

# Global warming potentials and radiative efficiencies of halocarbons and related compounds: a comprehensive review

Article

**Accepted Version** 

Open Access

Hodnebrog, O., Etminam, M., Fuglestvedt, J. S., Marston, G., Myhre, G., Nielsen, C. J., Shine, K. P. ORCID: https://orcid.org/0000-0003-2672-9978 and Wallington, T. J. (2013) Global warming potentials and radiative efficiencies of halocarbons and related compounds: a comprehensive review. Review of Geophysics, 51 (2). pp. 300-378. ISSN 1944-9208 doi: https://doi.org/10.1002/rog.20013 Available at https://centaur.reading.ac.uk/31338/

It is advisable to refer to the publisher's version if you intend to cite from the work. See <u>Guidance on citing</u>.

Published version at: http://onlinelibrary.wiley.com/doi/10.1002/rog.20013/abstract To link to this article DOI: http://dx.doi.org/10.1002/rog.20013

Publisher: Wiley

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the End User Agreement.

www.reading.ac.uk/centaur



## **CentAUR**

Central Archive at the University of Reading Reading's research outputs online

## 1 Global Warming Potentials and Radiative Efficiencies of

# **2 Halocarbons and Related Compounds: A Comprehensive**

- 3 Review
- 4 Ø. Hodnebrog<sup>1</sup>, M. Etminan<sup>2</sup>, J. S. Fuglestvedt<sup>1</sup>, G. Marston<sup>3</sup>, G. Myhre<sup>1</sup>, C. J. Nielsen<sup>4</sup>,
- 5 K. P. Shine<sup>2</sup>, T. J. Wallington<sup>5</sup>
- 6 <sup>1</sup>Center for International Climate and Environmental Research-Oslo (CICERO), P.O. Box
- 7 1129 Blindern, N-0318 Oslo, Norway
- 8 <sup>2</sup>Department of Meteorology, University of Reading, Earley Gate, P.O. Box 243, Reading,
- 9 RG6 6BB, Berks, UK
- <sup>3</sup>Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading,
- 11 RG6 6AD, Berks, UK
- <sup>4</sup>Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo,
- 13 Norway
- <sup>5</sup>Ford Motor Company, Research & Advanced Eng. Dept., Mail Drop RIC-2122, Dearborn,
- 15 MI 48121-2053, USA
- 16 Correspondence to: j.s.fuglestvedt@cicero.oslo.no
- 18 2<sup>nd</sup> revision, draft version 2. Date: 17 April 2013.

19

17

21

2223

24

25

26

#### 

#### Abstract

In the mid-1970s it was recognized that, as well as being substances that deplete stratospheric ozone, chlorofluorocarbons (CFCs) were strong greenhouse gases that could have substantial impacts on radiative forcing of climate change. Around a decade later, this group of radiatively active compounds was expanded to include a large number of replacements for ozone-depleting substances such as chlorocarbons, hydrochlorocarbons, hydrochlorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), bromofluorocarbons, and bromochlorofluorocarbons.

This paper systematically reviews the published literature concerning the radiative efficiencies (REs) of CFCs, bromofluorocarbons and bromochlorofluorocarbons (halons), HCFCs, HFCs, PFCs, SF6, NF3, and related halogen containing compounds. In addition we provide a comprehensive and self-consistent set of new calculations of REs and global warming potentials (GWPs) for these compounds, mostly employing atmospheric lifetimes taken from the available literature. We also present Global Temperature change Potentials (GTPs) for selected gases. Infrared absorption spectra used in the RE calculations were taken from databases and individual studies, and from experimental and *ab initio* computational studies. Evaluations of REs and GWPs are presented for more than 200 compounds. Our calculations yield REs significantly (> 5%) different from those in the Intergovernmental Panel on Climate Change Fourth Assessment Report (AR4) for 49 compounds. We present new RE values for more than 100 gases which were not included in AR4. A widely-used simple method to calculate REs and GWPs from absorption spectra and atmospheric lifetimes is assessed and updated. This is the most comprehensive review of the radiative efficiencies and global warming potentials of halogenated compounds performed to date.

## **Table of Contents**

55	1 Intro	duction	5
56	2 Back	ground concepts	9
57	2.1	Molecular radiative properties	9
58	2.2	Radiative forcing and radiative efficiency - concepts	11
59	2.3	Calculation of radiative efficiency	13
60	2.4	Atmospheric lifetimes	15
61	2.5	Climate impact metrics	18
62	3 Data	and method	20
63	3.1	Absorption cross-sections	20
64	3.1.1	Laboratory measurements of infrared absorption cross-sections	20
65	3.1.2 Theoretical calculations of infrared absorption cross sections		22
66	3.1.3 Database and sources of cross-section data		24
67	3.2	Atmospheric lifetimes	25
68	3.3	Radiative forcing efficiency	27
69	3.3.1	Spectrally-varying radiative efficiency	27
70	3.3.2	Stratospheric temperature adjustment	29
71	3.3.3	Simulations of atmospheric distributions and lifetimes	30
72	3.3.4	Fractional correction versus lifetime	33
73	3.4	Discussion of impact of functional groups on spectra/radiative forcing	36
74	3.5	Description of metrics	37
75	3.5.1	The Global Warming Potential (GWP)	37
76	3.5.2	The Global Temperature change Potential (GTP)	39
77	3.5.3	The reference gas CO <sub>2</sub>	39
78	3.6	Uncertainty – sensitivity to assumptions	41
79	3.6.1	Absorption cross-sections	41

80	3.6.2	Radiative forcing calculations	42
81	3.6.3	Atmospheric lifetimes	46
82	3.6.4	GWP	47
83	4 Results	s and Discussion	49
84	4.1 Inf	Frared Spectra, REs and GWPs	49
85	4.1.1	Chlorofluorocarbons (CFCs)	50
86	4.1.2	Hydrochlorofluorocarbons (HCFCs)	53
87	4.1.3	Hydrofluorocarbons (HFCs)	59
88	4.1.4	Chlorocarbons and Hydrochlorocarbons	73
89	4.1.5	Bromocarbons, Hydrobromocarbons, and Halons	76
90	4.1.6	Fully Fluorinated Species	80
91	4.1.7	Halogenated Alcohols and Ethers	88
92	4.2 Ad	Iditional metrics for most important gases: GTPs and GWPs	for other time
93	horizons.		112
94	5 Summa	ary and conclusions	113
95			
96			

#### 1 Introduction

97

98

99

100

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

126

127

128

Concern was raised in the 1970s that emissions of chlorofluorocarbons (CFCs), a class of compounds developed for a range of industrial and domestic uses, could lead to stratospheric ozone depletion [Molina and Rowland, 1974]. This concern was realized a decade later with the discovery of the Antarctic ozone hole [Farman et al., 1985] and a less severe but global-scale stratospheric ozone depletion [e.g., Stolarski et al., 1992].

At about the same time, it was also recognized that the CFCs were strong absorbers of infrared radiation and that sustained emissions could lead to accumulations in the atmosphere which would have significant climate impacts [Ramanathan, 1975; Wang et al., 1976]. This climatic role was re-emphasized during the 1980s, and expanded to more classes of gases, including chlorocarbons, hydrochlorocarbons, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and the bromofluorocarbons and bromochlorofluorocarbons (referred to here as halons) [e.g., Hansen et al., 1989; Ramanathan et al., 1985; Ramanathan et al., 1987]. These studies indicated that the increase in atmospheric concentrations of CFCs and related compounds was contributing a decadal radiative forcing which was around 30-40% of that due to the increase in carbon dioxide concentrations. Furthermore, it was noted that this share could increase, if the growth in emissions of the CFCs and related molecules was unconstrained.

The landscape for considering the climate impact of halocarbons (organic compounds containing one, or more, halogen atom) changed as a result of global environmental agreements under the auspices of the United Nations. First, the Montreal Protocol on Substances that Deplete the Ozone Layer (http://ozone.unep.org/new\_site/en/montreal\_protocol.php) - signed in 1987 and entered into force two years later - and its subsequent amendments and adjustments, led to the phasing out of production and emissions (with some exceptions) of CFCs, chlorocarbons and halons; it also included a schedule for the phasing out of emissions of HCFCs. Then, the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) (http://unfccc.int/kyoto protocol/items/2830.php) - signed in 1997 and entered into force in 2005 - set limits on the emissions of a "basket" of greenhouse gases by developed countries. The basket of greenhouse gases included a number of PFCs and hydrofluorocarbons (HFCs), the latter being most commonly used as CFC replacements. The initial Kyoto Protocol covered emissions in the so-called first commitment period of 2008-2012. The Doha Amendment to the Kyoto Protocol covers emissions in a second commitment period of 2013-2020, and added nitrogen trifluoride to the basket of greenhouse gases.

Some of the issues concerning the halocarbons can be illustrated by reference to Figure 1 [WMO/GAW, 2011], which shows quasi-global average atmospheric concentrations of 10 of the more abundant halocarbons. During the 1980s, the halocarbon abundance and growth was dominated by two CFCs (CFC-11 (CCl<sub>3</sub>F) and CFC-12 (CCl<sub>2</sub>F<sub>2</sub>)). There were also significant contributions from CFC-113 (CCl<sub>2</sub>FCClF<sub>2</sub>), methyl chloroform, and carbon tetrachloride. During the 1990s there was a dramatic change in the growth rates of the three CFCs and methyl chloroform. The changes were driven by the effects of the Montreal Protocol which led to rapidly declining emissions of these gases. The influence of the atmospheric lifetime of the different gases is also clear from Figure 1. Methyl chloroform has a relatively short lifetime (5 years) and its atmospheric concentration responds rapidly to decreased emissions. In contrast, CFC-12 and CFC-113 have atmospheric lifetimes of 100 and 85 years, respectively, and their atmospheric concentrations respond more slowly to decreased emissions. CFC-11 has an atmospheric lifetime of 45 years and its atmospheric concentration is more responsive than CFC-12 but less responsive than methyl chloroform to decreased emissions. The fact that the atmospheric concentrations of carbon tetrachloride (35 year lifetime) have only declined modestly over the past 30 years reflects continued emissions from developing nations [WMO, 2011].

Figure 1 shows that concentrations of HCFC-22 (CHClF<sub>2</sub>), an important interim replacement for several CFCs, continue to grow, despite being controlled by the Montreal Protocol – its concentration is now close to that of CFC-11. HFC-134a (CH<sub>2</sub>FCF<sub>3</sub>), which is included within the Kyoto Protocol, has been the fastest growing HFC, mainly because of its use as a replacement for CFC-12 in refrigeration and vehicle air-conditioning applications. Its relatively short lifetime (13.4 years) compared to the CFCs means that for the same emission rate the atmospheric abundance of HFC-134a would be much lower than the CFCs it replaces (see section 2.4). Estimating future atmospheric concentrations of HCFCs and HFCs is challenging as it requires estimation of future emissions which are difficult to predict. For example, future concentrations of HFC-134a will depend on the growth of the global vehicle fleet and the impact of legislation and improved technology which would limit the use of HFC-134a or its leakage from that fleet. If the current emission rate (149±27 kt yr<sup>-1</sup> in 2008 [WMO, 2011]) were maintained, the tropospheric concentration of HFC-134a would stabilize

at  $120 \pm 20$  ppt within a few decades. In addition to the gases shown in Figure 1, there are other halogenated alkanes (e.g., HFC-125 (CF<sub>3</sub>CF<sub>2</sub>H), HFC-143a (CF<sub>3</sub>CH<sub>3</sub>), HFC-152a (CH<sub>3</sub>CHF<sub>2</sub>), HFC-32 (CH<sub>2</sub>F<sub>2</sub>), HFC-245fa (CHF<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>), C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub>) that have been detected in the atmosphere at levels of 1-10 ppt.

161

162

163

164

165

166

167

168

169

170

171

172

173

174

175

176

177

178

179

180

181

182

183

184

185

186

187

188

189

190

191

While the Montreal Protocol was designed to protect the ozone layer, its impact on climate change has been substantial, since it also controlled the atmospheric abundance of species that are powerful greenhouse gases – indeed it can be argued that it had a greater influence on the radiative forcing of climate change than the Kyoto Protocol [e.g., *Velders et al.*, 2007].

To make the multi-gas approach embedded in the UNFCCC operational, the Kyoto Protocol from 1997 adopted a framework whereby emissions of non-CO<sub>2</sub> greenhouse gases were placed on a "CO<sub>2</sub>-equivalent" scale. As will be discussed in section 2, there is no unique way of assigning a CO<sub>2</sub>-equivalence to an emission of a non-CO<sub>2</sub> gas, but the Kyoto Protocol adopted one available metric, the Global Warming Potential with a 100-year time-horizon (GWP(100)). The Protocol uses values of GWP(100) for specific gases as reported in the Intergovernmental Panel on Climate Change (IPCC) Second Assessment Report (SAR) [IPCC, 1995]. It has not, so far, taken into account either revisions to those GWP values (as a result of improved understanding, and changing background concentrations of gases) or the expansion of the list to include additional species (including, for example, hydrofluoroethers (HFEs)) that have been catalogued in subsequent IPCC reports [e.g., IPCC, 2001; 2007] and World Meteorological Organization (WMO) / United Nations Environment Programme (UNEP) Scientific Assessment of Ozone Depletion [WMO, 2003; 2007; 2011]. In addition the parties to the UNFCCC have not considered in any detail and depth the use of alternative metrics to the GWP(100). For the second commitment period of the Kyoto Protocol, which is covered by the Doha Amendment, a draft decision (which is described in UNFCCC Decision 2/CMP.8 (http://unfccc.int/resource/docs/2012/cmp8/eng/13a01.pdf) which itself refers to Decision 4/CMP.7 (http://unfccc.int/resource/docs/2011/cmp7/eng/10a01.pdf)) has been made to adopt the GWP(100) values reported by the IPCC's Fourth Assessment Report in the Errata Table 2.14 of Working Group 1 to the report (see http://www.ipcc.ch/publications and data/ar4/wg1/en/errataserrata-errata.html#table214), but this decision has not been confirmed at the time of writing.

The GWP values for specific gases given in successive IPCC and WMO Ozone Assessment reports are drawn from a range of sources which use a variety of techniques to derive the input parameters (and in particular the "radiative efficiency" (RE) – which is, broadly, the "greenhouse" strength of a particular gas, on a per molecule basis – see section 2.2) needed to calculate the GWP. In addition, rather simplified considerations have sometimes been adopted to take into account discrepancies between values reported in the literature (e.g., averaging available values rather than assessing which are likely to be the more reliable).

The primary aim of this review is to provide a comprehensive and consistent analysis of the input parameters required to calculate values of the GWP and other metrics for a large number of CFCs, chlorocarbons, hydrochlorocarbons, HCFCs, HFCs, PFCs, HFEs and other related halogenated substances (including, for example, nitrogen trifluoride (NF<sub>3</sub>) and sulphur hexafluoride (SF<sub>6</sub>)). The particular emphasis will be on the method of calculation of the radiative efficiency. The review will also consider, in much less detail, atmospheric lifetimes, another important input parameter for the calculation of GWPs and other metrics – atmospheric lifetimes are, for the most part, taken from the existing literature, without detailed analysis. This then enables us to provide an extensive and self-consistent set of GWPs for halocarbon gases; we also provide tabulations of values for an alternative metric (the Global Temperature change Potential (GTP) – see section 4.2) for selected important gases.

In addition to their direct radiative effects, some halocarbons cause additional (indirect) effects on the climate system by influencing the abundance of other climatically-important gases – for example, stratospheric ozone, which is influenced by the CFCs and the halons. Such indirect effects are discussed elsewhere [e.g., *Daniel et al.*, 1995; *WMO*, 2011] and are not covered here.

Section 2 provides the necessary background concepts, section 3 presents the methodology we adopt to generate a consistent set of REs and lifetimes of the halocarbons, and related halogenated substances, including a discussion of the sensitivity of these parameters to uncertainties. Section 4 provides tabulations of the radiative efficiencies, lifetimes, GWPs and GTPs. Section 5 presents our conclusions.

#### 2 Background concepts

223

229

230

231

232

233

234

235

236

237

238

239

240

241

242

243

244

245

246

247

248

249

250

251

252

The computation of GWPs and similar metrics for a particular gas requires various inputs and model calculations. The two basic input parameters for the GWP calculations are, as will be described in section 2.5, the RE and the lifetime of the gas. The calculation of these two parameters requires, in turn, much additional information. Figure 2 summarizes the main steps required which are discussed in more detail below.

#### 2.1 Molecular radiative properties

The first stage in the determination of the RE is knowledge of the fundamental spectroscopic properties of a molecule. Here we are most concerned with its properties at thermal infrared (IR) wavelengths (i.e., wavelengths at which the Earth and its atmosphere emit significant amounts of infrared radiation) of roughly 4 to 200 µm (2500 to 50 cm<sup>-1</sup>). We will mostly work in terms of the frequency-like variable, wavenumber (the inverse of wavelength, normally auoted in cm<sup>-1</sup>). The emission of infrared radiation by the Earth and atmosphere and the radiative properties of the atmosphere are strong functions of wavenumber. Hence it is necessary to determine the spectroscopic properties of the target molecule as a function of wavenumber. A general introduction to atmospheric radiative transfer can be found in *Petty* [2006] and introductions to general molecular spectroscopy can be found in *Hollas* [2004] and Atkins and Friedman [2010]. Fundamentally, the molecules of interest here absorb and emit radiation by transitions between their vibrational-rotational energy levels. The characteristic wavenumber of absorption is determined by the spacing of the vibrational energy levels, with the transitions between particular vibrational-rotational energy levels leading to that absorption being spread by typically 50 cm<sup>-1</sup> around this characteristic wavenumber. For example, one of the simplest molecules, CF<sub>4</sub> absorbs over a narrow range of wavenumbers near 1300 cm<sup>-1</sup> which is associated with the stretching of the carbon-fluorine bonds in the molecule. Molecules containing the carbon-chlorine bond absorb characteristically around 800 cm<sup>-1</sup>. The more complex the structure of the molecule, the greater the number of possible modes of vibrations (including different stretching and bending modes) and hence the more complex the infrared absorption spectrum becomes. Figure 3 shows IR spectra of representative halocarbons and illustrates the increased number of IR absorption bands observed with larger, more complex and less symmetric molecules.

In principle, it would be desirable to characterize the strength of each discrete vibrational-rotational transition, and indeed this is necessary for some atmospheric greenhouse gases such as water vapor and carbon dioxide, where the absorption spectrum consists of many sharp individual spectral lines with rapid variations of absorption with wavenumber. However, for halocarbons the individual transitions are so close together (as a result of the large masses of the atoms), and sufficiently broad, that under atmospheric conditions the individual transitions merge together leading to a spectrum that consists of broad absorption bands (see Figure 3). The spectrally-resolved absorption cross-sections (units of cm<sup>2</sup> molecule<sup>-1</sup> with typical peak cross-sections of order 10<sup>-18</sup>-10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup> for the molecules considered here) can be integrated over infrared wavenumbers to give the *integrated cross-section* (typical values for halocarbons are of the order of 10<sup>-16</sup> cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup>). The integrated cross-section gives a useful measure of the overall strength of IR absorption but the variation of absorption with wavenumber (i.e., the absorption spectrum) must be known for calculation of the potential climate impact [e.g., *Pinnock et al.*, 1995; *Wallington et al.*, 2010].

The most common way for determining the absorption cross-sections of halocarbons is via laboratory measurements using Fourier Transform Infrared Spectrometry. Measurements are made at typically  $0.5 \text{ cm}^{-1}$  or better spectral resolution. In general, the absorption cross-sections for halocarbons are only rather weakly dependent on temperature and pressure over the atmospherically relevant range and this dependence is generally neglected in RE calculations and likely uncertainties are about  $\pm 5\%$  [*Highwood and Shine*, 2000]. The absorption cross-section measurements are typically assessed to have an accuracy of approximately  $\pm 5\%$  [e.g., *Ballard et al.*, 2000b; *Clerbaux et al.*, 1993; *Pinnock et al.*, 1995].

More recently, absorption cross-sections have begun to be determined by quantum mechanical electron structure calculations (we will refer to these as *ab initio* methods), which in principle only rely on the basic laws of nature. In practice, however, *ab initio* calculations involve approximations to solving the Schrödinger equation and residual errors remain [e.g., *Blowers et al.*, 2007; *Bravo et al.*, 2010b; *Papasavva et al.*, 1997]. The *ab initio* methods show considerable promise, but it has been found that they need empirical corrections (particularly for the wavenumbers of the main vibrational modes) to agree with laboratory measurements. In addition, their capabilities have not been assessed for the full range of molecules considered here. Nevertheless they have already proven to be useful adjuncts to

laboratory measurements and can provide data at wavenumbers that are difficult to study in the laboratory and allow rapid surveying of a broad range of compounds for which laboratory samples may not be easy to procure.

#### 2.2 Radiative forcing and radiative efficiency - concepts

Once the absorption cross-sections have been obtained, the next step is to compute the impact that the addition of a particular halocarbon to the atmosphere has on the radiation budget. The resulting change in the radiation budget is generally referred to as "radiative forcing" (RF), but there are a number of nuances to the definition of RF that need to be elaborated on. Also, in general, radiative forcing (in units of W m<sup>-2</sup>) refers to the effect of a specified change in the concentration of a species, often over some given time period. In this review, we focus on the radiative forcing per unit change in halocarbon mixing ratio – this is referred to as *radiative efficiency* (RE) (W m<sup>-2</sup> ppb<sup>-1</sup>). RE assumes that the RF is linear in mixing ratio – this is normally appropriate in the case of small perturbations in mixing ratio about current concentrations and is also appropriate for gases, such as the ones we consider here, which have low background concentrations.

IPCC Assessment Reports [e.g., Forster et al., 2007] have addressed the rationale for using RF, outlined caveats in its use, and also defined possible alternative definitions of RF [see also discussions in e.g., Fuglestvedt et al., 2010; Hansen et al., 2005]. Studies using climate models indicate that there is a direct relationship between global-averaged RF and the (equilibrium) global-mean surface temperature change, and so RF has been essentially used as a proxy for surface temperature change. RF is normally defined at the tropopause including stratospheric temperature adjustment [Forster et al., 2007], the rationale being that the tight coupling between the surface and troposphere means that they behave as a single thermodynamic system; hence it is the change in the input of energy into this system that drives the climate change.

Instantaneous RF [e.g., Forster et al., 2007] is defined as the change in net irradiance at the tropopause, following (for example) a change in a greenhouse gas concentration. Earlier studies indicated that the instantaneous RF had less utility (i.e., models indicated a less close relationship between it and the resulting surface temperature change) than RF with stratospheric temperature adjustment. Part of the rationale for this is that, following a perturbation, the response time of the stratosphere is fast (around a few months) compared to

the decadal time scale for the temperature of the surface-troposphere system to respond. It is found that for a number of forcings, the RF including stratospheric temperature adjustment has a closer relationship with modeled surface temperature change, than the instantaneous RF. For this definition of forcing, stratospheric temperatures are assumed to adjust in response to the change in greenhouse gas concentration – this change in temperature leads to a further change in the irradiance, as the downward emission by the stratosphere to the troposphere is dependent on this temperature. Some gases (notably  $CO_2$ ) lead to a cooling of the stratosphere which makes the stratospheric-adjusted forcing less than the instantaneous forcing. For others (including many halocarbons) the reverse is true, as the stratosphere warms – see section 3.3.2 for further discussion.

Early studies [Jain et al., 2000; Myhre and Stordal, 1997; Naik et al., 2000; Pinnock et al., 1995] quantified the difference between the instantaneous and stratospheric-adjusted RF for a range of halocarbons, indicating that the instantaneous forcing is typically 5-10% lower than the stratospheric-adjusted RF. One drawback with the stratospheric-adjusted RF is that its calculation is computationally much more demanding; in this review, because of the large number of gases involved, we calculated instantaneous RE and then applied a correction, based on the available literature, to account for the effect of stratospheric adjustment (see section 3.3.2).

More recently, there has been much work investigating alternative definitions of forcing [e.g., Andrews and Forster, 2008; Forster et al., 1997; Gregory et al., 2004; Hansen et al., 2005] – for example, fixing surface temperatures (sometimes sea-surface temperature only) but allowing tropospheric temperatures, humidity and cloudiness to adjust, in addition to the stratosphere. The rationale here is that there are so-called "fast feedbacks" or "rapid adjustments" operating in the troposphere that can change, for example, cloudiness in the absence of surface temperature change. Hence it is conceptually attractive to separate climate responses that operate on day-to-month timescales and are independent of changes in surface temperature from the "traditional" climate feedbacks (for example, water vapor feedback, ice albedo feedback and various cloud feedbacks) which are mediated by surface temperature change and hence act on decadal to century timescales.

These rapid tropospheric adjustments can be particularly important for other forcings, such as those resulting from black carbon aerosols. Few model results are available on the effect of tropospheric adjustments for the gases considered here. Computation of such

forcings requires long simulations using sophisticated climate models, and results would likely depend significantly on the climate model chosen. In addition, because of the inherent "unforced" natural variability in such climate models, it would be necessary to impose a large forcing (in excess of 1 W m<sup>-2</sup>) to easily extract a reliable signal from the model; this is many times the present-day RF of the most abundant CFC (CFC-12 – about 0.17 W m<sup>-2</sup> [Forster et al., 2007]) and orders of magnitude more than most other gases considered here, raising concerns about the linearity of the rapid tropospheric adjustments. Since research on these more advanced definitions of forcing is still at an early stage, and also because of the computational demands of performing these calculations, we believe it premature to adopt them here as a framework.

An additional and related issue concerns the so-called climate efficacy. An underlying assumption in early work in this area was that the global-mean surface temperature response to an RF of, say, 1 W m<sup>-2</sup>, was the same irrespective of the cause of the forcing. Climate model simulations now indicate that this assumption is not strictly justified. Efficacy is a measure of the ability (per W m<sup>-2</sup>) of a particular forcing to change surface temperature relative to, for example, a 1 W m<sup>-2</sup> forcing due to a change in carbon dioxide. Relatively little research has been performed on the efficacy of the halocarbons. Forster and Joshi [2005] found an efficacy of CFC-12 (using the stratosphere adjusted forcing) to be 0.94 in their model. Hansen et al. [2005], by contrast, found an equivalent value (for a combination of CFC-11 and CFC-12) of 1.3, but also demonstrated that the efficacy depends on the definition of forcing that is adopted. An additional issue for the short-lived halocarbons, is that the efficacy likely depends on the spatial distribution of the halocarbon [Joshi et al., 2003] which in turn depends on the halocarbon's lifetime (see section 2.4) and the distribution of emissions. Given these uncertainties, we assume an efficacy of 1 throughout this review, although it is in principle possible to include non-unity values of efficacy within the GWP and GTP metrics.

#### 2.3 Calculation of radiative efficiency

The calculation of radiative efficiency requires, in addition to the absorption spectrum for the halocarbon in question, a calculation of atmospheric irradiances, accounting for atmospheric properties, such as the amounts, distributions and radiative properties of other infrared-absorbing components (water vapor, carbon dioxide, ozone, clouds, etc.), and temperatures. As the RE is a globally- and annually-averaged quantity, in principle it should be calculated

locally and, say, monthly, and then averaged to produce the global and annual mean. In practice, it is possible, with about 5-10% accuracy, to calculate the RE using a globally-averaged atmospheric profile or using two or three profiles representative of the tropics and mid/high latitudes [Freckleton et al., 1998; Myhre and Stordal, 1997]. Myhre et al. [2006] found that for calculations of the CFC-12 RE, the use of two atmospheric profiles (one for tropics and one extra-tropics) represents global simulations with a horizontal resolution of  $2.5^{\circ} \times 2.5^{\circ}$  within 1%. In addition, there are several possible choices of tropopause definition that impact on the calculated forcing at the 5% level [Freckleton et al., 1998].

The radiative transfer models that can be used for such calculations vary in complexity. The most complex (line-by-line (LBL) models) perform calculations at high (typically 0.01 cm<sup>-1</sup>) spectral resolution and resolve explicitly the individual spectral lines of atmospheric gases such as water vapor, carbon dioxide and ozone. These are computationally expensive and parameterized models are often used (for example to compute the effect of stratospheric adjustment). Narrow Band Models resolve the infrared spectrum at typically 10 cm<sup>-1</sup> resolution, while computationally-fast Wide Band Models (suitable for use in climate models) may resolve the thermal infrared region into typically 5 to 10 spectral intervals. Intercomparisons of such models both for greenhouse gases in general [e.g., Collins et al., 2006; Oreopoulos et al., 2012] and for halocarbons in particular [e.g., Forster et al., 2005; Gohar et al., 2004; Jain et al., 2000] are of importance in assessing the capabilities of the parameterized models. When these models are combined with vertical profiles of temperature, cloudiness and greenhouse gas concentrations, it is necessary to ensure that the model's global-and-annual outgoing longwave radiation, and the impact of clouds on the outgoing longwave budget, are in reasonable agreement with satellite observations; otherwise, biases in the resulting RE calculations can occur.

In addition to the direct use of radiative transfer models to calculate REs, it is possible to use these models to produce simple techniques to compute the radiative forcing directly from the absorption cross-sections. *Pinnock et al.* [1995] used a narrow-band model to compute the RE per unit absorption cross-section as a function of wavenumber, using a global and annual mean atmosphere. This then indicates the spectral regions at which halocarbon radiative forcing is most effective. As shown in Figure 5 and discussed in section 3.3.1, where an update to the *Pinnock et al.* [1995] method is presented, molecules are most effective if they absorb in the 800-1200 cm<sup>-1</sup> spectral region (a so-called "atmospheric window"), but can

remain effective outside this region. If a halogenated compound absorbs at a wavelength where there is already substantial atmospheric absorption (for example by carbon dioxide near 670 cm<sup>-1</sup>) then the additional absorption by this compound will not contribute significantly to radiative forcing.

Hence, if the spectrally-varying radiative forcings calculated by *Pinnock et al.* [1995] are multiplied by the absorption cross-sections representing a real halocarbon (averaged to the same spectral resolution as the radiation calculations) then an estimate of the RE can be achieved easily by summing over all wavenumbers, using a spreadsheet for example, without the need for a complex radiation code. *Pinnock et al.* [1995] demonstrated for a wide range of halocarbons that this simple technique could generate instantaneous REs that were accurate to within 0.3%, relative to full calculations using the same radiation code that was used to generate the values in the simple technique, and using the same atmospheric profile. (It is emphasized that this is not the technique's absolute accuracy, as this is dependent on the accuracy of the radiation code and its input parameters). Consequently, the method developed by Pinnock *et al.* is simple and effective, and has been widely used.

A further consideration in calculating the RE is that the horizontal and vertical distribution of the molecule must be specified – often the baseline assumption is that the molecule is well-mixed within the atmosphere (both horizontally and vertically); corrections to approximately account for the departure from this assumption are then applied – see section 2.4 and 3.3.4. However, it should be noted that for short-lived gases in particular, there is no unique value of RE, as its value depends to some extent on the geographical (and seasonal) distribution of emissions, as these in turn influence the horizontal and vertical distribution of the gas.

#### 2.4 Atmospheric lifetimes

The global atmospheric lifetime (yr) of a gas is defined in the IPCC Third Assessment Report [IPCC, 2001] as "the burden (Tg) divided by the mean global sink (Tg/yr) for a gas in steady state (i.e., with unchanging burden)." The report also identifies two important consequences of this definition, namely that: (i) "when in steady state (i.e., source strength = sink strength) the atmospheric burden of a gas equals the product of its lifetime and its emissions"; and (ii) "the integrated atmospheric abundance following a single emission is equal to the product of the steady-state lifetime for that emission pattern and the amount emitted [Prather, 1996]".

As will be discussed in section 2.5, the most frequently used climate metrics consider the impact of a pulse emission of a gas.

The global atmospheric lifetime has also been referred to as simply as "lifetime", or "turnover time" [Bolin and Rodhe, 1973; IPCC, 1995] reflecting the fact that it characterizes the time required to turn over the global atmospheric burden of the gas in question. It is sometimes thought of as the decay time (e-fold) following a perturbation, with its magnitude determined by chemical or photolytic loss rates. While conceptually appealing, this approach applies rigorously only for a gas whose local chemical lifetime is constant in space and time, such as for the noble gas radon, whose lifetime is fixed by the rate of its radioactive decay [IPCC, 2001]. In reality the chemical losses of pollutants vary in time and space and, if the magnitude of emissions are sufficient (e.g., for methane), the emissions themselves can influence the chemistry of the atmosphere and hence the pollutant's lifetime. As discussed in sections 3.3.3 and 3.3.4, many halocarbons have short lifetimes, are not well mixed in the atmosphere, and the spatial and temporal emission pattern needs to be accounted for in assessments of their radiative efficiencies.

Halocarbons are removed from the atmosphere by two main mechanisms; reaction with OH radicals and photolysis. As a crude guide to understanding how the molecular structure of a halocarbon affects its reactivity towards OH radicals, for a given carbon backbone (e.g., C<sub>2</sub>, C<sub>3</sub>, *n*-C<sub>4</sub>, etc.) the more fluorine atoms in a haloalkane the longer its lifetime and the more bromine or iodine atoms the shorter its lifetime. For molecules containing hydrogen such as HCFCs, HFCs, HFEs and hydrochlorocarbons, the primary removal mechanism in the troposphere is reaction with the hydroxyl radical OH. Lifetimes range from a few days to millennia, depending on the structure of the molecule – to first order, the more heavily halogenated a molecule, the longer its lifetime, although the precise arrangement and nature of those halogens in the molecule plays an important role [*Atkinson et al.*, 2008; *Sander et al.*, 2010]. Unsaturated molecules containing >C=C< double bonds react rapidly with OH radicals. Including one, or more >C=C< double bond is a particularly effective method of reducing the atmospheric lifetime of halocarbons. For example, CF<sub>3</sub>CF<sub>2</sub>CH<sub>3</sub> (HFC-245cb) has a lifetime of 47.1 years while CF<sub>3</sub>CF=CH<sub>2</sub> (HFC-1234yf) has a lifetime of 10.5 days.

For CFCs and halons, the primary destruction mechanism is ultraviolet photolysis in the stratosphere. CFCs are inert in the troposphere as sufficiently short wavelength ultraviolet radiation does not penetrate in to the troposphere. Indeed, it is their chemical inertness that made the CFCs so attractive in industrial and domestic usages. It is interesting and worth noting that when detection of CFCs in the atmosphere was first reported, the conclusion included the comment "The presence of these compounds [CFC-11 and CFC-12] constitutes no conceivable hazard" [Lovelock and Maggs, 1973]. Halons have atmospheric lifetimes in the approximate range of 10 to 70 years, while CFCs have atmospheric lifetimes ranging from about 45 to more than a thousand years. Calvert et al. [2008] have reviewed the mechanisms in the atmospheric photolysis of haloalkanes. Absorption at ultra-violet wavelengths involves an  $n \to \sigma^*$  transition with a non-bonding electron of the halogen promoted into an antibonding sigma orbital of the C-X bond. Ultra-violet absorption spectra for haloalkanes (RX) of similar carbon backbone structure move to lower energy (longer wavelength absorption) along the series X = F, Cl, Br, to I, reflecting a trend of lower electron affinity of the halogen atom [Calvert et al., 2008]. Absorption by C-F and C-Cl bonds only occurs at wavelengths below approximately 240 nm. CFCs, HFCs, HCFCs, chlorocarbons, and hydrochlorocarbons do not photolyze in the troposphere as sufficiently short wavelength ultra-violet radiation does not reach the troposphere. In contrast to C-F and C-Cl bonds, C-I bonds absorb strongly at tropospherically relevant wavelengths and iodine-containing haloalkanes have atmospheric lifetime of days, or less, with respect to photolysis in the troposphere (e.g., 4.9 days for CH<sub>3</sub>I, 4.3 days for C<sub>2</sub>H<sub>5</sub>I, 4.9 hours for CH<sub>2</sub>ICl, and 4.9 minutes for CH<sub>2</sub>I<sub>2</sub> [Calvert et al., 2008]). Absorption by C-Br bonds at tropospherically relevant wavelengths is generally weak but photolysis can contribute to determining the atmospheric lifetime of some bromoalkanes such as CHBr<sub>3</sub> [Calvert et al., 2008]. Because of the inherent strength of the C-F bond, the PFCs are chemically inert and, are the longest lived of the halocarbons, with lifetimes ranging from about a thousand years to approximately 50,000 years for CF<sub>4</sub>.

475

476

477

478

479

480

481

482

483

484

485

486

487

488

489

490

491

492

493

494

495

496

497

498

499

500

501

502

503

504

505

506

507

The atmospheric lifetime plays a further role in the determination of the radiative efficiency, because it helps determine the degree of heterogeneity in the distribution of the halogenated molecules in the atmosphere. For molecules with lifetimes of less than a few months, the atmospheric distribution is dependent on where and when the gases are emitted, reflecting the spatial and temporal distribution of OH radicals which determines the local atmospheric lifetimes. Since the radiative efficiency of a gas depends on its location (in general, a gas at low latitudes is more effective, as more radiative energy is available to be absorbed at high temperatures), a unique radiative efficiency cannot be defined for such shortlived molecules without a detailed knowledge of the spatial and temporal emission pattern. In

addition, the vertical profile of a gas is also influenced by the atmospheric lifetime. Mixing processes are most efficient within the troposphere with molecules mixed vertically on the typical timescales of days to weeks. Within the stratosphere the vertical profile of a particular species depends strongly on the relationship between the timescales for transport within the stratosphere and the rate at which the molecule is destroyed. *Jain et al.* [2000] and *Naik et al.* [2000] [see also *Freckleton et al.*, 1998] used chemical transport models to simulate the distributions of a range of halocarbons, and quantify the difference in the RE between using these distributions and the assumption that the gases are well mixed. Their results were used by *Sihra et al.* [2001] to develop a simplistic method to approximately account for the effect of atmospheric lifetime on the radiative efficiency. This will be further discussed in section 3.3.4. (A non-constant atmospheric profile of a species can also result when the rates of surface emissions are growing rapidly, because of the multi-year timescale for the molecule to reach deep into the stratosphere.)

The products of the reactions that destroy halocarbons could in principle themselves be climatically-important gases. However, it is well established that the atmospheric degradation of halocarbons gives oxygenated compounds which have relatively short atmospheric lifetimes and are typically removed by wet and dry deposition on a time scale of days or weeks [Wallington et al., 1994b]. The oxidation products do not accumulate in the atmosphere and do not contribute significantly to radiative forcing of climate change.

#### 2.5 Climate impact metrics

A key objective of this review is to provide values for the GWP and GTP metrics for the halocarbons. The rationale and challenges in developing climate impact metrics have been reviewed in detail by *Fuglestvedt et al.* [2010] and so only a relatively brief discussion is given here.

One of the prime drivers of the development of emission metrics is the need for their use in multi-gas climate policies (such as the Kyoto Protocol) where emissions of different compounds must be placed on a common scale, usually referred to as a "CO<sub>2</sub>-equivalent" scale. There is no unique method of doing this, and the choice of method should be consistent with the climate policy that the metric aims to serve [e.g., *Plattner et al.*, 2009]. The Kyoto Protocol's choice of the GWP(100) has been a matter of much discussion and debate [e.g., *Fuglestvedt et al.*, 2003; *Manne and Richels*, 2001; *O'Neill*, 2000; *Shine*, 2009]. One often

cited reason for its original use and retention has been the lack of a widely-accepted alternative, and, latterly, the difficulties that might arise within policymaking if the metric (more specifically, the numerical value that converts a given emission to a CO<sub>2</sub>-equivalent emission) was substantially changed.

There are a number of elements that have to be considered in metric design. What kind of emission is considered - for example, a pulse or a sustained emission? What "impact" is considered - for example, radiative forcing, surface temperature change, sea-level rise, economic impact, or the rate of change of these quantities? Which indirect effects and feedbacks should be included? Is the impact considered integrated over some time period, or at one particular time? Is the impact given as global mean or with a regional resolution? What time period is considered? And, of significance to their wider acceptability, particularly within the policymaking community, how transparent are the formulations of the metrics?

Here we present results for two metrics. The GWP (with time horizons of 20, 100 and 500 years) is presented to be consistent with reporting in previous IPCC assessments and its wide usage. The GWP definition we use here is as used in the first IPCC Assessment Report [IPCC, 1990] which itself was based on then-recent studies suggesting ways of intercomparing the climate effect of emissions of different gases [Derwent, 1990; Fisher et al., 1990; Lashof and Ahuja, 1990; Wuebbles, 1989]. The GWP represents the time-integrated radiative forcing due to a pulse emission of a gas. It can be presented as the absolute GWP (AGWP – with units of, for example, W m<sup>-2</sup> kg<sup>-1</sup> year) or, more normally, as a ratio to the AGWP of CO<sub>2</sub>. One difficulty is that the AGWP of CO<sub>2</sub> has been subject to periodic revision in IPCC assessments, as a result of atmospheric changes (the RE of CO<sub>2</sub> decreases as CO<sub>2</sub> concentrations increase) and changes in understanding of how long CO2 concentrations remain perturbed following a pulse emission. Hence the GWP of a halocarbon may change solely because of a change in AGWP of CO<sub>2</sub> rather than revisions to its own lifetime and radiative efficiency, as happened, for example, in the IPCC Third Assessment Report IPCC [2001]. The precise method used here to determine the AGWPs, and hence the GWPs, will be presented in section 3.5.

The GTP [Shine et al., 2005a] is also chosen for presentation here, partly because it has attracted more attention than other alternative metrics, including at the policymaking level [e.g., Plattner et al., 2009] and partly because it has a quite different basis from, and hence provides an alternative perspective to, the GWP. The GTP represents the temperature change

due to a pulse emission of a gas, at some time (here 20, 50 and 100 years are chosen) in the future. Hence it is an "end-point" metric (unlike the GWP, which is a time-integrated metric) and hence retains less of a memory of the effect of emissions of short-lived species. It has been suggested that the GTP may be more suitable for target-based climate policies [e.g., *Shine et al.*, 2007], such as envisaged under the Copenhagen Accord of the UNFCCC, where the aim is to keep surface temperature change, relative to pre-industrial times, below 2 degrees C. The GTP method requires, in addition to the lifetime and radiative efficiency, some model to represent the response of global-mean surface temperature to radiative forcing, and hence requires the specification of additional parameters compared to the GWP. As with the GWP it can be presented as an absolute quantity (with units of, for example, K kg<sup>-1</sup>) or as a ratio to the absolute Global Temperature change Potential (i.e., AGTP) of CO<sub>2</sub>.

Since *Fuglestvedt et al.* [2010], there has been a significant literature on climate emission metrics including discussions of how these "physical" metrics relate to metrics which incorporate, additionally, an economics element [e.g., *Boucher*, 2012; *Johansson*, 2012; *Tol et al.*, 2012], the relationship amongst metrics (for example, *Peters et al.* [2011] discuss the similarities of the GWP with a time-integrated GTP) and evaluations of the sensitivities of GWPs and GTPs to uncertainties in input parameters and background scenarios [e.g., *Reisinger et al.*, 2011; *Reisinger et al.*, 2010].

#### 3 Data and method

## 3.1 Absorption cross-sections

## 3.1.1 Laboratory measurements of infrared absorption cross-sections

Analytical infrared instrumentation usually only covers the mid-infrared region, 4000-400 cm<sup>-1</sup>, and the majority of available IR absorption spectra — including most of the spectra covered in this review — were measured within this wavenumber range. As will be shown in detail in section 3.3.1, the effectiveness of the absorption in contributing to RE varies strongly with wavenumber, peaking at 300-600 and 750-1000 cm<sup>-1</sup>, significant at 1100-1300 cm<sup>-1</sup>, and of minor importance for wavenumbers above 1500 cm<sup>-1</sup> [*Pinnock et al.*, 1995].

Infrared spectra are measured in transmittance, which is defined as the ratio of spectral intensity transmitted through the sample at a given wavenumber  $\tilde{n}$ ,  $I_{tr}(\tilde{n})$ , to the incoming

spectral intensity,  $I_0(\tilde{n})$ . Transmittance is related to the wavenumber and temperature dependent absorption cross section,  $\sigma(\tilde{n}, T)$ , through the Beer-Lambert-Bouguer law:

$$\frac{I_{tr}\left(\tilde{n}\right)}{I_{0}\left(\tilde{n}\right)} = e^{-S\left(\tilde{n},T\right) \cdot nd}$$

where n is the molecule concentration (molecule cm<sup>-3</sup>), and l is the sample optical path length (cm). The absorption cross section (cm<sup>2</sup> molecule<sup>-1</sup>) is then given by:

$$S(\tilde{n},T) = \frac{1}{n \times l} \times \ln \int_{\tilde{T}}^{\tilde{T}} \frac{I_0(\tilde{n}) \ddot{V}}{I_{lr}(\tilde{n}) \dot{b}} = \frac{\ln(10)}{n \times l} \times \lg \int_{\tilde{T}}^{\tilde{T}} \frac{I_0(\tilde{n}) \ddot{V}}{I_{lr}(\tilde{n}) \dot{b}}$$

where ln is the napierian logarithm and lg is the common decadic logarithm.

The strength of an absorption band is given by the integral:

$$S(\tilde{n}_{1}, \tilde{n}_{2}, T) = \bigcup_{\tilde{n}_{1}}^{\tilde{n}_{2}} S(\tilde{n}, T) \times d\tilde{n}$$

608

612

613

614

615

616

617

618

619

620

621

622

623

624

625

626

627

where  $S(\tilde{n}_1, \tilde{n}_2, T)$  is the integrated absorption intensity (in units of cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup>) over the wavenumber range  $\tilde{n}_1$  to  $\tilde{n}_2$ .

The absorption cross section depends on temperature for several reasons. First, infrared absorption occurs from a range of rotational energy levels, and the relative populations of these levels are strongly temperature dependent. Secondly, and particularly for molecules containing heavier atoms and in bending vibrations, absorption will not only occur from the vibrational ground state but also from vibrationally excited states - so called hot bands. Since populations depend on the temperature, so will the measured net absorption. Further, molecules often have several stable conformations with different energies and slightly different infrared spectra. The conformational equilibrium and, consequently, the absorption spectrum of such molecules will therefore vary with temperature. While the infrared absorption bands of halocarbons narrow with decreasing temperature there is no significant change in the integrated infrared absorption over the atmospherically relevant range [Ballard et al., 2000b; Le Bris et al., 2011; Orlando et al., 1992]. Changes in temperature over the atmospherically relevant range result in narrowing of the absorption bands by a few cm<sup>-1</sup> [Orlando et al., 1992]. The error that results from the use of a single infrared spectrum measured at, or near, room temperature to calculate the RE of a molecule in the whole atmosphere is comparable to, or smaller than, the uncertainties in a single 628 measurement [*Ballard et al.*, 2000b] and so the temperature dependence is often ignored in RE calculations.

630

631

632

633

634

635

636

637

638

639

640

641

642

643

644

645

646

647

648

649

650

651

652

653

654

655

656

657

### 3.1.2 Theoretical calculations of infrared absorption cross sections

Theoretical calculations can be used to provide estimates of infrared vibrational band positions and the intensity of the transitions. The theory underpinning such calculations and their computational intricacies lie outside the scope of this review, but an introduction to the background can be found in Atkins and Friedman [2010]. Despite the complexities of the calculational methods, modern software packages are such that the non-specialist can use them and take advantage of the insights that theoretical calculations offer. Calculations are carried out using a combination of a calculational method and a basis set. Researchers have used traditional molecular orbital ab initio calculations using the 2nd-order Møller-Plesset (MP2) perturbation method, and more recently, the Density Functional Theory (DFT) method. The DFT method is becoming increasingly common, as it provides comparable accuracy to MP2, but at a considerably reduced computational cost. A commonly used DFT method is the Becke, 3-parameter, Lee-Yang-Parr method, commonly known as B3LYP. The basis sets used in modern calculations are comprised of Gaussian-type orbitals, which have characteristics similar to s-, p-, d-, etc. hydrogenic atomic orbitals. Basis sets are described with specific notation; common examples are, in order of increasing basis set size, 6-31G, 6-31G\* and 6-31G\*\*. A calculation might be described as B3LYP/6-31G\*\*, which would mean that the calculation had been carried out using the B3LYP method combined with the 6-31G\*\* basis set. There is always a tension between achieving the most accurate description of a molecule — which requires a large basis set — and the need to reduce the computational cost of the calculation — which requires a small basis set.

In principle, calculations should be carried out for all possible conformers of a compound, with the final spectrum being a weighted sum of the spectra of the individual conformers. The contribution of each conformer to the overall spectrum is determined by its relative population, which is calculated using the Boltzmann distribution. *Bravo et al.* [2010b] have tested the importance of including the contribution of conformers to the overall spectrum for n-C<sub>4</sub>F<sub>10</sub>. They concluded that the change to the RE of including the higher energy

conformers was less than 1%; most calculations use the lowest energy conformer to generate the spectrum used for RE calculations.

Theoretical calculations are subject to quite significant errors, with contributions arising from the method used and the limited size of the basis set. Fortunately, the outputs from the calculations generally provide an estimate of the positions of vibrational bands that differ in a systematic way from the experimentally observed band positions [Scott and Radom, 1996]. The extent to which these differences have a significant impact on radiative forcing efficiency calculations depends on the region of the spectrum where the transitions occur. For example, compounds containing C-F bonds have strong absorptions at around 1250 cm<sup>-1</sup>. In this region of the spectrum, the radiative efficiency function changes rapidly with wavenumber (see section 3.3.1) and so small errors in the band position can have a relatively large impact on calculated REs [Bravo et al., 2010b]. Different researchers have dealt with the systematic errors in different ways; the errors are sometimes ignored [Blowers and Hollingshead, 2009], accounted for by using a generic correction formula [Shine et al., 2005b], or corrected using methods specific to the particular class of compounds under consideration [Bravo et al., 2010b]. Integrated cross sections (over the appropriate wavenumber range) are generally in good agreement (within 5%) with those determined experimentally [Bravo et al., 2010b].

The output from calculations differs from experimental measurements in that rather than providing an absorption cross section as a function of wavenumber, an integrated absorption cross section (IAC) is calculated for each vibrational band. Conversion to a cross section can be achieved simply by dividing by the appropriate wavenumber interval to get an average cross section over that interval; for example, *Pinnock et al.* [1995] calculate REs using a 10 cm<sup>-1</sup> interval, so IACs are simply divided by 10 cm<sup>-1</sup> to get the average cross section over this interval for use in their calculations [*Bravo et al.*, 2010b]. An alternative approach is to 'spread' some of the absorption into neighboring wavenumber intervals. *Bravo et al.* [2010b] showed that spreading 50% of absorption equally into regions above and below the central interval did not have a significant effect on calculated radiative forcing efficiencies for a number of PFCs using the Pinnock method. However, the impact is likely to be more significant if a narrower wavenumber interval is chosen for the calculations.

For comparison with experiment, the integrated absorption cross sections can be used to simulate spectra assuming the vibrational bands are Gaussian in shape. Figure 4 shows an

experimentally determined spectrum of *n*-C<sub>4</sub>F<sub>10</sub> from *Bravo et al.* [2010b] along with spectra calculated using the B3LYP and MP2 methods. The calculated spectra have been corrected for the systematic errors discussed earlier. The agreement between theory and experiment is very good, particularly for calculations carried out using the B3LYP method. The spectra generated in this way can also be used to calculate radiative forcing efficiencies in the normal way. Again, using the Pinnock method with a 10 cm<sup>-1</sup> interval, *Bravo et al.* [2010b] found that converting the IACs to spectra in this way had only a modest impact on the calculated RE.

#### 3.1.3 Database and sources of cross-section data

The main sources of experimental infrared absorption cross-sections are Ford Motor Company [e.g., *Sihra et al.*, 2001], the SWAGG project (Spectroscopy and Warming potentials of Atmospheric Greenhouse Gases) [*Ballard et al.*, 2000c; *Highwood and Shine*, 2000], and the two databases HITRAN-2008 (High Resolution Transmission) [*Rothman et al.*, 2009] and GEISA-2009 (which is now referred to as GEISA-2011 on the GEISA website) (Gestion et Etude des Informations Spectroscopiques Atmosphériques) [*Jacquinet-Husson et al.*, 2011]. Theoretical absorption data from *ab initio* calculations [*Bravo et al.*, 2011a; *Bravo et al.*, 2010b] have also been included here.

The HITRAN-2008 database includes IR cross-sections of 31 different gases, many of which are measured at a range of temperatures and pressures. Updates since the previous edition, HITRAN-2004, have been described in detail in *Rothman et al.* [2009]. In GEISA-2009, IR spectra of 39 different gases are included, again for a wide range of temperatures and pressures. Some of the spectra in GEISA-2009 are from the same source as in HITRAN-2008, and when this is the case we disregard the spectrum from GEISA-2009 to avoid duplicates. *Jacquinet-Husson et al.* [2011] describes the GEISA-2009 database and the updates that have taken place since the 2003 edition.

The absorption cross-sections available in the literature have been summarized (Tables 2, 4, 6, 8, 10, 12 and 14) and the spectra which have been used in the calculation of new best estimate REs are highlighted. Each available spectrum has been evaluated and if several cross-sections exist from the same laboratory group, only the latest published spectrum has been used in our calculations. In particular, spectra from *Sihra et al.* [2001] supersede those from *Pinnock et al.* [1995] and *Christidis et al.* [1997] since the methodology of the Ford

laboratory measurements improved over time. Furthermore, cross-sections from laboratory measurements are favored over theoretical calculations, but the latter have been used if experimental spectra are not available for a compound and when significant differences in experimental data exist. The spectrum that was recorded nearest room temperature and atmospheric pressure was used when more than one spectrum was available from a source, as described further in section 3.6.1. The format of theoretical *ab initio* data differ from experimentally measured infrared spectra; theoretical data consist of values of the central wavenumber and the strength at the vibrational band center. To calculate the radiative efficiencies from these data, they were spread to the 1 cm<sup>-1</sup> bin size of our spectrally-varying radiative efficiency data (see section 3.3.1). All the cross-sections used in this study have been converted to the same format as in HITRAN (more information about this format can be obtained at the HITRAN web site at <a href="http://www.cfa.harvard.edu/hitran">http://www.cfa.harvard.edu/hitran</a>), and many of the cross-sections are available in the supplementary material.

## 3.2 Atmospheric lifetimes

The processes that remove halocarbons from the atmosphere have been described recently [WMO, 2011]; this publication included a discussion of the rationale for recent changes to the recommendations for the lifetimes of a number of species. It is outside of the scope of this review to re-examine these recommendations; we confine ourselves to a summary of the major atmospheric loss processes for halocarbons, which include chemical reaction and photolysis, as well as uptake by the oceans and terrestrial ecosystems. In addition, there are examples of compounds — e.g., SF<sub>5</sub>CF<sub>3</sub>, — where dissociative electron attachment may also be important [Takahashi et al., 2002].

The global atmospheric lifetime of a gas was defined in section 2.4 as its burden divided by its loss rate. Under locally defined conditions, lifetimes can be determined as the inverse of a (pseudo-)first-order loss process. For loss of compound Y by reaction with X, we can write the loss rate as:

$$748 \quad -\frac{\mathsf{d}[\mathsf{Y}]}{\mathsf{d}t} = k_{\mathsf{X}}[\mathsf{Y}][\mathsf{X}].$$

In this process, the pseudo-first-order rate constant for the loss of Y is equal to  $k_X[X]$ , and the lifetime of Y with respect to reaction with X,  $\tau_X$ , is  $1/(k_X[X]) = 1/k'_X$ , with an assumption (or

approximation) that [X] is constant. Integration over space and time yields a global and annual average lifetime of Y with respect to reaction with X. In the troposphere, the dominant oxidant is the hydroxyl radical, OH. For well-mixed compounds (lifetimes greater than a few months) lifetimes with respect to OH are determined relative to the lifetime of methyl chloroform, CH<sub>3</sub>CCl<sub>3</sub>. The lifetime of a gas is given as the product of the CH<sub>3</sub>CCl<sub>3</sub> lifetime and its rate constant for reaction with OH divided by the OH rate constant of the gas; see *WMO* [2011], *Prather and Spivakovsky* [1990], *Spivakovsky et al.* [2000] and *Montzka et al.* [2011] for further detailed discussion.

For photolytic processes, a photolysis rate constant, J, is defined with units of s<sup>-1</sup>, and is given by the expression:

761 
$$J = \int_{\lambda_1}^{\lambda_2} I(\lambda, z) \sigma(\lambda, T) \phi(\lambda, T) d\lambda$$

where  $I(\lambda, z)$  is the wavelength-dependent intensity of solar radiation at altitude z (sometimes known as the actinic flux),  $\sigma(\lambda, T)$  is the wavelength- and temperature-dependent ultraviolet/visible absorption cross section of the molecule of interest,  $\phi(\lambda, T)$  is the wavelength- and temperature-dependent photolysis quantum yield, and  $\lambda_1$  and  $\lambda_2$  define the wavelength range over which the calculation is carried out. Integration over space and time yields a global and annual average lifetime with respect to photolysis,  $\tau_J$ .

For a molecule destroyed by both chemical reaction and photolysis (and other processes), the overall global atmospheric lifetime,  $\tau_{total}$  can be written as a combination of the global and annual average lifetimes with respect to the various loss processes:

771 
$$1/\tau_{\text{total}} = 1/\tau_{\text{X}} + 1/\tau_{J} (+ 1/\tau_{\text{other}}).$$

As discussed in section 2.4, loss by chemical reaction within the troposphere is dominated by the reactivity of the hydroxyl radical, OH. For water soluble compounds such as perfluorinated esters, uptake by the oceans may also be important [*Kutsuna et al.*, 2005]. Compounds with lifetimes with respect to reaction with OH that are greater than a few years will reach the stratosphere, where destruction via photolysis and reaction with O(<sup>1</sup>D) may also contribute. Fully fluorinated compounds have lifetimes typically of several thousands of years and their loss is dominated by photolysis in the mesosphere and thermosphere, while CFCs

have lifetimes in the range 50-1000 years and are degraded by photolysis and reaction with  $O(^{1}D)$  in the stratosphere [Ravishankara et al., 1993].

The calculation of atmospheric lifetimes is complicated. Concentrations of reacting species show strong temporal and spatial variability, and it may be difficult to be confident of the absolute concentrations of these species. The intensity of solar radiation varies strongly with altitude, and the absorption cross sections and quantum yields may show significant dependence on temperature. There are also chemical feedbacks which can affect the lifetime. Given the spatial and temporal variability of reaction partners and photolysis and the potential for chemical feedbacks, it is necessary to use atmospheric models to accurately determine lifetimes, which adds significantly to the complexity of the lifetime determination [*Prather*, 2007]. There are no unique lifetimes for the shorter lived gases, as their lifetimes depend on the location of emissions and the chemical and physical conditions of the atmosphere. As discussed in section 3.6.3, there are often significant uncertainties associated with atmospheric lifetimes.

#### 3.3 Radiative forcing efficiency

## 3.3.1 Spectrally-varying radiative efficiency

The radiative efficiency calculations carried out here are based on the simple method outlined by *Pinnock et al.* [1995] in which a radiative transfer code is used to derive a wavelength-dependent RE for a unit absorption cross-section. With this method the instantaneous REs can be estimated directly from the absorption spectrum of a molecule without using a radiative transfer model, as explained in section 2.3. *Pinnock et al.* [1995] showed that results from their simple method agreed to within 0.3% with results from a narrowband model. This virtually eliminates the computational time needed and makes it straightforward to perform RE calculations for a large number of compounds. Additionally, when comparing the calculated REs between different compounds, uncertainties related to the absorption spectra are the only factor affecting the comparison, as uncertainties related to the use of different radiative transfer models can be ruled out. The Pinnock method is derived assuming the molecule causing the forcing to be well mixed in the atmosphere. The resulting RE has to be modified to take into account any non-uniformity in the horizontal and vertical distribution; the method by which this is done here is described in sections 3.3.3 and 3.3.4, and is

particularly important for emissions of short-lived gases. In principle, the RE should be calculated (in a similar manner to the lifetime, as discussed in section 3.2) by calculating the forcing locally and averaging in space and time to yield the global and annual average RE.

810

811

812

813

814

815

816

817

818

819

820

821

822

823

824

825

826

827

828

829

830

831

832

833

834

835

836

837

838

839

840

841

The method proposed by *Pinnock et al.* [1995] (plus the lifetime correction) is applicable for all compounds with low atmospheric concentrations and therefore weak absorption, such as the halogenated compounds considered here. When this requirement is met, the compound's radiative forcing per spectral interval is proportional to the product of its absorption cross section and its number column density. *Pinnock et al.* [1995] included a weak absorber with the same cross section at all wavelengths in a narrowband model to calculate the instantaneous, cloudy-sky, RF per unit cross section as a function of wavenumber.

We present here a revised calculation of the instantaneous, cloudy-sky, RF per unit cross section to reflect improvements in the radiative transfer calculations in the period since the *Pinnock et al.* [1995] curve was derived. Figure 5 illustrates the progression from the original to our final revised Pinnock curve. First we employ the same radiative transfer code (the Reading Narrow Band Model (NBM)) as used in *Pinnock et al.* [1995] to reproduce the original Pinnock curve, using the (rather dated) global-mean atmospheric profile presented in that paper – the specification of cloud amount was especially crude. We then recalculated the Pinnock curve, incorporating many minor updates to the NBM and in particular the use of a more modern global-mean atmosphere, based on European Centre for Medium-Range Weather Forecasts (ECWMF) and International Satellite Cloud Climatology Project (ISCCP) data [Freckleton et al., 1998]. Figure 5 (top) shows in particular a decrease in the Pinnock curve in the 800-1200 cm<sup>-1</sup> region, which mostly reflects an improved characterization of cloud (the longwave cloud forcing increased from 12 to 21 W m<sup>-2</sup> between the old and the new global-mean atmosphere). At other wavenumbers, the new and old Pinnock curves agree well. Next, we recalculated the Pinnock curve using area-weighted results using one tropical and two extratropical profiles [Freckleton et al., 1998], rather than a single global-mean profile. The most marked effect (see red curve on Figure 5 (top)) of using the new profiles is an increase in the Pinnock curve between 100 and 500 cm<sup>-1</sup>, which reflects the fact that the extratropical profiles are cooler (moving the peak of the Planck function to lower wavenumbers) and drier. At wavenumbers greater than 800 cm<sup>-1</sup> there are only small differences between the single and three atmosphere curves. Mixing ratios of other wellmixed gases used in the NBM were 389 ppm for  $CO_2$ , 1800 ppb for  $CH_4$  and 323 ppb for  $N_2O$ , reflecting contemporary values.

Since we wanted our new Pinnock curve to be based on a LBL code (as it is inherently more accurate and also at higher spectral resolution than the original (10 cm<sup>-1</sup>) curve) we next generated a Pinnock curve using the Oslo LBL model [*Myhre et al.*, 2006], employing their two (tropical/extratropical) atmosphere approach. Figure 5 (middle) shows a comparison of the NBM and LBL (averaged to 10 cm<sup>-1</sup> resolution) Pinnock curves – there is excellent agreement between the two models. Figure 5 (bottom) shows the final Pinnock curve, using the LBL but now averaged to 1 cm<sup>-1</sup> resolution. The effect of using the improved spectral resolution was found to have a negligible impact (<1-2%) on the RE calculations for most of the compounds presented in section 4. However, for a few compounds, this effect was stronger, as illustrated in Figure 6. The largest effect was for CF<sub>4</sub> because its main absorption band is at the edge of the atmospheric window. For this compound the RE was underestimated by about 8% when using 10 cm<sup>-1</sup> resolution compared to 1 cm<sup>-1</sup> resolution of the LBL Pinnock curve.

An Excel spreadsheet with both the updated 1 and 10 cm<sup>-1</sup> resolution LBL Pinnock curves is available in the supplementary material.

#### 3.3.2 Stratospheric temperature adjustment

Generally, halocarbons warm the lower part of the stratosphere because their strongest absorption bands normally occur in the atmospheric window region. For these wavelengths, in the stratosphere, the extra absorption of upwelling radiation by the halocarbon from the surface and troposphere exceeds the amount of extra radiation emitted by the halocarbon. Hence, there will be an increased heating rate of the stratosphere. When stratospheric temperature adjustment is applied, the increased heating rate leads to a warming of the stratosphere. In the new equilibrium state, the higher stratospheric temperatures lead to an increase in the amount of radiation emitted downwards into the troposphere so that the stratosphere-adjusted forcing is higher than the instantaneous forcing. (The reverse is true for CO<sub>2</sub> forcing, since it acts to cool the stratosphere so that the stratosphere-adjusted forcing is smaller than the adjusted forcing.).

Since the Pinnock et al. function used for calculating REs in this study does not take into account the stratospheric temperature adjustment, we have applied a factor to convert from instantaneous to adjusted forcing. Based on several studies [Forster et al., 2005; Jain et al., 2000; Myhre and Stordal, 1997; Naik et al., 2000; Pinnock et al., 1995], we have increased the calculated instantaneous RE for most compounds by 10% to account for stratospheric temperature adjustment. It should be kept in mind that the effect of stratospheric temperature adjustment can be quite variable for each compound [e.g., *Pinnock et al.*, 1995], particularly for gases which absorb outside the atmospheric window. For a few selected gases (CFC-11, CFC-12, HFC-41 and CF<sub>4</sub>) we have carried out explicit calculations, using the Oslo LBL model, to estimate the ratio between the RE including stratospheric temperature adjustment and the instantaneous RE. For CFC-11 and CFC-12, which have their main absorption bands in the atmospheric window region, the REs were 9.1% and 10.5% higher, respectively, when taking the stratospheric temperature adjustment into account. HFC-41 is a special case because its main absorption band overlaps strongly with ozone and our result from the LBL calculation shows a decrease in RE of 5.0% when accounting for stratospheric temperature adjustment (some of the radiation which would have been absorbed by ozone in the stratosphere is instead trapped by CH<sub>3</sub>F in the troposphere leading to a cooling of the stratosphere). As stated in section 3.3.1, CF<sub>4</sub> absorbs strongly at the edge of the atmospheric window (near 1,300 cm<sup>-1</sup>), and our results show an increase in RE of 10.5% due to stratospheric temperature adjustment for this compound. Based on these results and on previous literature [e.g., Myhre and Stordal, 1997; Pinnock et al., 1995] we consider a 10% increase a good approximation for most gases.

894

895

896

897

898

899

900

901

902

872

873

874

875

876

877

878

879

880

881

882

883

884

885

886

887

888

889

890

891

892

893

#### 3.3.3 Simulations of atmospheric distributions and lifetimes

The effect of non-uniform vertical profiles on radiative forcing has been investigated in several studies [e.g., Freckleton et al., 1998; Jain et al., 2000; Naik et al., 2000; Sihra et al., 2001], and is described in section 2.4. To further investigate and reduce the uncertainties associated with the correction factors for compounds which are mainly lost in the troposphere through reaction with OH, and normally have a relatively short lifetime, a number of simulations have been carried out with a 3-D Chemistry-Transport Model (CTM) in combination with a radiative transfer model. The models chosen for this purpose are the

global offline Oslo CTM2 model [Berglen et al., 2004; Søvde et al., 2008] and the Oslo broadband radiative transfer model [Myhre and Stordal, 1997].

903

904

905

906

907

908

909

910

911

912

913

914

915

916

917

918

919

920

921

922

923

924

925

926

927

928

929

930

931

932

933

934

The setup of the CTM simulations is similar to the studies of Acerboni et al. [2001] and Sellevag et al. [2004b] where a total of 6 short-lived halocarbons were implemented in the Oslo CTM2. Here we have implemented the following 9 halocarbons in the model, which were chosen to represent a range of atmospheric lifetimes (~10 days to 5.2 years): HFC-1234yf (CF<sub>3</sub>CF=CH<sub>2</sub>), HFE-356mmz1 (CH<sub>3</sub>OCH(CF<sub>3</sub>)<sub>2</sub>), HFE-254eb2 (CH<sub>3</sub>OCHFCF<sub>3</sub>), HFC-161 (CH<sub>3</sub>CH<sub>2</sub>F), CH<sub>3</sub>Br, HCFC-123 (CF<sub>3</sub>CCl<sub>2</sub>H), HFC-152a (CH<sub>3</sub>CHF<sub>2</sub>), HFC-143 (CH<sub>2</sub>FCHF<sub>2</sub>) and HFC-32 (CH<sub>2</sub>F<sub>2</sub>). The compounds were assumed to only react with the hydroxyl radical (OH), which is the main loss for most short-lived halocarbons, and their reaction rate coefficients were taken from the NASA/JPL database [Sander et al., 2010]. In a reference simulation, the geographical distribution of the emissions was the same as for CFC-11 [McCulloch et al., 1994], while in a sensitivity simulation the emission distribution was set the same as for black carbon (BC) [Bond et al., 2004; van der Werf et al., 2006] with the purpose of studying the impact of having a larger share of the emissions occurring at lower latitudes near the equator. It should be kept in mind that the sensitivity simulation is considered a rather extreme case as halocarbons are industrial chemicals and their emission distribution is more likely to follow that for other industrial compounds, such as CFC-11, than for species like black carbon which has significant non-industry related sources. In both cases, the anthropogenic emissions of other compounds were taken from the RETRO [2006] database for year 2000. The model was run repeatedly for the meteorological year 2000 with uniform annual emissions, and a sufficient amount of spin-up time was allowed to obtain chemical steady-state at levels that yield globally averaged surface mixing ratios of approximately 1 ppb. The model has been driven by meteorological forecast data from the ECMWF IFS model cycle 36, as explained by Søvde et al. [2011], and run at a horizontal resolution of approximately  $2.8^{\circ} \times 2.8^{\circ}$  (T42) and 60 vertical layers distributed from the surface to 0.1 hPa.

Figure 7 shows the calculated atmospheric distribution of HFC-161, which has a lifetime with respect to OH of 84 days in the reference simulation. In the sensitivity simulation with a "BC-like" emission distribution, the global burden is smaller, and hence the lifetime is shorter (71 days), due to the higher concentrations of OH found near the tropics. Due to the relatively short lifetime of HFC-161, the distribution of surface concentrations

reflects the regions of emissions quite well (Figure 7, top). The reference simulation reveals large concentrations in the northern hemisphere, and particularly over the industrial areas in US and Europe, while the sensitivity simulation shows a weaker gradient between the hemispheres, and with surface maxima over Southeast Asia and the biomass burning regions in Africa. Furthermore, the vertical profile is different between the two runs with a stronger decay of mixing ratios with altitude in the simulation with "CFC-11-like" emission distribution compared to the simulation with "BC-like" emission distribution.

The Oslo CTM2 simulated distributions of the halocarbons have been used for RF calculations with the Oslo broadband model [Myhre and Stordal, 1997]. In the radiative transfer calculations we also use 60-layer meteorological data from the ECMWF-IFS model, but with a reduced horizontal resolution of  $5.6^{\circ} \times 5.6^{\circ}$  (T21). Annual mean cloudy-sky RF (with stratospheric temperature adjustment included) has been calculated using the radiative transfer model (based on monthly-mean data), which has been run both with a constant global and annual mean vertical profile (so that the global and annual mean surface mixing ratio is used at all heights, latitudes, longitudes and times), and with the monthly mean atmospheric distribution calculated by Oslo CTM2. A quantification of the importance of using realistic vertical profiles rather than constant profiles was then obtained by calculating the fractional difference between the resulting RF from the two radiative transfer simulations.

In addition to the model runs explained above, simulations were carried out with the Oslo LBL model to quantify the effect of a non-uniform vertical profile for compounds which are mainly lost by photolysis in the stratosphere. Such compounds (i.e., mainly CFCs and halons) are well-mixed in the troposphere but their mixing ratios decay with increasing altitude in the stratosphere. Hence, they have a different vertical profile, and their atmospheric concentrations are also much less influenced by the horizontal distribution of emissions, than the compounds with lifetimes governed by OH destruction. The three compounds Halon-1211, CFC-11 and CFC-12 were chosen for the LBL model experiments because they span a relatively wide range of lifetimes (16 to 100 years [WMO, 2011]), and because vertical profiles of these compounds were available from CTM simulations. The vertical profiles of the two CFCs were taken from Myhre and Stordal [1997] while the Halon-1211 profiles were fit to the annual mean output from Oslo CTM2, averaged separately over the tropics and the extra-tropics. For all three compounds the mixing ratios were assumed to decrease exponentially above the tropopause in the radiation code.

To validate the vertical profiles of CFC-11 mixing ratio used in the Oslo radiative transfer model (results presented in section 3.3.4), we have compared these data with a recently derived climatology from the MIPAS satellite instrument [Hoffmann et al., 2008] in Figure 8. This MIPAS data set has been thoroughly validated against several other satellite observations, as well as airborne and ground-based measurements [Hoffmann et al., 2008]. For comparison the CFC-11 vertical profiles from the Oslo CTM2 simulations are also included in Figure 8, although these results are not used here directly (only the Halon-1211 profiles were used, as explained above). It should be noted that the mixing ratios of CFC-11 calculated by Oslo CTM2 are largely governed by the top and bottom boundary conditions taken from the Oslo 2-D stratospheric chemistry model [Stordal et al., 1985] which is based on WMO recommendations. CFC-11 has a relatively long lifetime of about 45 years [WMO, 2011] and its main loss is photolysis in the stratosphere. As a consequence, CFC-11 is wellmixed throughout the troposphere, while its concentration decreases with height in the stratosphere. This reduction with height has a major impact on the compound's radiative forcing [e.g., Freckleton et al., 1998], and it is therefore important that the models include realistic vertical profiles. The comparison between the Oslo radiation code and the Oslo CTM2 model shows that the assumption of an exponential decay of CFC-11 mixing ratios above the tropopause in the radiation code works relatively well (Figure 8). Furthermore, the CFC-11 vertical profiles employed in both models are in relatively good agreement with the climatology derived from MIPAS observations. Some discrepancies can be seen, especially near the tropical tropopause region, but it should be noted that differences between climatologies derived from satellite observations are also evident [Hoffmann et al., 2008] (their Figure 11), and that tropical stratospheric measurements of CFC-11 is a major source of uncertainty [Minschwaner et al., 2012] (see also their Figure 6). The vertical profiles are shown separately for the tropics (30°S-30°N) and the extra-tropics (90°S-30°S and 30°N-90°N) in Figure 8 due to the different tropopause heights. These two regions are also the same as used in the two-atmosphere setup of the Oslo radiation code.

994

995

996

997

998

967

968

969

970

971

972

973

974

975

976

977

978

979

980

981

982

983

984

985

986

987

988

989

990

991

992

993

## 3.3.4 Fractional correction versus lifetime

Results from the experiments described in section 3.3.3 are shown in Figure 9 together with results from previous studies [Acerboni et al., 2001; Jain et al., 2000; Sellevag et al., 2004b]. Our calculations differ from previous studies in three important respects. First, a number of

hypothetical "HFC-1234yf-like" molecules were studied. These compounds all had the infrared spectrum of HFC-1234yf but had different atmospheric lifetimes ranging from approximately 1 day to 7 years. Variation of the lifetime within the model was achieved by assuming rate coefficients for reaction with OH radicals in the range  $4.3 \times 10^{-15} - 3.5 \times 10^{-11}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The results are shown by the filled circles in Figure 9. Second, the literature values for the rate coefficients for reactions of OH radicals with the remaining 8 compounds were used, but this time we did not use the actual absorption spectra for the compound for the radiative transfer calculations. Instead, we chose to span the vertical axis, representing the fractional correction, by repeating the RE calculation 6 times for each gas, using different absorption bands which were either within or at the borders of the atmospheric window region. More specifically, these bands were centered at wavenumbers of 631 (absorption band of CF<sub>4</sub>), 714 (C<sub>2</sub>F<sub>6</sub>), 948 (SF<sub>6</sub>), 1116 (C<sub>2</sub>F<sub>6</sub>), 1250 (C<sub>2</sub>F<sub>6</sub>), and 1283 (CF<sub>4</sub>) cm<sup>-1</sup>. Figure 9 shows the fractional correction for the mean (filled squares) and standard deviation (vertical lines) of these 6 bands for each of the 8 gases. It should be noted that the fractional correction depends primarily on lifetime, but to some extent also on the position of the absorption bands; absorption bands inside the atmospheric window region has the weakest correction. Third, the correction factors for compounds with stratospheric photolysis as the primary loss mechanism have been calculated using a two-atmosphere approach, and are shown by the red symbols in Figure 9.

Several interesting features can be seen in Figure 9. The lifetimes calculated by the Oslo CTM2 are shorter when the geographical distribution of emissions was "BC-like" rather than "CFC-11-like", especially for lifetimes shorter than approximately 0.5 years. This is not surprising as the levels of OH are highest near the tropics (where a large share of the "BC-like" emissions takes place) because of higher humidity and more incoming solar radiation at low latitudes. Another interesting feature is that the fractional correction is weaker (i.e., closer to 1) in the run with "BC-like" emissions than the reference run with "CFC-11-like" emissions for lifetimes longer than about 0.003 years, or 1 day, while it is stronger for lifetimes shorter than 1 day. One reason for this is the higher RF for well-mixed greenhouse gases near the equator than at higher latitudes, because of higher temperatures [Shine and Forster, 1999].

For the compounds with similar lifetimes as in *Jain et al.* [2000], the fractional corrections in our reference simulation roughly agree with their corrections, except for the

compound in Jain et al. [2000] that has a lifetime of 0.25 years and a fractional correction of 0.61, which is closer to our results from the simulation with "BC-like" emission distribution. Part of the reason is probably that Jain et al. [2000] used a 2-D model with geographically constant surface mixing ratios, while we use a 3-D model with an assumed (and likely more realistic) emission distribution. In fact, another Oslo CTM2 sensitivity simulation with surface mixing ratios fixed at 1 ppb globally (results not shown) gives a very similar vertical profile and fractional correction factor as the simulation with "BC-like" emission distribution. Interestingly, the three compounds studied in Sellevag et al. [2004b] have smaller fractional correction factors than our results, and they do not always show an increase of fractional correction proportional with the lifetime. As the models and simulation setup are quite similar to this study, the differences can probably be attributed to the absorption spectra, which are different for the various compounds. Figure 9 shows that the spectral position has some influence on the fractional correction and causes a maximum deviation from the mean of ±10%. On the other hand, the results from Acerboni et al. [2001] show slightly higher fractional correction factors than in our study, presumably because they used a constant surface mixing ratio all over the globe instead of an assumed emission distribution.

Sihra et al. [2001] derived an empirical curve fit (see grey curve in Figure 9) to the values in Jain et al. [2000] and this has been used in later studies [e.g., Bravo et al., 2011a; Gohar et al., 2004]. Their fit is given by  $f(\tau) = 1 - 0.241 \tau^{-0.358}$ , where f is the fractional correction and  $\tau$  is the lifetime in years for lifetimes greater than 0.25 years. Here we have derived two new empirical curve fits, one for compounds dominated by loss in the troposphere through OH reaction, and one for compounds dominated by loss through stratospheric photolysis. In the latter case we have used a similar approach as Sihra et al. [2001] and derived an exponential fit, but this time only results from explicit LBL calculations discussed in section 3.3.3 have been used. We further assumed that f = 1 for very long lifetimes. The resulting exponential function is given by

1057 
$$f(\tau) = 1 - 0.1826 \,\tau^{-0.3339},\tag{1}$$

and is shown in Figure 9 by the red curve for  $10 < \tau < 10,000$  years. Equation (1) has been used to calculate lifetime-corrected RE for some of the compounds presented in section 4. In the case for compounds dominated by tropospheric OH loss, the empirical fit was restricted to results from 3-D model experiments where a "CFC-11-like" emission distribution was assumed. This means that the results from *Acerboni et al.* [2001] and the 2-D model of *Jain et* 

al. [2000] were not considered when deriving the fit (but still shown in Figure 9 for comparison), while the results of *Sellevag et al.* [2004b] were included along with results from the present study. As we now want to include compounds with very short lifetimes, the empirical curve fit was constrained to form an *S*-shaped curve in Figure 9 with the following formula:

$$---, (2)$$

where a, b, c and d are constants with values of 2.962, 0.9312, 2.994, and 0.9302, respectively. The curve was further constrained to give f = 0 for very short lifetimes and f = 1 for very long lifetimes. The resulting S-shaped function is shown in Figure 9 by the dark blue curve for  $10^{-4} < \tau < 10^4$  years, and has been used to calculate lifetime corrected RE values for most of the compounds presented in section 4.

# 3.4 Discussion of impact of functional groups on spectra/radiative forcing

The infrared spectra of polyatomic molecules are made up of a number of vibrational bands, each containing rotational fine structure that may, or may not, be resolved. For a non-linear molecule containing N atoms, there are 3N-6 normal vibrations, although this number of bands may not be visible in the spectrum. Bands may overlap with each other, may lie outside of the spectral range of the measurements, may be forbidden or the vibrational mode may be degenerate. For example, the tetrahedral molecule,  $CF_4$  has a total of 9 normal vibrations, but only one band is observed in its infrared spectrum (as illustrated in Figure 3). The molecule has stretching and a variety of bending vibrations, but the bending vibrations occur at lower wavenumber (ca.  $400 \text{ cm}^{-1}$ ) than can usually be observed in an infrared measurement. At the same time, as it contains four C-F bonds, it is expected to have four stretching normal vibrations. A simple analysis of the symmetry properties of the stretching modes shows that one is the totally symmetric (A<sub>1</sub>) stretch, which cannot be accessed in an allowed infrared transition. The other three vibrations turn out to be three-fold degenerate (symmetry species  $T_2$ ) and give rise to a single allowed transition at around 1280 cm<sup>-1</sup>. Molecules with lower symmetry will exhibit more bands, as degenerate vibrations are less likely to occur.

In the case of  $CF_4$ , it is clearly possible to identify the  $T_2$  vibration as a C-F stretching vibration, which is a specific example of a group vibration. In general, a normal mode of

vibration involves movement of all the atoms in a molecule and it is not always possible to assign transitions to particular group vibrations. From the perspective of determining radiative efficiencies, the majority of spectral features of importance occur in the region between 1500 and 500 cm<sup>-1</sup>. This region is called the *fingerprint region* and usually contains a complicated series of absorptions, and it is often difficult to clearly identify group vibrations within this region. Nevertheless, some features may be identified. Molecules containing H atoms will have C-H stretching vibrations that produce transitions in the 3000 cm<sup>-1</sup> region of the spectrum, well outside of the region of interest here. On the other hand, C-H bending vibrations are expected at around 1400 cm<sup>-1</sup> and are a common feature of many HFCs [e.g., Sihra et al., 2001]. We have already seen that C-F stretching gives rise to a band at 1280 cm<sup>-1</sup>, and bands in this region are observed in a wide range of fluorine-containing compounds [e.g., Bravo et al., 2010b; Sihra et al., 2001]. However, it should be noted that the electronwithdrawing properties of neighboring groups can have a significant influence on band position. While molecules with a relatively high fluorine content show a C-F stretching feature at around 1200-1300 cm<sup>-1</sup>, HFC-41 (CH<sub>3</sub>F) shows only a feature at 1000-1100 cm<sup>-1</sup>, which corresponds to the expected position for a C-F group vibration given in standard spectroscopy textbooks such as Hollas [2004]. For this reason, care must be used when assigning observed bands to individual group vibrations in the spectra of heavily halogenated molecules.

1112

1113

1093

1094

1095

1096

1097

1098

1099

1100

1101

1102

1103

1104

1105

1106

1107

1108

1109

1110

1111

# 3.5 Description of metrics

- The motivation for the choice of metrics adopted here (GWP and GTP) was given in section
- 1115 2.5.

# 1116 3.5.1 The Global Warming Potential (GWP)

- 1117 The Global Warming Potential (GWP) is based on the time-integrated radiative forcing due to
- 1118 a pulse emission of a unit mass of gas. It can be given as an absolute GWP for gas i (AGWP<sub>i</sub>)
- 1119 (usually in W m<sup>-2</sup> kg<sup>-1</sup> year) or as a dimensionless value by dividing the AGWP<sub>i</sub> by the
- 1120 AGWP of a reference gas, normally CO<sub>2</sub>. Thus, the GWP is defined as:

1121

A user choice is the time horizon (*H*) over which the integration is performed. IPCC has usually presented GWP for 20, 100 and 500 years and the Kyoto Protocol has adopted GWPs for a time horizon of 100 years.

For a gas i, if  $A_i$  is the RE,  $\tau_i$  is the lifetime (and assuming its removal from the atmosphere can be represented by exponential decay), and H is the time horizon, then the integrated RF up to H is given by:

This is an approximation that holds for long-lived gases but is less accurate for shorter lived gases whose lifetimes depend on location of emissions and physical and chemical conditions of the atmosphere. *Prather* [2007] developed a concept of atmospheric chemistry as a coupled system across different trace species with transport between different regions and radiative feedbacks. Due to these processes a perturbation to one species in one location will lead to a global response on a wide range of time scales, often involving many other chemical components. The chemistry-transport system can be linearized and represented by eigenvalue decomposition [*Prather*, 2007] that are perturbation patterns of trace gas abundances, also known as chemical modes. Any perturbation to atmospheric composition can be expressed as a sum of chemical modes, each with a fixed decay term.

The AGWP for  $CO_2$  is more complicated, because its atmospheric response time (or lifetime of a perturbation) cannot be represented by a simple exponential decay. This situation arises because  $CO_2$  is absorbed into the various regions of the oceans (surface water, thermocline, deep ocean) on a range of different timescales. As a consequence, following a pulse emission of  $CO_2$  the perturbation of the atmospheric concentration of  $CO_2$  remains significant (>20%) even after 1000 years. The decay of a perturbation of atmospheric  $CO_2$  following a pulse emission at time t is usually approximated by *Joos et al.* [2013]:

**—** 

where the parameter values are  $a_0$ =0.2173,  $a_1$ =0.2240,  $a_2$ =0.2824,  $a_3$ =0.2763,  $\alpha_1$ =394.4,  $\alpha_2$ =36.54 and  $\alpha_3$ =4.304. The parameter values for the impulse response function (IRF) are based on a recent multi-model study [*Joos et al.*, 2013], and these values have been used here. For comparison the parameter values from *Forster et al.* [2007] were  $a_0$ =0.217,  $a_1$ =0.259,  $a_2$ =0.338,  $a_3$ =0.186,  $\alpha_1$ =172.9,  $\alpha_2$ =18.51 and  $\alpha_3$ =1.186 (see footnote a, Table 2.14 in *Forster et al.* [2007]).

1153	Then the AGWP $_{CO2}$ can be given as
1177	Then the ACTW Poor can be given as
1100	Then the Tio Wil (1), can be given as

 $- \qquad (3)$ 

- Note that the parameters used in calculating the AGWP are dependent on the choice of background state, but it is convention to use present-day conditions. While the models used to calulate IRF for CO<sub>2</sub> usually include climate carbon cycle feedbacks, usually no climate
- feedbacks are included for the non-CO<sub>2</sub> gases.

1159

# 1160 3.5.2 The Global Temperature change Potential (GTP)

- 1161 GTP is presented as an alternative to the GWP and uses the change in global mean
- 1162 temperature for a chosen point in time as the impact parameter. While GWP is a metric
- integrative in time, the GTP is based on the temperature change per unit emissions for a
- selected year, t. As for the GWP, the impact of  $CO_2$  is normally used as reference, thus,
- 1165  $GTP(t)_i = AGTP(t)_i / AGTP(t)_{CO2} = \Delta T(t)_i / \Delta T(t)_{CO2},$
- where AGTP (K kg<sup>-1</sup>) is the absolute GTP. The assumed lifetime of CO<sub>2</sub> is the same as that
- given for the GWP in section 3.5.1.
- In the calculations here, we represent the thermal inertia of the climate system
- following the method used by Fuglestvedt et al. [2010]. This includes a representation of the
- deep ocean as well as the ocean mixed layer based on a temperature response function with
- two time-constants derived from climate model results [Boucher and Reddy, 2008]. The
- derived GTPs are dependent on the assumed value of climate sensitivity [Shine et al., 2005a;
- 1173 Shine et al., 2007], which is implicit in the Boucher and Reddy response functions, and is
- 1174 equal to about 1 K (W m<sup>-2</sup>)<sup>-1</sup>.

1175

1176

# 3.5.3 The reference gas CO<sub>2</sub>

- 1177 The metric values need updating due to new scientific knowledge about various properties,
- but also due to changes in lifetimes and radiative efficiencies caused by changing atmospheric
- 1179 background conditions.
- For the reference gas CO<sub>2</sub>, such changes (i.e., in AGWP<sub>CO2</sub> and AGTP<sub>CO2</sub>) will affect
- all the other gases. With increasing CO<sub>2</sub> levels in the atmosphere the marginal radiative

forcing is reduced, while at the same time the ocean uptake is reduced and airborne fraction increased. These changes (working in opposite directions) lead to changes in AGWP<sub>CO2</sub> and AGTP<sub>CO2</sub>. Updates to AGWP<sub>CO2</sub> are often presented in IPCC and WMO Ozone assessments.

1185

1186

1189

1190

1191

1192

1193

1194

1195

1196

1197

1198

1199

1200

1201

1202

1203

1204

1205

1206

1207

1208

1209

1210

1211

1212

The radiative forcing for CO<sub>2</sub> can be approximated using the expression based on radiative transfer models [*Myhre et al.*, 1998]:

1187  $RF = \alpha \ln((C_0 + \Delta C)/C_0)$ , where  $\alpha = 5.35$  W m<sup>-2</sup> and C is the atmospheric mixing ratio of CO<sub>2</sub>.

Based on this and for a small  $\Delta C$ , the radiative efficiency of  $CO_2$  can be approximated. The RE of  $CO_2$  changed from 0.0147 W m<sup>-2</sup> ppm<sup>-1</sup> to 0.0141 W m<sup>-2</sup> ppm<sup>-1</sup> when atmospheric  $CO_2$  levels increased from 364 to 378 ppm, as used by IPCC Third Assessment Report (TAR) [IPCC, 2001] and IPCC Fourth Assessment Report (AR4) [IPCC, 2007], respectively. At current  $CO_2$  levels of ~391 ppm [WMO/GAW, 2012], a 1 ppm change in the  $CO_2$  concentration ( $\Delta C$ =1 ppm) gives a radiative efficiency for  $CO_2$  of 0.013665 W m<sup>-2</sup> ppm<sup>-1</sup>.

The airborne fraction and the impulse response function have also been updated and Figure 10 shows the IRFs from the four IPCC assessment reports together with the updated IRF from Joos et al. [2013]. In this review we have updated the AGWP<sub>CO2</sub> and AGTP<sub>CO2</sub> values based on the new IRF and RE of CO<sub>2</sub>. The latter value is converted from per ppb to per kg by multiplying with  $(M_A/M_{CO2}) \times (10^9/T_{\rm M})$ , where  $M_A$  and  $M_{CO2}$  are the molecular weight of dry air (28.97 g mol<sup>-1</sup>) and CO<sub>2</sub> (44.01 g mol<sup>-1</sup>), respectively, and T<sub>M</sub> is the mean dry mass of the atmosphere  $(5.135 \times 10^{18} \text{ kg} [Trenberth and Smith, 2005])$ . The RE of CO<sub>2</sub> given per mass is then  $1.75 \times 10^{-15}$  W m<sup>-2</sup> kg<sup>-1</sup>, and the resulting AGWPs for CO<sub>2</sub> (using Equation 3) are  $2.495 \times 10^{-14}$ ,  $9.171 \times 10^{-14}$  and  $32.17 \times 10^{-14}$  W m<sup>-2</sup> vr (kgCO<sub>2</sub>)<sup>-1</sup> for time horizons of 20, 100 and 500 years, respectively. These values are higher than the AGWP<sub>CO2</sub> used in AR4 (calculated based on the IRF and RE of CO<sub>2</sub> given in AR4) by approximately 1.4, 6.0 and 13%, respectively, mainly due to the change in IRF. As a consequence the GWP<sub>100</sub> values presented for all compounds in section 4 will be about 6% lower than if the AGWP<sub>CO2</sub> from AR4 was used. The AGTP<sub>CO2</sub> values used in the calculations of GTPs in section 4.2, have been updated (using Equation A3 in Fuglestvedt et al. [2010]) to  $6.841 \times 10^{-16}$ ,  $6.167 \times 10^{-16}$ ,  $5.469 \times 10^{-16}$  K (kgCO<sub>2</sub>)<sup>-1</sup> for time horizons of 20, 50 and 100 years, respectively. As for AGWP<sub>CO2</sub> the new AGTP<sub>CO2</sub> values take into account the updated IRF and radiative efficiency of CO<sub>2</sub>, while the remaining parameters are taken from Fuglestvedt et al. [2010].

# 3.6 Uncertainty – sensitivity to assumptions

# 3.6.1 Absorption cross-sections

Uncertainties related to the measurements of IR absorption spectra are dependent on many factors, and can differ for each compound. Some compounds have been subject to extensive laboratory measurements by several groups, such as for HCFC-22 [Ballard et al., 2000b] and HFC-134a [Forster et al., 2005], while others may lack reliable experimental cross-section data. Typical sources of uncertainties related to spectra include, but are not limited to, temperature and pressure for the measurement and in the sample, spectral range and resolution in the measurement, purity of sample, spectrometer and methods used, and noise in the measurements. A comprehensive intercomparison of laboratory measurements of absorption spectra was reported by Ballard et al. [2000b] for HCFC-22. They examined a range of sources of uncertainties and identified a limited set of aspects, related both to sample and photometric uncertainty sources, which should be given special attention when measuring other molecules. Overall, the total error in the absorption cross-section measurements for each of the five laboratory groups considered by Ballard et al. [2000b] were generally less than 5% and for the most part in the range 3-5%.

Integrated absorption cross sections from theoretical calculations are often in good agreement with experimentally determined values; for example, *Bravo et al.* [2010b] report theoretical integrated absorption cross sections for a range of PFCs that are within 5% of the experimentally determined values. Because band overlap often makes it difficult to compare individual vibrational bands, agreement at this level may be somewhat worse than for the total integrated cross sections. As discussed in section 3.1.2, theoretical calculations generally provide infrared absorption band positions that differ systematically from those observed experimentally. These differences are wavenumber dependent and are usually only a few percent, but because band position is so important in determining radiative efficiencies, corrections for these differences are usually made.

The absorption spectra used in this study have for the most part been used as reported in the literature when performing the radiative forcing calculations. However, each spectrum has been the subject of a visual inspection and in some cases it was necessary to remove noise around the baseline. As the noise often does not average out to precisely zero, inclusion of

noise occurring outside the absorption bands may lead to biases in the RE calculations. Furthermore, for some compounds measurements were often available for a number of different temperatures and pressures, particularly for the HITRAN and GEISA databases. When this was the case, we used the data for which temperature and pressure were closest to room temperature, 296 K, and surface pressure, 760 Torr. *Forster et al.* [2005] have shown that variation of the diluent pressure over the range 0-740 Torr and temperature over the range 190-296 K has no discernible (<5%) effect on the integrated absorption band intensities of HFC-134a. To sum up, we estimate an uncertainty of 5 and 10% for the experimental and ab initio absorption cross-sections, respectively.

# 3.6.2 Radiative forcing calculations

Past studies estimating halocarbon radiative forcings have differed significantly for some compounds. For instance, a recent RE estimate of the very potent greenhouse gas sulphur hexafluoride (SF<sub>6</sub>) (0.68 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Zhang et al.*, 2011a] was more than 30% higher than the IPCC AR4 estimate (0.52 W m<sup>-2</sup> ppb<sup>-1</sup>). As noted in section 3.6.1, differences can arise due to uncertainties related to the absorption cross-sections, but a large part of the uncertainties is usually related to the radiative forcing calculations.

Multi-model studies have proved particularly useful in assessing and reducing uncertainties in the RF calculations. *Forster et al.* [2005] applied six detailed radiative transfer models (four line-by-line models and two narrowband models) and reduced the uncertainty in the radiative forcing of HFC-134a, a compound with a RE estimate that had differed significantly in the previous studies. They also concluded that for this compound the uncertainties arising from the RF calculations were larger than those caused by using different absorption cross-sections - up to 10 and 7%, respectively. Similarly, *Gohar et al.* [2004] obtained differences of less than 12% when using two different radiative transfer models to calculate REs of four compounds which had differed significantly in the past literature.

The assumptions related to RF calculations includes the choice of radiation scheme, temporal and spatial averaging, cloud data, background temperature and concentrations, tropopause height, stratospheric temperature adjustment, and accounting for non-uniform vertical profile. A wide range of radiative transfer schemes exist, each varying in complexity. Broadband schemes are among the simplest and are often used in General Circulation Models

(GCMs) due to the heavy computational requirements of such models. The intercomparison study of Collins et al. [2006] showed that there are often large differences in the calculated radiative forcing by well-mixed greenhouse gases between the various GCM schemes, and between the GCM schemes and the much more detailed and computationally expensive lineby-line (LBL) codes. However, the LBL codes were in excellent agreement with each other, and this type of code has previously been found to agree well with observations, at least in the spectral region between 800 and 2600 cm<sup>-1</sup> [Tjemkes et al., 2003], which covers the whole atmospheric window. Similarly, Forster et al. [2011] generally found agreement within 5% for four longwave LBL codes (slightly larger range for shortwave LBL codes) in an intercomparison study under clear sky conditions for various cases with changes in GHG concentrations, whereas differences were substantially larger for radiative transfer codes used in GCMs. One exception for the agreement between the LBL codes was for changes in stratospheric water vapor [Maycock and Shine, 2012]. In a recent study by Oreopoulos et al. [2012], a LBL model was validated against several high-resolution spectral measurements and used as reference when comparing a number of different LBL and GCM radiative transfer codes. They concluded that the longwave radiative transfer schemes were generally in agreement with the reference results, and that the current generation schemes perform better than the GCMs from two decades ago [Ellingson and Fouquart, 1991]. The fact that we apply a detailed LBL model, should lead to less uncertainty compared to if a narrowband or broadband code was used. In Forster et al. [2005], the estimated contribution to total RF uncertainty for HFC-134a due to radiative transfer scheme was taken to be 3%. Here, we consider this value to be too optimistic and estimate an uncertainty of ~5%. We underscore that this uncertainty is for detailed radiative transfer codes and codes which have been through careful validation in intercomparison studies such as Forster et al. [2005] and does not apply to radiative transfer codes traditionally used in GCMs.

1275

1276

1277

1278

1279

1280

1281

1282

1283

1284

1285

1286

1287

1288

1289

1290

1291

1292

1293

1294

1295

1296

1297

1298

1299

1300

1301

1302

1303

1304

1305

1306

Different methodologies in how clouds are treated lead to additional uncertainties in radiative transfer models [e.g., *Gohar et al.*, 2004]. Clouds lead to reduced upward irradiance and therefore the cloudy-sky radiative forcing is normally about 25-35% lower than the clear-sky RF [*Jain et al.*, 2000]. Inter-model differences of up to 10% in the cloud radiative effects were found by *Oreopoulos et al.* [2012], while *Forster et al.* [2005] estimated an additional uncertainty of about 5% in the RE of HFC-134a due to the inclusion of clouds. The detailed radiative transfer codes used in *Forster et al.* [2005] all had a global-mean outgoing longwave

radiative flux at the top of the atmosphere close to observations and they span the range of realistic longwave cloud radiative effects [*Kiehl and Trenberth*, 1997; *Trenberth et al.*, 2009].

The effect of spectral overlap is important, including in the atmospheric window where most of the halocarbons absorb. Spectral overlap with H<sub>2</sub>O is the most important for most compounds, and according to Pinnock et al. [1995] and Jain et al. [2000], removing all water vapor lead to increases in cloudy-sky instantaneous RF typically in the range ~10-30%. However, there is less than 1% increase when reducing the water vapor by 10% [Pinnock et al., 1995], indicating that the uncertainty induced by spectral overlap is negligible. On the other hand, omitting N<sub>2</sub>O and CH<sub>4</sub>, which was common in some models, could lead to substantially larger errors as they increase the instantaneous RF by about 10% for some compounds [Pinnock et al., 1995]. In Forster et al. [2005], one model was used to test the effect of a 0.2 K uncertainty in surface temperature and of using two different climatologies for water vapor and pressure, and found approximately 1 and 2% differences in the radiative forcings, respectively. Previous studies have also assessed uncertainties associated with spectroscopic measurements in new releases of HITRAN data of the greenhouse gases H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, and CH<sub>4</sub> [Kratz, 2008; Pinnock and Shine, 1998]. In general, they found that improvements in absorption spectra for these compounds during the preceding couple of decades had a relatively small impact on radiative forcing estimates.

Another factor influencing the radiative forcing estimates is the definition of the tropopause (recall from section 2.2 that the radiative forcing is normally defined at the tropopause). Previous studies have highlighted the role of choosing an appropriate tropopause height, and found differences up to 10% in the global mean instantaneous RF when testing various tropopause definitions [Forster et al., 2005; Freckleton et al., 1998; Myhre and Stordal, 1997]. The error when using more than one vertical profile to represent the global atmosphere is lower, and we have estimated this uncertainty to be ~5%. Furthermore, the effect of global and annual averaging may lead to additional errors due to non-linearities in the radiative forcing calculations. For well-mixed gases, Myhre and Stordal [1997] found only small differences (less than 1%) in RF due to temporal averaging, while spatial averaging to one global mean profile induced errors up to 10%, partly due to the strong sensitivity to tropopause height for the halocarbons. However, the use of three profiles representing the tropics and the extra-tropics of each hemisphere was found sufficient by

*Freckleton et al.* [1998]. The RF calculations presented in this study use two or three profiles, representing the tropics and the extra-tropics (see section 3.3.1).

As explained in section 3.3.2, stratospheric temperature adjustment typically leads to an increase in cloudy-sky RF for the halocarbons of typically about 10%. *Forster et al.* [2005] have provided an estimate of the contribution to the RF uncertainty arising from this factor, namely ~4%, based on the results of four different radiative transfer models. The two models in *Gohar et al.* [2004] differed by a maximum of 3 percentage points when calculating the increase in RF due to stratospheric temperature adjustment for four different HFCs.

One of the largest sources of uncertainties in RF estimates is the effect of a non-uniform vertical profile caused mainly by reaction with OH in the troposphere and photolysis in the stratosphere (section 3.3.4). *Sihra et al.* [2001] estimated this uncertainty to be in the order of 5-10%, while we note from Figure 9 that this number is dependent on the lifetime. The fractional correction factors for compounds that are reasonably well-mixed in the atmosphere, with lifetimes typically longer than about 5 years, show less spread than the compounds with shorter lifetimes. One reason for the larger spread is differences caused by the various absorption bands, but is also due to uncertainties related to the geographical distribution of emissions which influence both the fractional correction and the atmospheric lifetime. However, it should be stressed here that for the sensitivity simulation using the "BC-like" emission distribution (section 3.3.3) is considered an extreme case and should be given less weight. Based on previous literature and the new simulations performed in this study, we estimate an uncertainty of ~5% for compounds with lifetimes longer than about 5 years and ~20% for compounds with shorter lifetimes.

Each source of uncertainty and their estimated contribution to the total RE uncertainty is listed in Table 1. The uncertainty estimates are based on available published studies and on subjective judgment, as discussed above. Using the root-sum-square (RSS) method, we find an overall uncertainty due to radiative forcing calculations (including uncertainties in the experimental absorption spectra described in section 3.6.1) of approximately 13% for compounds with lifetimes longer than around 5 years. When using properly corrected theoretical absorption spectra the total uncertainty increases to around 15%. We estimate the overall uncertainty to be valid for a 5 to 95% (90%) confidence range, which is the same confidence range used for the radiative forcing values in IPCC AR4. Our estimate of 13% (valid for experimental cross-sections) is only slightly larger than the 10% uncertainty

reported for long-lived greenhouse gases in AR4. Due to the large uncertainties in the fractional correction, the total RF uncertainty increases to ~23% for compounds with lifetimes shorter than around 5 years. It should also be noted that the radiation schemes used to produce our updated "Pinnock curve" is a detailed LBL code and therefore has less uncertainties than models with coarser spectral resolution, such as broadband models.

# 3.6.3 Atmospheric lifetimes

Uncertainties in atmospheric lifetimes arise from a range of factors. For short-lived compounds, accurate determinations of the temperature-dependent rate coefficients for reactions with OH are needed. The NASA Data Evaluation Panel [Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 17 NASA Panel for Data Evaluation:2011] indicates uncertainties in OH rate constants at room temperature of up to about 20% for the compounds considered here. Combined with uncertainties in the temperature dependence gives an overall uncertainty of about 30% in the rate coefficient of the reactions at tropospheric temperatures. It is also important to note that lifetimes with respect to reaction with OH are determined relative to the lifetime of methyl chloroform, which in turn is dependent on the global OH field (see section 3.4). As an example, *Prather et al.* [2012] have used a recently published analysis of methyl chloroform data [*Montzka et al.*, 2011] to estimate a total lifetime for HFC-134a of 14.2 yr as against the WMO [*WMO*, 2011] recommendation of 13.4 yr. While this change is within our stated uncertainty, the important point is that changes in our understanding of the methyl chloroform lifetime can have an impact on the lifetimes of a great many compounds.

For some longer-lived compounds, photolysis in the stratosphere is the dominant loss process. Estimates of lifetimes for such compounds can be made from their ultraviolet absorption cross sections and quantum yields, and the altitude-dependent actinic flux. The NASA Data Evaluation Panel provides combined cross section/quantum yield uncertainties for some of the compounds considered here. For well-studied CFCs (CFC-11 and CFC-12) these uncertainties are well-constrained and are quoted at 10%, while for halons, uncertainties of a factor of two are quoted. Combined with uncertainties in the actinic flux, it is clear that there can be very significant uncertainties in photolysis lifetimes. This can be particularly true when considering very long-lived compounds such as the PFCs [Ravishankara et al., 1993].

However, it should be noted that for such long-lived species, GWPs on a one hundred year time horizon are insensitive to atmospheric lifetimes. Uncertainties in other processes such as deposition can be very large, but as *Prather et al.* [2012] point out, these uncertainties often have a relatively small impact on total lifetimes. In general, uncertainties in lifetimes are large compared to uncertainties in other parameters such as cross sections. A follow up study could assess the uncertainties in lifetimes and the combined effect of RE and lifetimes uncertainties on GWP and GTP.

# 1408 3.6.4 GWP

Some studies have investigated uncertainty in GWP and GTP values [Boucher, 2012; Olivié and Peters, 2012; Reisinger et al., 2010; Wuebbles et al., 1995] and they have been either based on model comparisons or Monte-Carlo approaches. Uncertainty can also be assessed using standard methods of uncertainty propagation. For a general function, f, with two independent variables, x and y, the uncertainty in f can be approximated as

$$1414 \qquad - \qquad - \tag{4}$$

This allows combination of different pieces of information on uncertainty (e.g., from independent studies) to assess the importance of the different components of metrics (e.g., RE versus lifetime). We use this approach for two chosen gases as examples (HFC-134a and CFC-11) and use uncertainties in RE obtained in this study with uncertainties in lifetimes from the literature. Based on Equation (4) the uncertainty for AGWP is given by

assuming Gaussian distributions and no correlation between RE and  $\tau$ . The derivatives of AGWP with respect to RE and  $\tau$  were obtained analytically. For HFC-134a, the relative uncertainty (for the 5–95% (90%) confidence range) is estimated to be  $\pm 18\%$  for  $\tau$  [*Prather et al.*, 2012] and  $\pm 13\%$  for RE (from Table 1). Using Equation (5) with these uncertainties, the total uncertainty for AGWP<sub>HFC-134a</sub> is  $\pm 16\%$  for a 20 year time horizon,  $\pm 22\%$  for 100 years, and  $\pm 22\%$  for 500 years. For CFC-11, the relative uncertainty is estimated to be  $\pm 33\%$  for  $\tau$  [*Minschwaner et al.*, 2012] and  $\pm 13\%$  for RE (from Table 1). Note that uncertainties related to indirect effects caused by e.g., the influence of CFC-11 on stratospheric ozone, are not

taken into account here. The total uncertainty for AGWP<sub>CFC-11</sub> is then  $\pm 15\%$  for a 20 year time horizon,  $\pm 28\%$  for 100 years, and  $\pm 36\%$  for 500 years.

The uncertainty in the AGWP<sub>CO2</sub> can be obtained using the  $\pm 10\%$  estimated uncertainty in RE [*IPCC*, 2007] and uncertainty in the time-integrated IRF<sub>CO2</sub> (see definition of IRF<sub>CO2</sub> in section 3.5.1) of  $\pm 15\%$ ,  $\pm 25\%$ , and  $\pm 28\%$  for a 20, 100, and 500 year time horizon [*Joos et al.*, 2013]. The uncertainty for the product , i.e., the uncertainty in AGWP<sub>CO2</sub>, is given by

leading to an uncertainty of AGWP<sub>CO2</sub> of  $\pm 18\%$ ,  $\pm 26\%$ , and  $\pm 30\%$ , respectively, with the uncertainty dominated by the uncertainty in the integrated IRF<sub>CO2</sub>. These estimates are different from what is given by IPCC AR4 where it was stated that AGWP for CO<sub>2</sub> is estimated to be  $\pm 15\%$ , with equal contributions from the CO<sub>2</sub> response function and the RF calculation [*IPCC*, 2007]. The main reason for the difference is the new uncertainty range in the IRF for CO<sub>2</sub> based on a multi model study [*Joos et al.*, 2013]. Combining the uncertainty in the AGWP values for HFC-134a and CFC-11 with AGWP<sub>CO2</sub> (using the sum of the squares uncertainty propagation), the uncertainty in GWP<sub>HFC-134a</sub> is estimated to  $\pm 24\%$ ,  $\pm 34\%$ , and  $\pm 37\%$  for a 20, 100, and 500 year time horizon. For CFC-11 the GWP uncertainties are  $\pm 23\%$ ,  $\pm 38\%$  and  $\pm 47\%$  for a 20, 100, and 500 year time horizon.

*IPCC* [2007] gives GWP uncertainties of  $\pm 35\%$  for the 5 to 95% (90%) confidence range which is based on earlier IPCC assessments; i.e., the Second and Third Assessment reports [*IPCC*, 1995; 2001].

The stated uncertainties for HFC-134a and CFC-11 are probably representative of those for most other CFCs, HCFCs, HFCs and perfluorocarbons with similar or longer lifetimes and with experimentally determined absorption cross-sections. For shorter-lived gases ( $\tau$  less than 5 years), the uncertainties will be considerably greater (we estimate AGWP uncertainties about at least a factor of 2 larger than those given above), and the assumption that there is no correlation between RE and  $\tau$  will be less valid. In addition, for the shorter-lived gases, both RE and  $\tau$  will depend on the location (and time) of emission, and the validity of presenting a single globally-representative value of GWPs is more questionable.

#### 4 Results and Discussion

# 4.1 Infrared Spectra, REs and GWPs

Absorption cross-sections and radiative efficiency estimates in the literature are reviewed in this section. In addition we present new calculations of REs and GWPs for a large number of gases based on published absorption cross-sections and the updated Pinnock curve described in section 3.3. All the REs are given for cloudy-sky and with stratospheric temperature adjustment included (see definition of RE in section 2.2), unless explicitly noted in the text. When the atmospheric lifetime is available, a correction for non-homogeneous (vertical and horizontal) distribution is applied to the calculated REs, following the methods described in section 3.3.4. Each available spectrum has been evaluated and the most reliable spectra have been used in the calculations of new best estimate REs, as explained in section 3.1.3.

For each compound our results are compared to the values presented in AR4. In a few cases, the best estimate RE from AR4 has been retained when new calculations were not carried out due to unavailability of reliable absorption cross-section data. Best estimate RE and GWP for each compound are indicated in bold in the tables. Additionally, we provide best estimate REs and GWPs for a number of compounds which were not included in AR4, but where absorption cross-sections were available or where RE values have been published. The atmospheric lifetimes necessary for the GWP calculations have been taken from *WMO* [2011] unless stated otherwise in the text. Note that indirect effects caused by e.g., the influence of CFCs on stratospheric ozone, have not been studied here but are covered elsewhere [e.g., *Daniel et al.*, 1995; *WMO*, 2011]. In the following, a brief discussion is given for each compound in each of the categories: chlorofluorocarbons, hydrochlorofluorocarbons, hydrochlorocarbons, chlorocarbons, bromocarbons and halons, fully fluorinated species, and halogenated alcohols and ethers. Additional information, such as the REs reported in each of the individual studies, and the calculated REs of all available spectra, is given in Tables S1-S7 in the supplementary material.

In the following, when we refer to IPCC AR4 [*IPCC*, 2007] it should be noted that a number of compounds were inadvertently omitted in the printed version of AR4 WGI Table 2.14; we have used the erratum to this table which is available at <a href="http://www.ipcc.ch/publications\_and\_data/ar4/wg1/en/errataserrata-errata.html">http://www.ipcc.ch/publications\_and\_data/ar4/wg1/en/errataserrata-errata.html</a>.

# 4.1.1 Chlorofluorocarbons (CFCs)

CFCs are long-lived compounds which are mainly removed in the stratosphere by UV photolysis or reaction with excited oxygen atoms, O(<sup>1</sup>D). Their GWPs are generally high due to long lifetimes, and despite substantial emission reductions of CFCs during the past couple of decades, their radiative forcing of climate will remain large for many decades [*WMO*, 2011]. The CFCs are relatively homogeneously distributed in the troposphere, but due to photolysis their mixing ratios decrease with increasing altitude in the stratosphere. The IR absorption by the CFCs occurs to a large extent in the 'atmospheric window' from 800 – 1200 cm<sup>-1</sup>, as illustrated for CFC-11 in Figure 11. Previously published absorption cross-sections are listed in Table 2, while updated atmospheric lifetimes, REs, and GWP(100) values for CFCs are presented in Table 3 and discussed below. Unless stated otherwise, the exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) has been used to account for a non-uniform vertical profile for the compounds presented in this subsection.

# CFC-11 (CCl<sub>3</sub>F)

Several studies have calculated the RE of CFC-11 [*Christidis et al.*, 1997; *Fisher et al.*, 1990; *Good et al.*, 1998; *Hansen et al.*, 1997; *Heathfield et al.*, 1998; *Jain et al.*, 2000; *Myhre and Stordal*, 1997; *Myhre et al.*, 1998; *Naik et al.*, 2000; *Ninomiya et al.*, 2000; *Pinnock et al.*, 1995; *Sihra et al.*, 2001]. Many of these studies report RE equal to, or close to, 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>, (range: 0.22-0.29 W m<sup>-2</sup> ppb<sup>-1</sup>, mean: 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>), which is the value that was used in AR4. (It should be noted that the RE values for all compounds reported by *Fisher et al.* [1990] were given relative to CFC-11 in *IPCC* [1990], assuming a RE of 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> for CFC-11. *WMO* [1999] scaled the REs from *Fisher et al.* [1990] by a factor 1.14 to account for the change in the recommended forcing for CFC-11 (from 0.22 to 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>), and these values were then adopted in subsequent IPCC assessments.) *Good et al.* [1998] estimated a value of RE using vibrational integrated absorption cross sections calculated using *ab initio* methods and obtained a value some 18% larger than those experimentally-derived band strengths.

In the present study we have used absorption spectra from several sources [*Heathfield et al.*, 1998; *Imasu et al.*, 1995; *Li and Varanasi*, 1994; *Orkin et al.*, 2003; *Sihra et al.*, 2001] and calculated the RE of CFC-11, assuming it to be well mixed, to be in the range 0.27 – 0.29

W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.28 W m<sup>-2</sup> ppb<sup>-1</sup>) (see Tables 2-3). For CFC-11 we have carried out explicit simulations using the Oslo LBL model and derived factors to account for stratospheric temperature adjustment and lifetime adjustment (see sections 3.3.3 and 3.3.4 for details and validation against satellite observations of CFC-11). The stratospheric adjustment, which is accounted for in the mean value of 0.28 W m<sup>-2</sup> ppb<sup>-1</sup>, is assumed to increase the forcing by 9.1%, while the lifetime correction reduces this value by 7.3%. Our final value, 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> is in relatively good agreement with AR4. As noted above, the RE in some studies is given relative to the RE of CFC-11, and have been scaled in previous assessments to the former recommended CFC-11 RE of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>. Here we choose to list the absolute REs of these studies [mainly *Fisher et al.*, 1990; *Imasu et al.*, 1995] as scaled to our new recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>.

A significant source of uncertainty related to the GWP of CFC-11 is the lifetime. In recent assessments [IPCC, 2007; WMO, 2011] the lifetime has been estimated as 45 years, based on observational studies [Cunnold et al., 1997; Volk et al., 1997] and model studies [WMO, 1999]. However, new studies, based on both models and observations, suggest a longer lifetime for CFC-11. Douglass et al. [2008] estimated a CFC-11 lifetime of 56-64 years using models that have realistic age of air and reproduce the observed relationship between the mean age and the fractional release. In Wuebbles et al. [2009] the lifetime was estimated to be 54 and 57 years, using a 3-D and a 2-D atmospheric chemistry model, respectively. Recent studies based on satellite and ground-based observations have estimated a CFC-11 lifetime of 50 years (range: 34-67 years) [Minschwaner et al., 2012], 52 years (range: 40-66 years) [Rigby et al., 2013], and 59 years (range: 53-66 years) [Laube et al., 2012]. In Table 2 we choose to keep the lifetime of 45 years from WMO [2011] as our best estimate.

#### CFC-12 (CCl<sub>2</sub>F<sub>2</sub>)

Literature values for the RE of CFC-12 [Fisher et al., 1990; Good et al., 1998; Hansen et al., 1997; Jain et al., 2000; Myhre and Stordal, 1997; Myhre et al., 1998; Myhre et al., 2006; Orkin et al., 2003; Sihra et al., 2001] provide results in the range 0.30 – 0.33 W m<sup>-2</sup> ppb<sup>-1</sup> with a mean of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup>, while a value of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> was used in AR4 (based on Myhre and Stordal [1997]). Differences are caused by differing impact of clouds, absorption cross-section data and the vertical profile of decay of the mixing ratio in the

stratosphere [*IPCC*, 2001]. Detailed LBL calculations were performed by *Myhre et al.* [2006] who calculated a RE of 0.33 W m<sup>-2</sup> ppb<sup>-1</sup>. Here we have used absorption cross sections from several sources [*Clerbaux et al.*, 1993; *Myhre et al.*, 2006; *Orkin et al.*, 2003; *Sihra et al.*, 2001; *Varanasi and Nemtchinov*, 1994] to calculate an average RE due to CFC-12 of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.29 – 0.33 W m<sup>-2</sup> ppb<sup>-1</sup>) (Tables 2-3). As for CFC-11 we have carried out explicit simulations of CFC-12 using the Oslo LBL model and derived factors to account for stratospheric temperature adjustment and lifetime adjustment. The instantaneous RE is increased by 10.5% when stratospheric temperature adjustment is taken into account, while the lifetime correction reduces the RE by 3.0%. Our final estimate (0.32 W m<sup>-2</sup> ppb<sup>-1</sup>) is in excellent agreement with that used in AR4. In contrast to CFC-11, the atmospheric lifetimes of CFC-12 derived in the new model study by *Douglass et al.* [2008] are in good agreement with those used in previous IPCC and WMO assessments, and we here adopt the lifetime of 100 years which has been used since the assessment of *WMO* [1999].

#### **CFC-13 (CCIF<sub>3</sub>)**

- A value of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> for the RE of CFC-13 has been used in the previous IPCC and
- 1569 WMO assessments and is from *Myhre and Stordal* [1997] who used a broadband model. The
- same value was calculated with a narrowband model in *Jain et al.* [2000], and was obtained in
- this study using absorption cross-section data from *McDaniel et al.* [1991].

# CFC-113 (CCl<sub>2</sub>FCClF<sub>2</sub>)

- Literature measurements of the RE of CFC-113 fall in the range  $0.28 0.33 \text{ W m}^{-2} \text{ ppb}^{-1}$  with
- a mean of 0.31 W m<sup>-2</sup> ppb<sup>-1</sup> [Fisher et al., 1990; Jain et al., 2000; Myhre and Stordal, 1997],
- which is the same value as in AR4 (based on Myhre and Stordal [1997]). We have used
- absorption cross-sections from a recent study by Le Bris et al. [2011] and from McDaniel et
- 1578 al. [1991] to obtain values of 0.31 and 0.29 W m<sup>-2</sup> ppb<sup>-1</sup>, respectively. Our average RE (0.30
- 1579 W m<sup>-2</sup> ppb<sup>-1</sup>) is in excellent agreement with AR4.

# CFC-114 (CClF<sub>2</sub>CClF<sub>2</sub>)

Literature measurements of the RE of CFC-114 are in the range 0.29 - 0.38 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.33 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Jain et al., 2000; Myhre and Stordal, 1997]. AR4 reports a RE of 0.31 W m<sup>-2</sup> ppb<sup>-1</sup> (based on *Myhre and Stordal* [1997]) which is the same as calculated here using absorption cross-section from McDaniel et al. [1991]. Although our RE estimate is in excellent agreement with AR4, the best estimate GWP of CFC-114 is about 15% lower (Table 3) due to the shorter lifetime and higher AGWP<sub>CO2</sub> used here. We have used the lifetime from WMO [2011] of 190 years, which is based on new model calculations by *Prather and Hsu* [2008; 2010], and is approximately 40% shorter than the AR4 estimate of 300 years...

# CFC-115 (CClF<sub>2</sub>CF<sub>3</sub>)

Literature reports of the RE of CFC-115 fall in the range 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> to 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.24 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Jain et al., 2000; Myhre and Stordal, 1997], while the latest assessments (since IPCC [2001]) have used the instantaneous forcing of 0.18 W m<sup>-2</sup> ppb<sup>-1</sup> from Myhre and Stordal [1997] (note that the value from AR4 falls outside the range quoted for the range of literature values because they reported the instantaneous RE while we consider the RE from Myhre and Stordal [1997]). The much higher RE of CFC-115 calculated by Fisher et al. [1990] compared to Myhre and Stordal [1997] and Jain et al. [2000] is most likely caused by the much higher integrated absorption cross-section in the first study compared to the work of McDaniel et al. [1991] which has been used in the two latter studies (Table 2). We calculate a RE value of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup>, which is in agreement with Myhre and Stordal [1997] and close to the RE of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> estimated by Jain et al. [2000]. As for CFC-114, new model calculations [Prather and Hsu, 2008; 2010] suggested a significantly shorter lifetime of 1,020 years for CFC-115 (compared to 1,700 years in AR4). Nevertheless, the GWP(100) of CFC-115 is still ~4% higher than in AR4 due to the higher RE of CFC-115 calculated here (Table 3).

# 4.1.2 Hydrochlorofluorocarbons (HCFCs)

HCFCs are controlled by the Montreal Protocol, but they have been common substitutes for CFCs due to their lower potential for ozone depletion. As a consequence, atmospheric concentrations of some HCFCs have grown rapidly over the last decade, as illustrated for HCFC-22 in Figure 1. The atmospheric lifetimes of HCFCs are generally lower than for CFCs, but some of these compounds still have sufficiently long lifetimes to yield significant global warming potentials. The absorption cross-section of one of the most well-studied gases, HCFC-22, is shown in Figure 12. Similarly to the CFCs, most of the absorption from HCFCs occurs in the atmospheric window region (800 – 1200 cm<sup>-1</sup>). Previously published absorption cross-sections are listed in Table 4, while best estimate lifetimes, radiative efficiencies and GWP(100) values for HCFCs are given in Table 5 and discussed below. Since the main loss mechanism for HCFCs is through reaction with OH in the troposphere, the *S*-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) has been used to account for the non-uniform vertical profile and horizontal distribution of all compounds presented in this subsection.

# HCFC-21 (CHCl<sub>2</sub>F)

REs of 0.19 W m<sup>-2</sup> ppb<sup>-1</sup> [*Christidis et al.*, 1997] and 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> [*Sihra et al.*, 2001] have been reported for HCFC-21. The difference in the results between the studies reflects different vertical profile assumptions; *Christidis et al.* [1997] assumed a constant vertical profile while *Sihra et al.* [2001] accounted for the fall-off in concentration of this relatively short-lived species (1.7 years atmospheric lifetime) above the troposphere. The RE from *Sihra et al.* [2001] is used for the recommended RE in AR4, and the cross-section from that study has been used in our RE and GWP calculations. Both the HITRAN 2008 and GEISA 2009 databases include the spectrum from *Massie et al.* [1985], but this spectrum contains only one of the absorption bands (785-840 cm<sup>-1</sup>) and has therefore not been employed in our calculations. Our estimate of 0.15 W m<sup>-2</sup> ppb<sup>-1</sup> is in good agreement (3.8% higher prior to rounding) with the AR4 (see Table 5).

#### HCFC-22 (CHClF<sub>2</sub>)

HCFC-22 is one of the most well-studied compounds with RE estimates in the literature ranging from 0.18 to 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.21 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Good et al., 1998; Highwood and Shine, 2000; Jain et al., 2000; Myhre and Stordal, 1997; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001]. Papasavva et al. [1997] used an ab initio spectrum which is approximately 10% more intense than the experimentally

derived spectra (Table 4) and consequently report a RE of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> which is 10% higher than the average from the experimental studies. AR4 reports a RE of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Highwood and Shine* [2000]. We have based our calculations on the spectrum from *Ballard et al.* [2000b] which is a composite of measurements from five laboratory groups, and is in good agreement with other reported experimental spectra (see Table 4). Our calculations yield a RE value of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup>, which is the same as recommended by AR4. We note that calculated RE values using absorption cross-sections available from other studies [*Clerbaux et al.*, 1993; *Highwood and Shine*, 2000; *Orkin et al.*, 2003; *Pinnock et al.*, 1995; *Sihra et al.*, 2001] (see SI Table 2 for individual results) agree to within 4% of the RE value calculated using the spectrum from *Ballard et al.* [2000b], indicating that the uncertainty in the HCFC-22 spectrum is rather small (the spectrum reported by *Varanasi et al.* [1994] was not included in this comparison because one of the absorption bands was missing).

#### HCFC-122 (CHCl<sub>2</sub>CF<sub>2</sub>Cl)

One study has estimated the instantaneous RE of HCFC-122 with a value 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> [*Orkin et al.*, 2003] (scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We have used their absorption spectrum and calculated a RE value of 0.17 W m<sup>-2</sup> ppb<sup>-1</sup>. The main reasons for the lower value calculated here are probably that *Orkin et al.* [2003] used a simplified approach which were not based on radiative transfer calculations, and that they did not account for stratospheric temperature adjustment and inhomogeneous distribution in the troposphere. The lifetime of 1.0 year is taken from *Orkin et al.* [2003].

### HCFC-122a (CHFClCFCl<sub>2</sub>)

One study has estimated instantaneous RE due to HCFC-122a, with a value 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> [*Orkin et al.*, 2003] (scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We calculate a RE value of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> when using their absorption cross-section and lifetime estimate of 3.4 years.

#### HCFC-123 (CHCl<sub>2</sub>CF<sub>3</sub>)

1674 Literature estimations of the RE of HCFC-123 derived from experimental measurements of the IR spectrum lie in the range 0.14 - 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.18 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et 1675 al., 1990; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et 1676 al., 2001]. As seen from Table 4, the infrared spectrum reported in the ab initio study of 1677 1678 Papasavva et al. [1997] is more intense than measured in the experimental studies and consequently the instantaneous RE of 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> is higher than those determined in the 1679 experimental studies. AR4 report a RE of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> which is based on both *Sihra et al.* 1680 [2001] and Jain et al. [2000]. We calculate a slightly higher RE value of 0.15 W m<sup>-2</sup> ppb<sup>-1</sup> for 1681 1682 all three sources of absorption spectra [Clerbaux et al., 1993; Orkin et al., 2003; Sihra et al., 2001] (Tables 4-5). It should be noted here that for this compound we have applied a 1683 1684 correction for stratospheric temperature adjustment of 6.5% (the average of the values found by Jain et al. [2000] (5%) and Pinnock et al. [1995] (8%)) rather than the generic 10% 1685 1686 correction used elsewhere in section 4.1.2.

1687

1688

#### HCFC-123a (CHClFCF<sub>2</sub>Cl)

- One study has estimated instantaneous RE of HCFC-123a with a value 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> [*Orkin et al.*, 2003] (scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We have
- used their absorption spectrum and calculated a slightly lower RE value of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup>.

1692

1693

#### HCFC-124 (CHClFCF<sub>3</sub>)

1694 Previous studies of RE due to HCFC-124 are in relatively good agreement with a range of 0.19 - 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.21 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Jain et al., 2000; Naik 1695 et al., 2000; Pinnock et al., 1995; Sihra et al., 2001]. As for HCFC-123, Papasavva et al. 1696 [1997] calculated a higher RE of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> (instantaneous RE) based upon an *ab initio* 1697 absorption cross-section. IPCC AR4 report a RE of 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from 1698 Fisher et al. [1990] (note that AR4 scaled the RE value from Fisher et al. [1990] to the 1699 previously recommended CFC-11 RE of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> – see the discussion concerning 1700 CFC-11 in section 4.1.1 – while we refer to the Fisher et al. [1990] value as scaled to our 1701 recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We have used absorption cross-sections 1702 from Sihra et al. [2001] and Clerbaux et al. [1993] to calculate a mean RE value of 0.20 W m 1703 <sup>2</sup> ppb<sup>-1</sup> (range: 0.19 - 0.20 W m<sup>-2</sup> ppb<sup>-1</sup>) (Tables 4-5), which is lower than in Fisher et al. 1704

- 1705 [1990]. However, our calculated RE is in agreement with the newer studies of Sihra et al.
- 1706 [2001], Jain et al. [2000] and Naik et al. [2000], most likely due to the higher integrated
- absorption cross-section of Fisher et al. [1990] (Table 4).

1708

### 1709 HCFC-132c ( $CH_2FCFCl_2$ )

- One study has estimated instantaneous RE due to HCFC-132c, with a value 0.19 W m<sup>-2</sup> ppb<sup>-1</sup>
- 1711 [Orkin et al., 2003] (scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We
- 1712 calculate a RE value of 0.17 W m<sup>-2</sup> ppb<sup>-1</sup> when using their absorption cross-section and
- lifetime estimate of 4.3 years.

1714

1715

# HCFC-141b (CH<sub>3</sub>CCl<sub>2</sub>F)

- 1716 Radiative efficiencies for HCFC-141b reported in the published literature are in the range
- 1717 0.12 0.18 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.15 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Imasu et al., 1995; Jain
- 1718 et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001], and
- the value of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> from *Fisher et al.* [1990] has been used by AR4 (scaled to the
- previously recommended CFC-11 RE of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>). *Papasavva et al.* [1997]
- 1721 calculated a much higher RE (instantaneous RE of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup>) using an ab initio
- absorption spectrum. We calculate a slightly higher RE than AR4 with a mean value of 0.16
- W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.15 0.17 W m<sup>-2</sup> ppb<sup>-1</sup>) when using absorption cross-sections from
- several sources [Clerbaux et al., 1993; Imasu et al., 1995; Orkin et al., 2003; Sihra et al.,
- 1725 2001]. We note that the value of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> from Fisher et al. [1990] has been scaled
- by AR4 to account for changes in the recommended RE of CFC-11 (from 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> in
- 1727 Fisher et al. [1990] to 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> in AR4), and that a scaling to our recommended
- 1728 CFC-11 forcing of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> results in a RE of 0.15 W m<sup>-2</sup> ppb<sup>-1</sup> from Fisher et al.
- 1729 [1990] in better agreement with our calculations.

1730

1731

# HCFC-142b (CH<sub>3</sub>CClF<sub>2</sub>)

- Previous reports of RE of HCFC-142b are in the range 0.16 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.18 W
- 1733 m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; Sihra
- 1734 et al., 2001]. Again, the ab initio study of Papasavva et al. [1997] is at the higher end of the

range based on experimental studies as they calculate an instantaneous RE of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup>. AR4 report a RE of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Fisher et al.* [1990]. We calculate a mean RE value of 0.19 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.18 - 0.20 W m<sup>-2</sup> ppb<sup>-1</sup>) when using absorption cross-sections from *Sihra et al.* [2001] and *Clerbaux et al.* [1993] (Tables 4-5). Our estimate is lower than *Fisher et al.* [1990] and *Pinnock et al.* [1995], but higher than the more recent studies [*Jain et al.*, 2000; *Naik et al.*, 2000; *Sihra et al.*, 2001].

# HCFC-225ca (CHCl<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)

A range of 0.20 - 0.27 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.22 W m<sup>-2</sup> ppb<sup>-1</sup>) for the RE of HCFC-225ca has been reported in the literature [Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; Sihra et al., 2001]. Three of the studies are in good agreement (<3% difference) while Pinnock et al. [1995] is an outlier with a value of 0.27 W m<sup>-2</sup> ppb<sup>-1</sup>, despite the lower integrated absorption cross-section in their study (Table 4). The reason is that Pinnock et al. [1995] did not take into account the non-uniform tropospheric distribution, which gives a reduction in the RE of 16% when using our fractional correction method described in section 3.3.4 and a lifetime of 1.9 years [WMO, 2011]. AR4 has based their RE recommendation of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> on Sihra et al. [2001] and Jain et al. [2000]. We calculate a mean RE value of 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.22 - 0.23 W m<sup>-2</sup> ppb<sup>-1</sup>) when using absorption cross-sections from Sihra et al. [2001] and Clerbaux et al. [1993] (Tables 4-5). 

# HCFC-225cb (CHClFCF<sub>2</sub>CClF<sub>2</sub>)

The RE of HCFC-225cb has differed considerably in the past literature with a range of 0.25 - 0.35 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.29 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Imasu et al.*, 1995; *Jain et al.*, 2000; *Naik et al.*, 2000; *Pinnock et al.*, 1995; *Sihra et al.*, 2001]. A value of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> has been used in previous assessments and is based on Granier (pers. comm.) [*IPCC*, 1994]. We calculate a mean RE value of 0.29 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.28 - 0.31 W m<sup>-2</sup> ppb<sup>-1</sup>) when using absorption cross-sections from *Sihra et al.* [2001], *Clerbaux et al.* [1993] and *Imasu et al.* [1995] (Tables 4-5). Our result differs by almost 10% from the AR4 recommendation. As the AR4 value is not based on published literature it is difficult to assess the reasons to why our estimate is significantly lower than their value, but we note that our estimate is in agreement with the

mean of published values and close to the most recent published RE estimate of HCFC-225cb of 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> [*Sihra et al.*, 2001].

#### (E)-1-Chloro-3,3,3-trifluoroprop-1-ene (CF<sub>3</sub>CH=CHCl(E))

The radiative efficiency of (E)-1-chloro-3,3,3-trifluoroprop-1-ene has not been assessed in AR4, but was estimated by *Andersen et al.* [2008]. They used the original *Pinnock et al.* [1995] method and calculated an instantaneous RE of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup>. Their absorption cross-section has been used in this study to calculate a lifetime-corrected RE of 0.04 W m<sup>-2</sup> ppb<sup>-1</sup> (Table 5). The short lifetime of 26 days [*WMO*, 2011] for this compound leads to a strong effect of the fractional correction factor which has been applied to account for non-uniform mixing (vertical and horizontal). It should be noted here that the uncertainties associated with this correction factor are very large on a percentage basis for such short-lived species (see Figure 9 and associated discussion in section 3.3.4), and we further note that our calculated RE is in good agreement with *Andersen et al.* [2008] if we assume uniform mixing.

# 4.1.3 Hydrofluorocarbons (HFCs)

HFCs do not destroy stratospheric ozone [Ravishankara et al., 1994; Wallington et al., 1995] and have emerged as important replacements for ozone-depleting substances such as the CFCs. The main removal mechanism for the HFCs is through reaction with OH. The atmospheric lifetime of HFCs depends on their reactivity towards OH radicals and ranges from 2.1 days for CH<sub>2</sub>=CHF to 242 years for CF<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub> (HFC-236fa). Compounds with lifetimes greater than a decade tend to be well mixed in the troposphere. Compounds with lifetimes less than a year are not well mixed and have an inhomogeneous distribution within the troposphere and needs to be accounted for in RE estimates. HFCs have strong absorption bands within the atmospheric window region (800 – 1200 cm<sup>-1</sup>) and hence have the potential to be potent greenhouse gases, especially for long-lived gases such as HFC-23 and HFC-236fa which have lifetimes greater than 200 years. At the other extreme, fluorinated alkenes such as CF<sub>3</sub>CF=CH<sub>2</sub> (HFC-1234yf) have very short atmospheric lifetimes (1-2 weeks) and are not significant greenhouse gases. HFC-134a (CF<sub>3</sub>CFH<sub>2</sub>) is the most abundant HFC in the atmosphere and is currently present at a concentration of approximately 60 ppt (Figure 1). HFC-134a has a lifetime of 13.4 years and its potency as a greenhouse gas lies between those

of the long-lived and short lived HFCs. Figure 13 shows the absorption spectrum of HFC-134a which, because of its industrial importance, has been studied extensively and is perhaps the best established of all the HFCs. Published absorption cross-sections for HFCs are listed in Table 6, atmospheric lifetimes, radiative efficiencies, and GWP(100) values for HFCs are presented in Table 7 and discussed below. The *S*-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) has been used to account for a non-uniform vertical profile and geographic distribution for all compounds presented in this subsection.

1803

1804

1805

1806

1807

1808

1809

1810

1811

1812

1813

1814

1815

1816

1817

1818

1819

1820

1821

1822

1823

1824

1825

1826

1827

1796

1797

1798

1799

1800

1801

1802

#### **HFC-23 (CHF<sub>3</sub>)**

Published estimates of the RE of HFC-23 span the range 0.16 – 0.27 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.21 W m<sup>-2</sup> ppb<sup>-1</sup>) [Gohar et al., 2004; Highwood and Shine, 2000; Jain et al., 2000; Naik et al., 2000; *Pinnock et al.*, 1995; *Sihra et al.*, 2001]. AR4 adopted the value of 0.19 W m<sup>-2</sup> ppb<sup>-1</sup> from Gohar et al. [2004], who used two different radiative transfer methods to estimate forcings of 0.18 and 0.19 W m<sup>-2</sup> ppb<sup>-1</sup>. The small differences between results from the two models used by Gohar et al. [2004] were attributed to slight differences in the treatment of clouds in the models. The large difference between the results of Gohar et al. [2004] and those of Jain et al. [2000] (0.248 W m<sup>-2</sup> ppb<sup>-1</sup>) and Naik et al. [2000] (0.271 W m<sup>-2</sup> ppb<sup>-1</sup>) is difficult to explain because all three studies used essentially the same IR spectrum. Two studies have used ab initio methods to estimate HFC-23 RE to be 0.18 W m<sup>-2</sup> ppb<sup>-1</sup> [Blowers and Hollingshead, 2009] and 0.19 W m<sup>-2</sup> ppb<sup>-1</sup> [Papasavva et al., 1997], but these are instantaneous REs and must be increased by approximately 11% [Gohar et al., 2004] to be comparable with the RE values (including stratospheric temperature adjustment) reported by Gohar et al. [2004]. We have used absorption cross-sections from Gohar et al. [2004] and Highwood and Shine [2000] to calculate RE values of 0.19 and 0.16 W m<sup>-2</sup> ppb<sup>-1</sup>, respectively, which are in excellent agreement with the REs reported in each of the two individual studies. The mean of our calculated REs (0.18 W m<sup>-2</sup> ppb<sup>-1</sup>) is slightly more than 5% lower than the AR4 recommendation. The relatively large range in the integrated absorption cross-sections for HFC-23 (Table 6), and subsequent large range of REs in our calculations, indicates that there are uncertainties related to the measurements of the absorption cross-section for this compound (the absorption band below 700 cm<sup>-1</sup>, which is only taken into account in Gohar et al. [2004], has only a negligible contribution to the integrated absorption cross-section).

#### HFC-32 ( $CH_2F_2$ )

Estimates for the RE of HFC-32 based on experimental absorption cross-sections range from 0.09 to 0.16 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.12 W m<sup>-2</sup> ppb<sup>-1</sup>) [Gohar et al., 2004; Highwood and Shine, 2000; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 2011b], while estimates based on absorption cross-sections from ab initio studies are in the range 0.12 - 0.13 W m<sup>-2</sup> ppb<sup>-1</sup> (instantaneous RE) [Blowers and Hollingshead, 2009; Papasavva et al., 1997]. As for HFC-23, the results of Gohar et al. [2004] were used in AR4 with a value of 0.11 W m<sup>-2</sup> ppb<sup>-1</sup>. We have used absorption spectra from Gohar et al. [2004], Highwood and Shine [2000] and Orkin et al. [2003] and derived a RE of HFC-32 of 0.11 W m<sup>-2</sup> ppb<sup>-1</sup> for all these spectra, in excellent agreement with AR4. It should be noted that additional absorption cross-sections are available e.g., through the HITRAN and GEISA databases (Table 6), but have not been included to avoid double-counting of absorption cross-sections from the same laboratory groups (e.g., both Highwood and Shine [2000] and Smith et al. [1996] are based on spectra from the Molecular Spectroscopy Facility / Rutherford Appleton Laboratory [M.S.F./R.A.L.]). The combination of a change in the recommended lifetime for this compound (5.2 years in WMO [2011] compared to 4.9 years in AR4) and the higher AGWP<sub>CO2</sub> used here, result in a GWP(100) value which is about the same as in AR4 (see Table 7). 

# **HFC-41 (CH<sub>3</sub>F)**

A radiative efficiency for HFC-41 of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> has been used in previous assessments and is taken from *Pinnock et al.* [1995] (note that stratospheric decay was accounted for in the assessments, but not in the original study). A range of 0.02 – 0.03 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.03 W m<sup>-2</sup> ppb<sup>-1</sup>) has been reported from studies using measured absorption cross-sections [*Pinnock et al.*, 1995; *Sihra et al.*, 2001]. The *ab initio* studies have the same range and mean, but they have only reported instantaneous RE [*Blowers and Hollingshead*, 2009; *Papasavva et al.*, 1997]. We used the absorption spectrum from *Sihra et al.* [2001] and derived a RE value of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup>, which is in excellent agreement with AR4. It should be noted that stratospheric temperature adjustment normally leads to a stronger forcing compared to instantaneous RE (recall from section 3.3.2 that we apply a 10% increase for most compounds), while for HFC-41 it leads to a weakening due to the strong overlap with the

absorption spectrum of ozone [*Pinnock et al.*, 1995]. We have carried out explicit LBL model calculations and estimated a 5.0% decrease for the stratospheric temperature adjustment for HFC-41 (see section 3.3.2), and this result has been used (instead of the 10% increase) to calculate the RE of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> above. Due to a change in the recommended lifetime for this compound (2.8 years in *WMO* [2011] compared to 2.4 years in AR4) our recommended GWP value is higher than in AR4 (see Table 7).

1866

1867

1868

1869

1870

1871

1872

1873

1874

1875

1876

1877

1878

1879

1880

1881

1882

1883

1884

1885

1886

1887

1888

1860

1861

1862

1863

1864

1865

# HFC-125 ( $CHF_2CF_3$ )

Previous studies have reported a fairly wide range of RE values for HFC-125: 0.21 - 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Highwood and Shine, 2000; Imasu et al., 1995; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001; Young et al., 2009b; Zhang et al., 2011b]. Ab initio studies for this compound have calculated REs that are at the high end of the range of experimental studies with instantaneous RE of 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> [Papasavva et al., 1997] and RE of 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> [Good et al., 1998]. The recent study by Zhang et al. [2011b] is an outlier with a value of 0.30 W m<sup>-2</sup> ppb<sup>-1</sup>, but they did not identify any clear reason for the large difference between their result and the results from all other studies. Zhang et al. [2011b] calculate their RE from a combination of forcings from three standard atmospheres; they do not show to what extent this combination is representative of a true global-mean atmosphere, nor do they show how their outgoing longwave radiation or cloud forcing, using this combination of atmospheres, compare with satellite observed values, which is an important diagnostic of model behavior [e.g., Forster et al., 2005]. Recent assessments have used the value of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> estimated in Highwood and Shine [2000]. We have used absorption cross-sections from several sources [Clerbaux et al., 1993; Highwood and Shine, 2000; Imasu et al., 1995; Orkin et al., 2003; Young et al., 2009b] (see also Table 6; note that the spectrum from Young et al. [2009b] supersede that of Sihra et al. [2001]) and calculated a mean RE value of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.21 - 0.24 W m<sup>-2</sup> ppb<sup>-1</sup>) (Table 7), which is in excellent agreement with AR4 (note that our use of a lifetime of 28.2 years recommended by [WMO, 2011] is shorter than that of 29 years used in AR4, but this does not affect the GWP(100) value significantly).

1889

1890

#### HFC-134 ( $CHF_2CHF_2$ )

Studies of the radiative efficiency of HFC-134 have reported values in the range 0.18 - 0.271891 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.20 W m<sup>-2</sup> ppb<sup>-1</sup>) [Christidis et al., 1997; Jain et al., 2000; Naik et al., 1892 2000; Sihra et al., 2001; Zhang et al., 2011b]. Again, Zhang et al. [2011b] is an outlier with a 1893 RE value of 0.27 W m<sup>-2</sup> ppb<sup>-1</sup>, which is more than 30% higher than reported in any of the 1894 1895 other studies (see also the HFC-125 section above for a discussion of Zhang et al. [2011b]). 1896 The ab initio studies are in good agreement with the mean of experimental studies for this 1897 compound as both Papasavva et al. [1997] and Good et al. [1998] calculated REs of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> (the first study calculated instantaneous RE). Previous assessments have used the 1898 value of 0.18 W m<sup>-2</sup> ppb<sup>-1</sup> based on *Christidis et al.* [1997] (a scaling factor to account for 1899 decreased concentrations in the stratosphere was applied). We calculate a mean RE value of 1900 0.19 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.18 - 0.20 W m<sup>-2</sup> ppb<sup>-1</sup>) when using absorption cross-sections from 1901 two sources [Sihra et al., 2001; Smith et al., 1998]. Our GWP(100) estimate is similar to AR4 1902 1903 due to the combination of a slightly higher RE, a slightly longer lifetime, and a higher 1904 AGWP<sub>CO2</sub> used here.

1905

1906

# HFC-134a (CH<sub>2</sub>FCF<sub>3</sub>)

Calculations of the RE of HFC-134a are in the range 0.15 - 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.18 W 1907 m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Forster et al., 2005; Gohar et al., 2004; Highwood and Shine, 1908 1909 2000; Imasu et al., 1995; Jain et al., 2000; Naik et al., 2000; Orkin et al., 2003; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 2011b], while one ab initio study estimated an 1910 instantaneous RE of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> [Papasavva et al., 1997]. AR4 adopted a value of 0.16 1911 W m<sup>-2</sup> ppb<sup>-1</sup> based on the multi-model studies of *Gohar et al.* [2004] and *Forster et al.* [2005]. 1912 1913 Particularly, Forster et al. [2005] derived a "recommended" absorption cross section and applied four radiative transfer models to yield an average RE with relatively low uncertainty 1914 (0.16±0.02 W m<sup>-2</sup> ppb<sup>-1</sup>), and attributed most of the uncertainty to the radiative forcing 1915 calculation rather than the absorption cross section. In this study we have used the 1916 1917 recommended absorption spectrum from Forster et al. [2005] (Table 6), which is based on measurements from six different laboratory groups, and calculated a radiative forcing of 0.16 1918 W m<sup>-2</sup> ppb<sup>-1</sup>, the same as used in AR4 (Table 7). The lifetime has been updated to 13.4 years 1919 1920 from WMO [2011] compared to the 14 years used in AR4.

1921

1922

#### HFC-143 ( $CH_2FCHF_2$ )

The average RE of HFC-143 reported in the literature based on experimentally measured absorption spectra is 0.12 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.11 – 0.14 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Clerbaux and Colin*, 1925 1994; *Jain et al.*, 2000; *Naik et al.*, 2000; *Pinnock et al.*, 1995; *Sihra et al.*, 2001], while the *ab initio* study of [*Papasavva et al.*, 1997] estimated an instantaneous RE of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup>. AR4 used 0.13 W m<sup>-2</sup> ppb<sup>-1</sup> taken from *Clerbaux and Colin* [1994]. We calculate the same mean RE value (range: 0.12 - 0.13 W m<sup>-2</sup> ppb<sup>-1</sup>) using absorption cross-sections from two sources [*M.S.F./R.A.L.*; *Sihra et al.*, 2001].

1930

1931

1932

1933

1934

1935

1936

1937

1938

1939

1940

1941

1942

1943

1944

1945

1946

1947

1948

1949

1950

1951

1952

1953

#### HFC-143a (CH<sub>3</sub>CF<sub>3</sub>)

The estimated RE of HFC-143a ranges from 0.13 to 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.16 W m<sup>-2</sup> ppb<sup>-1</sup>) in previous studies [Fisher et al., 1990; Highwood and Shine, 2000; Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 2011b]. Ab initio studies have calculated RE of 0.15 W m<sup>-2</sup> ppb<sup>-1</sup> [Good et al., 1998] and instantaneous RE of 0.16 W m<sup>-2</sup> ppb<sup>-1</sup> [Papasavva et al., 1997]. AR4 adopted the value from Highwood and Shine [2000] of 0.13 W m<sup>-2</sup> ppb<sup>-1</sup>, which is at the lower end of this range. The recent study of Zhang et al. [2011b] calculated almost 70% higher RE (0.22 W m<sup>-2</sup> ppb<sup>-1</sup>) than in AR4, but they did not provide adequate reasons for these discrepancies (see also discussion of HFC-125). By using absorption cross-sections from three different sources [Di Lonardo and Masciarelli, 2000; Sihra et al., 2001; Smith et al., 1998], we calculate a mean RE value of 0.16 W m<sup>-2</sup> ppb<sup>-</sup> <sup>1</sup> (range: 0.15 - 0.17 W m<sup>-2</sup> ppb<sup>-1</sup>), which is 22% higher than the AR4 value, but in line with the mean of estimates from literature measurements. The low value of RE in the AR4 reflects the use of the infrared spectrum from Highwood and Shine [2000] which has an integrated absorption cross section which is significantly lower than in any of the other studies (Table 6). We did not include the *Highwood and Shine* [2000] spectrum here as this was taken from a lower temperature (253 K) pure gas measurement of Di Lonardo and Masciarelli [2000] who note that their lower temperature measurements may be more inaccurate if they fail to properly resolve the sharper spectral features at the lower temperature. Another contribution to the discrepancy is the use of different factors to correct for a non-uniform vertical profile. Whereas we use a fractional correction factor of 0.98 based on the method in section 3.3.4 and a lifetime of 47.1 years, Highwood and Shine [2000] used the crude factor of 0.95 based on Freckleton et al. [1998].

# HFC-152 ( $CH_2FCH_2F$ )

1956 The ab initio study by Papasavva et al. [1997] is the only published investigation of the RE for HFC-152. An instantaneous RE value of 0.09 W m<sup>-2</sup> ppb<sup>-1</sup> was reported and this value has 1957 been used in previous IPCC assessments. Using experimentally determined absorption cross-1958 sections from Wallington et al. [1994a] (Tables 6-7) and accounting for the non-uniform 1959 distribution we calculate a much lower RE value of 0.04 W m<sup>-2</sup> ppb<sup>-1</sup>. The large difference is 1960 mainly due to the short lifetime of 146 days for HFC-152 [WMO, 2011] which leads to a 1961 reduction from 0.08 to 0.04 W m<sup>-2</sup> ppb<sup>-1</sup> when taking into account the non-uniform 1962 1963 distribution (Table 7). Recommended RE and GWP values are updated based on our 1964 calculations.

1965

1966

1955

# **HFC-152a** (CH<sub>3</sub>CHF<sub>2</sub>)

Literature calculations of the RE of HFC-152a, using measured cross-sections, lie in the range 1967 0.09 - 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.11 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Highwood and Shine, 1968 1969 2000; Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; Sihra et al., 2001; Zhang et al., 1970 2011b], while the ab initio study of Papasavva et al. [1997] estimated an instantaneous RE of 0.11 W m<sup>-2</sup> ppb<sup>-1</sup>. AR4 reports a RE of 0.09 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Highwood and* 1971 Shine [2000]. We calculated a slightly higher RE value of 0.10 W m<sup>-2</sup> ppb<sup>-1</sup> when using 1972 1973 absorption cross-sections from either of the three different sources [Clerbaux et al., 1993; 1974 Sihra et al., 2001; Vander Auwera, 2000], showing that the uncertainty associated with 1975 measurements of the HFC-152a spectrum is low. The higher GWP value calculated here 1976 reflects the higher RE value, a longer lifetime estimate in the latest review by WMO [2011] (1.5 years) compared to that used in AR4 (1.4 years), and an updated AGWP<sub>CO2</sub> value used 1977

1979

1980

1978

here.

# HFC-161 (CH<sub>3</sub>CH<sub>2</sub>F)

Values of 0.02 - 0.04 W m<sup>-2</sup> ppb<sup>-1</sup> have been reported for RE of HFC-161 (mean: 0.03 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Christidis et al.*, 1997; *Jain et al.*, 2000; *Naik et al.*, 2000; *Sihra et al.*, 2001]. The *ab initio* study of *Papasavva et al.* [1997] is at the high end of this range with an instantaneous RE of 0.04 W m<sup>-2</sup> ppb<sup>-1</sup>. A value of 0.03 W m<sup>-2</sup> ppb<sup>-1</sup> has been used in previous IPCC assessments and is based on *Christidis et al.* [1997] (a scaling factor of 0.8 based on

1986 Freckleton et al. [1998] was applied to account for decreased concentrations in the stratosphere). We calculate a RE value of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> when using the absorption cross-sections from Sihra et al. [2001]. The lower RE in our study compared to that in AR4 is explained by the different lifetime correction factors used as we use a factor of 0.37 to account for the non-homogeneous mixing while a factor 0.8 was applied to the Christidis et al. [1997] result.

1992

1993

# HFC-227ca (CF<sub>3</sub>CF<sub>2</sub>CHF<sub>2</sub>)

- 1994 The radiative efficiency of HFC-227ca has not been assessed in AR4. Values in the range
- 1995 0.25 0.33 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.29 W m<sup>-2</sup> ppb<sup>-1</sup>) are available for this compound [*Christidis*
- 1996 et al., 1997; Sihra et al., 2001]. We have used the absorption cross-section from Sihra et al.
- 1997 [2001] to calculate a RE value of 0.27 W m<sup>-2</sup> ppb<sup>-1</sup>, which is slightly higher than the RE of
- 1998 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> calculated in their study. The lifetime of 28.2 years is taken from *Christidis*
- 1999 et al. [1997].

2000

2001

# HFC-227ea (CF<sub>3</sub>CHFCF<sub>3</sub>)

- 2002 Published values of the RE of HFC-227ea lie in the range 0.26 to 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> (mean:
- 2003 0.28 W m<sup>-2</sup> ppb<sup>-1</sup>) [Gohar et al., 2004; Jain et al., 2000; Naik et al., 2000; Pinnock et al.,
- 2004 1995; Sihra et al., 2001]. AR4 used a RE value of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> which is an average
- derived from the two models used in *Gohar et al.* [2004]. The absorption cross-section from
- 2006 that study has been used here to calculate a RE value of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>, in agreement with
- 2007 that in AR4 (Tables 6-7). Our best estimate GWP value is higher than that in AR4 reflecting
- the latest information on the atmospheric lifetime of HFC-227ea [WMO, 2011].

2009

2010

#### HFC-236cb (CH<sub>2</sub>FCF<sub>2</sub>CF<sub>3</sub>)

- 2011 Two studies have been conducted to determine the RE of HFC-236cb. The average of results
- from the two studies is  $0.24 \text{ W m}^{-2} \text{ ppb}^{-1}$  (range:  $0.22 0.26 \text{ W m}^{-2} \text{ ppb}^{-1}$ ) [Christidis et al.,
- 2013 1997; Sihra et al., 2001]. Previous assessments have adopted the value of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup>
- based on *Christidis et al.* [1997] (a scaling factor to account for decreased concentrations in

the stratosphere was applied). We calculate the same RE value of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> when 2015 using the absorption cross-section from Sihra et al. [2001] (Tables 6-7). 2016

2017

2018

# HFC-236ea (CHF<sub>2</sub>CHFCF<sub>3</sub>)

- Previous IPCC and WMO assessments have used a value of 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> based on 2019 Gierczak et al. [1996] (a factor 0.8 was applied to yield cloudy-sky adjusted forcing from 2020 2021 their clear-sky instantaneous forcing), which is the only study that have estimated RE due to 2022 HFC-236ea. No new calculations have been carried out here for this compound, thus we 2023 retain the RE from AR4 as our best estimate. The GWP(100) value has been updated,
- 2024 however, to account for the change in AGWP<sub>CO2</sub> and the updated lifetime (11.0 years in
- 2025 *WMO* [2011] compared to 10.7 years in AR4).

2026

2027

#### HFC-236fa (CF<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub>)

- Literature estimates of the RE of HFC-236fa range from 0.23 to 0.29 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.26 2028
- W m<sup>-2</sup> ppb<sup>-1</sup>) [Gierczak et al., 1996; Jain et al., 2000; Naik et al., 2000; Pinnock et al., 1995; 2029
- Sihra et al., 2001] (note that the upper estimate of 0.29 W m<sup>-2</sup> ppb<sup>-1</sup> from Gierczak et al. 2030
- [1996] have been scaled by a factor 0.8 to convert from clear-sky instantaneous forcing to 2031
- cloudy-sky stratospheric temperature adjusted forcing following WMO [1999]). In previous 2032
- assessments, an average of the results from Pinnock et al. [1995] and Gierczak et al. [1996] of 2033
- 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> has been used. Using the absorption spectrum from Sihra et al. [2001] we 2034
- calculate a RE value of 0.24 W m<sup>-2</sup> ppb<sup>-1</sup>, 13% lower than the AR4 value (Tables 6-7). We 2035
- 2036 note that the estimate of Gierczak et al. [1996] was crudely scaled to account for clouds and
- 2037 stratospheric temperature adjustment, and that the resulting RE is at the higher end of the
- range of REs from the literature. Furthermore, the difference between our RE estimate and the 2038
- calculation of *Pinnock et al.* [1995] (0.27 W m<sup>-2</sup> ppb<sup>-1</sup>) can be partly explained by the higher 2039
- 2040 integrated absorption cross-section in their study (Table 6).

2041

2042

#### HFC-245ca (CH<sub>2</sub>FCF<sub>2</sub>CHF<sub>2</sub>)

- An RE estimate of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> for HFC-245ca has been used in all IPCC and WMO 2043
- assessments since *IPCC* [1994] and is based on Fisher (pers. comm.) (original value was 0.20 2044

W m<sup>-2</sup> ppb<sup>-1</sup>, but it was scaled to 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> in WMO [1999] because of a change in the 2045 recommended forcing of CFC-11 – see the discussion of CFC-11 in section 4.1.1), and no 2046 2047 newer estimates were found in the literature. No new calculations have been carried out here 2048 for this compound, thus we retain the RE from AR4 as our best estimate, except that we scale the value by a factor 0.26/0.25=1.04 to account for the update in our recommended RE of 2049 CFC-11. Our recommended RE of HFC-245ca is then 0.24 W m<sup>-2</sup> ppb<sup>-1</sup>. Also, the GWP(100) 2050 value has been updated to account for the change in AGWP<sub>CO2</sub> and the updated lifetime (6.5 2051 2052 years in WMO [2011] compared to 6.2 years in AR4).

2053

2054

# HFC-245cb (CF<sub>3</sub>CF<sub>2</sub>CH<sub>3</sub>)

- The radiative efficiency of HFC-245cb was not assessed in AR4. Published studies give RE in
- 2056 the range 0.25 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.27 W m<sup>-2</sup> ppb<sup>-1</sup>) [Christidis et al., 1997; Sihra et
- 2057 al., 2001]. We used the absorption spectrum from two sources [Orkin et al., 2003; Sihra et al.,
- 2058 2001] and calculated a mean RE value of 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.23 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>)
- 2059 (Tables 6-7), which is slightly lower than the 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> reported by *Sihra et al.* [2001].
- 2060 However, they assumed a constant vertical profile for this compound, and we note that our
- 2061 RE estimate when assuming a constant vertical profile (0.25 W m<sup>-2</sup> ppb<sup>-1</sup>) is consistent with
- their result. The lifetime of 47.1 years is taken from *Christidis et al.* [1997] who assumed the
- same lifetime as HFC-143a, based on the similar molecular structure of the two compounds.

2064

2065

# HFC-245ea (CHF<sub>2</sub>CHFCHF<sub>2</sub>), HFC-245eb (CH<sub>2</sub>FCHFCF<sub>3</sub>) and HFC-263fb

2066 (CH<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub>)

- The REs of HFC-245ea, HFC-245eb and HFC-263fb have not been assessed in AR4, but
- 2068 Rajakumar et al. [2006] used a LBL model to calculate REs of 0.18, 0.23 and 0.13 W m<sup>-2</sup>
- 2069 ppb<sup>-1</sup>, respectively. Clouds and stratospheric temperature adjustment were included in their
- study, but they did not include the effect of a non-homogeneous vertical profile. When using
- 2071 lifetimes from WMO [2011] and our method described in section 3.3.4, the lifetime-corrected
- 2072 REs from *Rajakumar et al.* [2006] are 0.16, 0.20 and 0.10 W m<sup>-2</sup> ppb<sup>-1</sup> for HFC-245ea, HFC-
- 2073 245eb and HFC-263fb, respectively. Using these REs we derive the recommended GWPs
- given in Table 7.

2075

# 2076 **HFC-245fa** (**CHF**<sub>2</sub>**CH**<sub>2</sub>**CF**<sub>3</sub>)

Published estimates of the RE of HFC-245fa lie in the range 0.24 - 0.29 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 2077 0.27 W m<sup>-2</sup> ppb<sup>-1</sup>) [Jain et al., 2000; Ko et al., 1999; Naik et al., 2000; Orkin et al., 2003; 2078 Sihra et al., 2001], and the value of 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> from Ko et al. [1999] has been used in 2079 recent assessments. We calculate a lower mean RE value of 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.24 -2080 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>) when using the absorption cross-sections from Sihra et al. [2001] and 2081 Orkin et al. [2003] (Tables 6-7). Part of the reason for the weaker RE in this study is the 2082 lower integrated absorption cross-section in Sihra et al. [2001] compared to Ko et al. [1999] 2083 2084 (Table 6), but it could also be related to differences in how the non-homogeneous distribution is accounted for. We note further that the RE estimate of Ko et al. [1999] is at the high end of 2085 the range of literature REs and that our estimate is in agreement with the 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> 2086 calculated by Sihra et al. [2001]. Our RE estimate of 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> is approximately 13% 2087 lower than the value of 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> used in AR4 (see Table 7). 2088

2089

2090

# HFC-272ca (CH<sub>3</sub>CF<sub>2</sub>CH<sub>3</sub>)

Previous studies of RE due to HFC-272ca are in the range 0.08 - 0.09 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 2091 0.09 W m<sup>-2</sup> ppb<sup>-1</sup>) [Pinnock et al., 1995; Sihra et al., 2001]. We calculate a RE value of 0.08 2092 W m<sup>-2</sup> ppb<sup>-1</sup> using the absorption spectrum from Sihra et al. [2001] (Tables 6-7). While there 2093 is no lifetime estimate for CH<sub>3</sub>CF<sub>2</sub>CH<sub>3</sub> in the literature, using the structure activity 2094 relationship developed by Calvert et al. [2008] with  $k(-CH_3) = 1.35 \times 10^{-13}$  and  $F(-CF_{2-}) =$ 2095 0.045 we estimate  $k(OH + CH_3CF_2CH_3) = 1.21 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. Combining 2096 this rate coefficient with an average tropospheric OH concentration of 1 x 10<sup>6</sup> cm<sup>-3</sup> provides 2097 an estimate for the atmospheric lifetime of 2.6 years. Using this estimated lifetime we derive 2098 the GWP value given in Table 7. 2099

2100

2101

# HFC-329p (CHF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)

The RE of HFC-329p has not been assessed by AR4, but was estimated to 0.31 W m<sup>-2</sup> ppb<sup>-1</sup> (instantaneous RE) by *Young et al.* [2009b] who used the original *Pinnock et al.* [1995] method. We have used the absorption cross-section from *Young et al.* [2009b] and calculated the same RE value of 0.31 W m<sup>-2</sup> ppb<sup>-1</sup> (Tables 6-7).

2106

# 2107 **HFC-365mfc** (CH<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>)

A range of 0.21 – 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.22 W m<sup>-2</sup> ppb<sup>-1</sup>) is available from literature 2108 estimations of the RE of HFC-365mfc [Barry et al., 1997; Inoue et al., 2008; Naik et al., 2109 2000]. AR4 adopted the value of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> from Barry et al. [1997], while WMO 2110 [2011] used an average of the results from Barry et al. [1997] and the more recent study of 2111 *Inoue et al.* [2008]. The latter study calculated a slightly higher RE of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> 2112 (instantaneous RE) reflecting an approximately 10% more intense infrared absorption 2113 2114 spectrum reported by *Inoue et al.* [2008]. A precise comparison of the spectra recorded by 2115 Barry et al. [1997] and Inoue et al. [2008] is not possible because Barry et al. [1997] did not 2116 report an integrated absorption cross section. Here we have used the better documented absorption cross-section from *Inoue et al.* [2008] to calculate a radiative forcing of 0.22 W m 2117 <sup>2</sup> ppb<sup>-1</sup>. Our RE estimate is approximately 6% higher (prior to rounding) than the value used 2118 2119 in AR4 (see Table 7).

2120

2121

2122

2123

2124

2125

2126

2127

2128

2129

2130

# HFC-43-10mee (CF<sub>3</sub>CHFCHFCF<sub>2</sub>CF<sub>3</sub>)

AR4 reports a RE of HFC-43-10mee of 0.40 W m<sup>-2</sup> ppb<sup>-1</sup> which is based on Fisher (pers. comm.) [*IPCC*, 1994] (original value was scaled in *WMO* [1999] because of a change in the recommended forcing of CFC-11 – see the discussion of CFC-11 in section 4.1.1). No published estimates of the RE of this compound exist and no new calculations have been carried out here, thus we retain the RE from AR4 as our best estimate, except that we scale the value by a factor 0.26/0.25=1.04 to account for the update in our recommended RE of CFC-11. Our recommended RE of HFC-43-10mee is then 0.42 W m<sup>-2</sup> ppb<sup>-1</sup>. Also, the GWP(100) value has been updated to account for the change in AGWP<sub>CO2</sub> and the updated lifetime (16.1 years in *WMO* [2011] compared to 15.9 years in AR4).

2131

2132

# HFC-1132a (CH<sub>2</sub>=CF<sub>2</sub>), HFC-1141 (CH<sub>2</sub>=CHF) and (Z)-HFC-1336 (CF<sub>3</sub>CH=CHCF<sub>3</sub>(Z))

The REs of HFC-1132a, HFC-1141 and (Z)-HFC-1336 were not assessed in AR4. Baasandorj et al. [2010] have estimated the radiative efficiencies of HFC-1132a and HFC-1141 to be 0.09 and 0.08 W m<sup>-2</sup> ppb<sup>-1</sup>, respectively. Baasandorj et al. [2011] estimated the radiative efficiency of (Z)-HFC-1336 to be 0.38 W m<sup>-2</sup> ppb<sup>-1</sup>. The RE values from both studies are instantaneous REs derived using the original *Pinnock et al.* [1995] method for the

- 2138 forcing calculations. We apply a 10% increase to account for stratospheric temperature
- 2139 adjustment, and an additional correction factor to account for the non-homogeneous mixing
- 2140 (see section 3.3.4) to derive recommended REs of 0.004, 0.002 and 0.074 W m<sup>-2</sup> ppb<sup>-1</sup> for
- 2141 HFC-1132a, HFC-1141 and (Z)-HFC-1336, respectively. Lifetimes necessary for the RE
- 2142 lifetime correction and GWP calculation were taken from WMO [2011] for HFC-1132a and
- 2143 HFC-1141, and from *Baasandorj et al.* [2011] for (Z)-HFC-1336.

2145

## (Z)-HFC-1225ye ( $CF_3CF=CHF(Z)$ )

- 2146 Literature values of the RE of (Z)-HFC-1225ye are in close agreement with a range 0.25 -
- 2147 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>) [Hurley et al., 2007; Papadimitriou et al., 2008a].
- 2148 Our RE calculation using the absorption spectrum from Hurley et al. [2007] and assuming
- 2149 homogeneous mixing throughout the troposphere is 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>, in good agreement with
- 2150 the literature data. However, when we account for the substantially non-homogeneous mixing
- of this short-lived species we arrive at the much lower RE value of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> (Tables
- 2152 6-7). Neither of the two literature studies account for the non-homogeneous mixing of
- 2153 CF<sub>3</sub>CF=CHF in the troposphere. Our recommended RE and GWP values are given in Table 7.

2154

## 2155 (E)-HFC-1225ye ( $CF_3CF=CHF(E)$ )

- There has been one published study of the RE of (E)-HFC-1225ye which gave a value 0.24 W
- 2157 m<sup>-2</sup> ppb<sup>-1</sup> [Hurley et al., 2007]. We have used the absorption spectrum from Hurley et al.
- 2158 [2007] and calculated a RE value of 0.01 W m<sup>-2</sup> ppb<sup>-1</sup> (Tables 6-7). As for the (Z)-HFC-
- 2159 1225ye compound discussed above, our RE estimate is in close agreement with the published
- value when we assume homogeneous mixing of (E)-HFC-1225ye.

2161

2162

#### (Z)-HFC-1234ze $(CF_3CH=CHF(Z))$

- There has been one published study of the RE of (Z)-HFC-1234ze which gave a value 0.20 W
- 2164 m<sup>-2</sup> ppb<sup>-1</sup> [Nilsson et al., 2009]. We calculate a RE value of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> using absorption
- spectrum from Nilsson et al. [2009] (Tables 6-7). The RE value estimated here is in good
- agreement with the published value when homogeneous distribution is assumed. The lifetime
- of 10 days is taken from *Nilsson et al.* [2009].

### 2169 **HFC-1234yf** ( $CF_3CF=CH_2$ )

- 2170 Literature values for the RE of HFC-1234yf fall in the range 0.22 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> (mean:
- 2171 0.23 W m<sup>-2</sup> ppb<sup>-1</sup>) [Nielsen et al., 2007; Orkin et al., 2010; Papadimitriou et al., 2008a]. We
- 2172 calculate a mean RE value of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> both when using the absorption cross-section
- from Orkin et al. [2010] and from Nielsen et al. [2007] (Tables 6-7). Neither of the previous
- studies accounted for the non-homogeneous mixing of this short-lived compound and we note
- 2175 that our estimate is in excellent agreement with the mean of published RE values when we
- 2176 assume uniform mixing of HFC-1234yf.

2177

2178

- (E)-HFC-1234ze (trans-CF<sub>3</sub>CH=CHF)
- 2179 Results from the published studies of the RE of (E)-HFC-1234ze lie in the range 0.24 0.27
- 2180 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>) [Orkin et al., 2010; Søndergaard et al., 2007]. We
- 2181 calculate a RE value of 0.04 W m<sup>-2</sup> ppb<sup>-1</sup> when using absorption cross-sections from both of
- these studies (Tables 6-7). The non-homogeneous mixing of this short-lived compound was
- 2183 not accounted for in the two studies; our estimate of RE is consistent with the published
- values if we assume uniform mixing.

- 2186 HFC-1243zf, HFC-1345zfc, 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene,
- 2187 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-
- 2188 heptadecafluorodec-1-ene ( $C_xF_{2x+1}CH=CH_2$  (x=1, 2, 4, 6 and 8))
- 2189 In the recent study by Andersen et al. [2012a], REs were calculated for five compounds that
- 2190 have not been included in previous assessments. They used the original *Pinnock et al.* [1995]
- method to calculate instantaneous REs of 0.16, 0.18, 0.34, 0.38 and 0.42 W m<sup>-2</sup> ppb<sup>-1</sup> for
- 2192 HFC-1243zf, HFC-1345zfc, 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene, 3,3,4,4,5,5,6,6,7,7,8,8,8-
- 2193 tridecafluorooct-1-ene and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene,
- 2194 respectively, assuming uniform mixing of these gases. As can be seen in Table 7, the
- corresponding REs calculated in this study are in close agreement to Andersen et al. [2012a],
- while they are substantially lower in the range 0.01 0.03 W m<sup>-2</sup> ppb<sup>-1</sup> when accounting
- 2197 for non-homogeneous mixing. It should be noted here that the uncertainties associated with
- 2198 the lifetime correction factor are very large on a percentage basis for such short-lived species

(see Figure 9 and associated discussion in section 3.3.4). The absorption cross-sections used here are from *Andersen et al.* [2012a] (Table 6), and the lifetimes necessary for the fractional correction and GWP calculation have been taken from *Andersen et al.* [2005].

2202

2203

2204

2205

2206

2207

2208

2209

2210

2211

2212

2213

2214

2215

2216

2217

2218

2219

2220

2221

2222

2199

2200

2201

## 4.1.4 Chlorocarbons and Hydrochlorocarbons

Chlorocarbons and hydrochlorocarbons are ozone-depleting substances and are therefore controlled under the Montreal Protocol. Lifetimes for the chlorocarbons hydrochlorocarbons considered here range from less than a year for CH<sub>2</sub>ClCH<sub>2</sub>Cl to 26 years for CCl<sub>4</sub> (carbon tetrachloride). Figure 1 shows the contrasting time-histories of the atmospheric concentrations of the most abundant chlorocarbon (CCl<sub>4</sub>) and hydrochlorocarbon (CH<sub>3</sub>CCl<sub>3</sub>, methyl chloroform). Methyl chloroform concentrations fell rapidly after implementation of the Montreal Protocol, due to a combination of rapidly-decreasing emissions and its short (5 year) lifetime. By contrast, due to continued emissions of carbon tetrachloride it remains the fourth most abundant of the compounds considered here (about 90 ppt), with concentrations decreasing only rather slowly (at a rate of about 1.2 ppt year<sup>-1</sup> [WMO, 2011]). Figure 14 shows the absorption spectrum of carbon tetrachloride – the symmetry of this molecule results in a quite simple spectrum, with most of the absorption concentrated in the 750 – 800 cm<sup>-1</sup> spectral region. Previously published absorption crosssections are listed in Table 8, while updated atmospheric lifetimes, radiative efficiencies, and 100-year GWP values for chlorocarbons and hydrochlorocarbons are presented in Table 9 and discussed below. With the exception of carbon tetrachloride, which is mainly lost by photolysis [WMO, 2011], the S-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) has been used to account for a non-uniform vertical profile and geographic distribution for all compounds presented in this subsection.

2223

2224

#### Methyl chloroform (CH<sub>3</sub>CCl<sub>3</sub>)

The studies that have calculated RE of methyl chloroform present values in the range 0.06 - 0.10 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.07 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Imasu et al., 1995; Jain et al., 2000; Orkin et al., 2003]. Both Fisher et al. [1990] and Jain et al. [2000] used the same absorption cross-section [Fisher et al., 1990]. Orkin et al. [2003] presented a 9% larger absorption cross-section and, based on the measured spectrum of the Earth's outgoing

radiation obtained by NIMBUS 4 [*Kunde et al.*, 1974], a relative RE to CFC-11 of 0.38. AR4 adopted the RE value of 0.06 W m<sup>-2</sup> ppb<sup>-1</sup> from *Fisher et al.* [1990]. We have used the absorption cross-sections from two sources [*Imasu et al.*, 1995; *Orkin et al.*, 2003] and calculated a slightly higher RE value of 0.07 W m<sup>-2</sup> ppb<sup>-1</sup> for both spectra.

2234

2235

2236

2237

2238

2239

2240

2241

2242

2243

2244

2245

2246

2247

2248

2249

2250

2251

2230

2231

2232

2233

#### Carbon tetrachloride (CCl<sub>4</sub>)

Previous studies of carbon tetrachloride RE present values in the range 0.09 - 0.13 W m<sup>-2</sup> ppb<sup>-</sup> <sup>1</sup> (mean: 0.11 W m<sup>-2</sup> ppb<sup>-1</sup>) [Fisher et al., 1990; Jain et al., 2000; Myhre and Stordal, 1997]; Fisher et al. [1990] and Jain et al. [2000] based their calculations on the absorption cross section presented by Fisher et al. [1990], while Myhre and Stordal [1997] employed the absorption cross section of Massie et al. [1985]. AR4 adopted the RE of 0.13 W m<sup>-2</sup> ppb<sup>-1</sup> from Jain et al. [2000]. We have used the more recent absorption cross-section from the study of Nemtchinov and Varanasi [2003], which includes temperature and pressure dependency and an inter-comparison of all previous data, and derive a RE value of 0.17 W m<sup>-2</sup> ppb<sup>-1</sup>. This is significantly higher (35% higher) than the AR4 value (Table 9) and entirely due to the higher absorption cross-section of the newer data (Table 8) than that was used in the RE calculation of Jain et al. [2000]. In contrast to the other compounds listed in this section, carbon tetrachloride is mainly lost by photolysis rather than reaction with OH [WMO, 2011]. Hence, we have used the exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) instead of the S-shaped fit to account for a non-uniform vertical profile, although this has only a small impact on the RE because this compound is relatively well-mixed in the atmosphere (lifetime of 26.0 years).

2252

2253

#### Methyl chloride (CH<sub>3</sub>Cl)

- Only one study has estimated the methyl chloride RE presenting a value of 0.01 W m<sup>-2</sup> ppb<sup>-1</sup>
- 2255 [Grossman et al., 1997], which is also the value that has been used in the AR4 assessment.
- 2256 Grossman and co-workers employed a combination of absorption cross-sections from *Brown*
- 2257 et al. [1987] and HITRAN. No new calculations have been carried out here for this
- compound, thus we retain the RE from AR4 as our best estimate. The GWP(100) value has,
- 2259 however, been updated to account for the change in AGWP<sub>CO2</sub>.

### 2261 Methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>)

- No estimate of the methylene chloride RE has been found in the published literature. AR4
- reports a RE of 0.03 W m<sup>-2</sup> ppb<sup>-1</sup> that has been used in all assessments since *IPCC* [1994] and
- is based on Fisher (pers. comm.) (scaled to the previously recommended CFC-11 RE of 0.25
- W m<sup>-2</sup> ppb<sup>-1</sup>). No new calculations have been carried out here for this compound, thus we
- 2266 retain the RE and GWP(100) from AR4 as our best estimate (the GWP(100) for this
- 2267 compound rounds to 9 after updating the AGWP<sub>CO2</sub> value).

2268

2269

## Chloroform (CHCl<sub>3</sub>)

- 2270 The two previous reports on chloroform RE are in the range 0.09 0.11 W m<sup>-2</sup> ppb<sup>-1</sup> (mean:
- 2271 0.10 W m<sup>-2</sup> ppb<sup>-1</sup>) [Highwood and Shine, 2000; Sihra et al., 2001] and are both based on the
- spectroscopic data from McPheat and Duxbury [2000]. AR4 has adopted the RE of 0.11 W m
- 2273 <sup>2</sup> ppb<sup>-1</sup> from *Highwood and Shine* [2000]. We have employed the absorption cross-section
- from McPheat and Duxbury [2000], but we derive a substantially lower RE value of 0.08 W
- 2275 m<sup>-2</sup> ppb<sup>-1</sup> (Tables 8-9). The reason for the ~30% lower value in the present study is linked to
- 2276 the different methods correcting for the non-homogeneous mixing of this short-lived species.
- 2277 Highwood and Shine [2000] used a factor of 0.8 from Freckleton et al. [1998] while we use a
- 2278 fractional correction factor of 0.55 based on the method described in section 3.3.4 and a
- 2279 lifetime of 0.4 years [WMO, 2011]. Recommended RE and GWP values, based on our
- calculations, are presented in Table 9.

2281

2282

## 1,2-Dichloroethane (CH<sub>2</sub>ClCH<sub>2</sub>Cl)

- 2283 1,2-dichloroethane has a relatively low RE with estimates of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> in the literature
- 2284 [Highwood and Shine, 2000; Sihra et al., 2001]; both studies use the absorption cross-section
- of Vander Auwera [2000]. The present calculations, employing the same spectroscopic data,
- 2286 yield a RE about half the magnitude, 0.01 W m<sup>-2</sup> ppb<sup>-1</sup> (Tables 8-9). As for chloroform, the
- 2287 calculated RE value is consistent with the previous studies when a homogeneous distribution
- 2288 is assumed.

# 4.1.5 Bromocarbons, Hydrobromocarbons, and Halons

The bromocarbons, hydrobromocarbons, and halons are ozone-depleting substances on account of both presences of bromine, and in some compounds, also chlorine. They are controlled under the Montreal Protocol. Lifetimes for the compounds considered here range from less than a year in the case of methylene bromide (CH<sub>2</sub>Br<sub>2</sub>) to 65 years in the case of Halon-1301 (CBrF<sub>3</sub>). The most abundant hydrobromocarbon in the atmosphere is methyl bromide (about 7.5 ppt, decreasing at 0.2 ppt year<sup>-1</sup> [WMO, 2011]) and the most abundant halon is Halon-1211 (about 4.2 ppt, decreasing at 0.05 ppt year<sup>-1</sup> [WMO, 2011]). Figure 15 shows the absorption spectrum of Halon-1301 (CBrF<sub>3</sub>) – the relatively simple structure of this molecule is reflected in an absorption spectrum where most of the intensity is concentrated in two narrow bands between 1,000 and 1,200 cm<sup>-1</sup>.

Previously published absorption cross-sections are listed in Table 10, while updated atmospheric lifetimes, radiative efficiencies, and GWP(100) values for bromocarbons, hydrobromocarbons, and halons are presented in Table 11 and discussed below. Three of the compounds are mainly lost by photolysis in the stratosphere (Halon-1211, Halon-1301 and Halon-2402 [WMO, 2011]), and we have therefore used the exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) to account for a non-uniform vertical profile for these compounds. The remaining compounds are mainly lost through reaction with OH and we have therefore used the S-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) to account for a non-uniform vertical profile and geographic distribution for these compounds.

### Methyl bromide (CH<sub>3</sub>Br)

The RE of methyl bromide is low with a mean of 0.006 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.005 - 0.007 W m<sup>-2</sup> ppb<sup>-1</sup>) from published estimates [*Christidis et al.*, 1997; *Grossman et al.*, 1997; *Jain et al.*, 2000; *Sihra et al.*, 2001]. AR4 has adopted a RE of 0.01 W m<sup>-2</sup> ppb<sup>-1</sup> based on the results of *Grossman et al.* [1997] and *Christidis et al.* [1997] (rounded to two decimals). *Grossman et al.* [1997] used the molecular parameters of *Anttila et al.* [1983] and *Graner and Blass* [1975] to model the CH<sub>3</sub>Br spectrum. We have used the absorption cross-section from *Sihra et al.* [2001] and derive RE = 0.004 W m<sup>-2</sup> ppb<sup>-1</sup> (Tables 10-11), which is lower than the AR4 value (0.006 W m<sup>-2</sup> ppb<sup>-1</sup>). The reason is that the previous studies assumed a constant vertical

profile, while we applied a lifetime correction factor of 0.70 using the method described in section 3.3.4 and a lifetime of 0.8 years [*WMO*, 2011]. The present calculations are in excellent agreement with the 0.007 W m<sup>-2</sup> ppb<sup>-1</sup> calculated by *Christidis et al.* [1997] when a constant vertical profile of methyl bromide is assumed. The best estimate RE and GWP are shown in Table 11.

2326

2327

### **Methylene bromide (CH<sub>2</sub>Br<sub>2</sub>)**

- 2328 Previous studies of RE due to methylene bromide are in the range 0.011 0.021 W m<sup>-2</sup> ppb<sup>-1</sup>
- 2329 (mean: 0.017 W m<sup>-2</sup> ppb<sup>-1</sup>) [Christidis et al., 1997; Jain et al., 2000; Sihra et al., 2001]; AR4
- recommends RE of 0.01 W m<sup>-2</sup> ppb<sup>-1</sup> (rounded to two decimals) from *Christidis et al.* [1997]
- 2331 (note that AR4 accounted for stratospheric decay [WMO, 1999]). When using the absorption
- 2332 cross-section from Sihra et al. [2001], we calculate a RE value of 0.008 W m<sup>-2</sup> ppb<sup>-1</sup>, which
- leads to a new recommended GWP(100) value of 1 (Tables 10-11).

2334

2335

## Halon-1201 (CHBrF<sub>2</sub>)

- 2336 Literature reports of Halon-1201 RE are in the range 0.15 0.18 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.17 W
- 2337 m<sup>-2</sup> ppb<sup>-1</sup>) [Christidis et al., 1997; Jain et al., 2000; Orkin et al., 2003; Sihra et al., 2001];
- 2338 AR4 adopted a RE of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Christidis et al.* [1997] (note that
- 2339 AR4 accounted for stratospheric decay [WMO, 1999]). We derive a mean RE of 0.15 W m<sup>-2</sup>
- ppb<sup>-1</sup> (range: 0.15 0.16 W m<sup>-2</sup> ppb<sup>-1</sup>) when using the absorption cross-sections from *Sihra et*
- 2341 al. [2001], Orkin et al. [2003] and the recent study by Charmet et al. [2010] (Tables 10-11).
- Our RE estimate is in agreement with the value from Sihra et al. [2001], but it is more than
- 2343 5% higher than the AR4 estimate (Table 11). Despite the higher RE, our recommended
- 2344 GWP(100) value is lower than in AR4 due to the shorter lifetime recommended by WMO
- 2345 [2011] (5.2 years compared to 5.8 years in AR4) and the higher AGWP<sub>CO2</sub> used here.

2346

2347

## **Halon-1202** (CBr<sub>2</sub>F<sub>2</sub>)

- One study has estimated RE due to Halon-1202 with a value 0.29 W m<sup>-2</sup> ppb<sup>-1</sup> [Orkin et al.,
- 2349 2003] (when scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We have used the
- 2350 absorption cross-section from the same study and calculated a slightly lower RE of 0.27 W m

<sup>2</sup> ppb<sup>-1</sup>. It should be noted that the recent study by *Papanastasiou et al.* [2013] suggests a

2352 lifetime of 2.52 years, which is shorter than the 2.9 years [WMO, 2011] used here.

2353

2354

### Halon-1211 (CBrClF<sub>2</sub>)

- 2355 Previous reports of the RE of Halon-1211 are in the range 0.25 0.33 W m<sup>-2</sup> ppb<sup>-1</sup> (mean:
- 2356 0.28 W m<sup>-2</sup> ppb<sup>-1</sup>) [Christidis et al., 1997; Jain et al., 2000; Sihra et al., 2001]. AR4 reports a
- 2357 RE of 0.30 W m<sup>-2</sup> ppb<sup>-1</sup>, which is based on the results of *Christidis et al.* [1997] (note that
- 2358 AR4 accounted for stratospheric decay [WMO, 1999]). We have used the absorption cross-
- 2359 section from Sihra et al. [2001] and calculated a RE value of 0.29 W m<sup>-2</sup> ppb<sup>-1</sup>, which is
- consistent (within 5% difference) with the AR4 value (Tables 10-11). For Halon-1211 we
- have carried out explicit simulations using the Oslo LBL model and derived a factor of 0.937
- 2362 to account for the non-uniform vertical profile induced by loss through photolysis in the
- stratosphere (see section 3.3.4 for details), and this factor has been used to derive the RE of
- 2364 0.29 W m<sup>-2</sup> ppb<sup>-1</sup>. It should be noted that *Papanastasiou et al.* [2013] have recently suggested
- a slightly longer lifetime of 16.4 years compared to the 16.0 years [WMO, 2011] which have
- been used here.

2367

2368

### Halon-1301 (CBrF<sub>3</sub>)

- 2369 Estimates of the RE of Halon-1301 in the literatures range from 0.27 to 0.33 W m<sup>-2</sup> ppb<sup>-1</sup>
- 2370 (mean: 0.30 W m<sup>-2</sup> ppb<sup>-1</sup>) [Charmet et al., 2008; Drage et al., 2006; Jain et al., 2000; Orkin et
- 2371 al., 2003; Ramanathan et al., 1985; Sihra et al., 2001]. AR4 used a RE of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup>
- taken from Ramanathan et al. [1985]. We have used absorption cross-sections from three
- 2373 sources [Charmet et al., 2008; Orkin et al., 2003; Sihra et al., 2001] and calculated a mean
- 2374 RE value of 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.29 0.31 W m<sup>-2</sup> ppb<sup>-1</sup>), about 6% lower than AR4.

2375

2376

# Halon-2301 (CH<sub>2</sub>BrCF<sub>3</sub>)

- One study has estimated RE due to Halon-2301 with a value 0.17 W m<sup>-2</sup> ppb<sup>-1</sup> [Orkin et al.,
- 2378 2003] (scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We have used their
- 2379 absorption cross-section and calculated a lower RE value of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup>. Our value
- 2380 includes corrections for stratospheric temperature adjustment and non-homogeneous mixing,

which were not accounted for in the published estimate. The lifetime of 3.4 years is taken

2382 from *Orkin et al.* [2003].

2383

2384

## Halon-2311 / Halothane (CHBrClCF<sub>3</sub>)

- The RE of Halon-2311 has not been assessed in AR4, but was estimated to be in the range
- 2386 0.17 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.19 W m<sup>-2</sup> ppb<sup>-1</sup>) in previous studies [Andersen et al., 2012b;
- 2387 Orkin et al., 2003]. Both these studies assumed homogeneous mixing throughout the
- 2388 troposphere and used the original *Pinnock et al.* [1995] method to calculate the instantaneous
- 2389 RE. We calculate a lower RE with a mean value of 0.13 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.13 0.14 W m<sup>-2</sup>
- 2390 <sup>2</sup> ppb<sup>-1</sup>) when using the absorption cross-sections from Andersen et al. [2012b] and Orkin et
- 2391 al. [2003] (Tables 10-11). The lower value calculated here primarily reflects the correction
- factor we have applied to account for non-homogeneous mixing, but it is also a result of the
- 2393 difference between the original Pinnock curve and the new curve presented in section 3.3.1,
- 2394 whereas the latter curve generally yields lower REs (in this case ~5% lower).

2395

2396

### Halon-2401 (CHFBrCF<sub>3</sub>)

- 2397 Orkin et al. [2003] have estimated the RE due to Halon-2401 with a value 0.23 W m<sup>-2</sup> ppb<sup>-1</sup>
- 2398 (when scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We have used their
- absorption cross-section and calculated a RE value of 0.19 W m<sup>-2</sup> ppb<sup>-1</sup>. Again, the lower
- value results mainly from the lifetime correction factor applied here to account for non-
- 2401 homogeneous mixing. The lifetime of 2.9 years is taken from *Orkin et al.* [2003].

2402

2403

#### Halon-2402 (CBrF<sub>2</sub>CBrF<sub>2</sub>)

- 2404 Sihra et al. [2001] estimated the RE of Halon-2402 presenting a value of 0.33 W m<sup>-2</sup> ppb<sup>-1</sup>,
- 2405 which is also the RE adopted by AR4. We have used the absorption cross-section from Sihra
- 2406 et al. [2001] and calculated a RE value of 0.31 W m<sup>-2</sup> ppb<sup>-1</sup>, about 6% lower than that used in
- AR4. We have used a lifetime of 20.0 years [WMO, 2011], but we note that the recent study
- by *Papanastasiou et al.* [2013] has estimated a significantly longer lifetime of 28.3 years, and
- consequently higher GWP values for this compound.

## 4.1.6 Fully Fluorinated Species

Fully fluorinated compounds are generally long-lived compounds removed by photolysis in the stratosphere, although unsaturated compounds may be very short-lived because of their reactivity towards OH radicals. Perfluorocarbons (PFCs) usually have strong absorption in the 1200-1300 cm<sup>-1</sup> region of the spectrum (as illustrated for CF<sub>4</sub> in Figure 16) and so are radiatively active in the atmosphere. As a result – and combined with their long lifetimes – saturated PFCs have some of the largest GWPs of any compounds detected in the atmosphere. These compounds are identified within the Kyoto Protocol as gases whose presence in the atmosphere must be controlled, as has sulphur hexafluoride. As noted in section 1, nitrogen trifluoride was added to the basket of greenhouse gases in the second commitment period of the Kyoto Protocol. Published absorption cross-sections are listed in Table 12, while updated atmospheric lifetimes, radiative efficiencies, and GWP(100) values for fully fluorinated species are presented in Table 13 and discussed below. For sulfuryl fluoride and six shortlived compounds we have used the S-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) to account for a non-uniform vertical profile and geographic distribution due to their reactivity towards OH. The remaining compounds have very long lifetimes (>500 years) and are lost by photolysis in the stratosphere, hence we have used the exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) to account for a non-uniform vertical profile for these compounds.

#### Nitrogen trifluoride (NF<sub>3</sub>)

There is one study of the RE for nitrogen trifluoride in the literature. *Robson et al.* [2006] calculated a cloudy-sky adjusted radiative forcing of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> by using a combination of line-by-line and narrow band radiative transfer models, and this value has been used in IPCC and WMO assessments (since *WMO* [2007]). Earlier assessments reported a much lower value of 0.13 W m<sup>-2</sup> ppb<sup>-1</sup> (instantaneous RE), but these calculations were based on incomplete cross-section data. We have used the spectrum from *Robson et al.* [2006] and calculated a RE value of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> (Table 12-13), which is consistent (within 5% difference) with AR4. Since AR4, the lifetime of NF<sub>3</sub> has been studied by *Prather and Hsu* [2008] who suggest a much shorter lifetime of 550 years, partly due to inclusion of the O(<sup>1</sup>D) + NF<sub>3</sub> reaction, compared to the 740 years recommended in AR4. *WMO* [2011] used an updated rate constant for the O(<sup>1</sup>D) reaction to obtain a lifetime of 500 years, which is the

- value we have used here. It should be noted that a very recent study by *Papadimitriou et al.*[2013] included temperature dependence of the NF<sub>3</sub> UV absorption spectrum and suggested a longer lifetime for NF<sub>3</sub> of 585 years (±20%).

  [2446]

  Sulphur hexafluoride (SF<sub>6</sub>)

  Previous studies of the RE for sulphur hexafluoride are in the range 0.49 0.68 W m<sup>-2</sup> ppb<sup>-1</sup>

  (mean: 0.56 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Jain et al.*, 2000; *Myhre and Stordal*, 1997; *Zhang et al.*, 2011a].
- 2450 Zhang et al. [2011a] estimated a much higher RE than the other studies, and this was also the
- case for several of the HFCs calculated by Zhang et al. [2011b] (see discussion of HFC-125
- in section 4.1.3). AR4 adopted a RE of 0.52 W m<sup>-2</sup> ppb<sup>-1</sup> from Myhre and Stordal [1997],
- 2453 while we calculate a 10% higher RE value of 0.57 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.54 0.59 W m<sup>-2</sup> ppb<sup>-1</sup>
- 2454 <sup>1</sup>) using absorption cross-sections from the GEISA and HITRAN databases (Tables 12-13).

2456

## (Trifluoromethyl)sulfur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>)

- 2457 Previous reports of RE of (trifluoromethyl)sulfur pentafluoride are in the range 0.57 0.59 W
- 2458 m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.58 W m<sup>-2</sup> ppb<sup>-1</sup>) [Nielsen et al., 2002; Sihra et al., 2001; Sturges et al.,
- 2459 2000], and AR4 adopted the RE of 0.57 W m<sup>-2</sup> ppb<sup>-1</sup> from Sturges et al. [2000]. We calculate
- 2460 a mean RE value of 0.59 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.58 0.61 W m<sup>-2</sup> ppb<sup>-1</sup>), consistent (within 5%
- 2461 difference) with the AR4, using absorption cross-sections from two sources [Nielsen et al.,
- 2462 2002; Rinsland et al., 2003] (Tables 12-13). Both of these spectra include an absorption
- 2463 feature at 612.5 cm<sup>-1</sup> which was not included in the measurements of *Sturges et al.* [2000],
- and this explains the slightly higher RE calculated here.

2465

2466

### Sulphuryl fluoride (SO<sub>2</sub>F<sub>2</sub>)

- 2467 Previous reports of RE of sulphuryl fluoride are in the range 0.20 0.22 W m<sup>-2</sup> ppb<sup>-1</sup> (mean:
- 2468 0.21 W m<sup>-2</sup> ppb<sup>-1</sup>) [Andersen et al., 2009; Papadimitriou et al., 2008b]. We calculate a RE
- value of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> using the absorption spectrum from *Andersen et al.* [2009] (Tables
- 2470 12-13) in good agreement with the previous literature.

2471

2472

## PFC-14 (CF<sub>4</sub>)

Previous reports of the RE of PFC-14 are in the range 0.08 - 0.12 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.10 W m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010b; Hurley et al., 2005; Jain et al., 2000; Myhre and Stordal, 1997; Roehl et al., 1995; Sihra et al., 2001; Zhang et al., 2011a]. Bravo et al. [2010b] report a relatively low RE value of 0.08 W m<sup>-2</sup> ppb<sup>-1</sup> (instantaneous RE) from their B3LYP/6-31G\*\* calculations, but it should be noted that CF<sub>4</sub> was part of the training set used to determine corrections to band positions. AR4 adopted a RE of 0.10 W m<sup>-2</sup> ppb<sup>-1</sup> from Hurley et al. [2005], and we calculate a similar mean RE of 0.09 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.09 - 0.10 W m<sup>-2</sup> ppb<sup>-1</sup>) when using absorption data from *Hurley et al.* [2005] (only the Ford data, and not the M.S.F./R.A.L. data) and from the HITRAN database (Tables 12-13). Interestingly, as PFC-14 has a very strong and narrow absorption band centered near 1280 cm<sup>-1</sup>, which is close to the edge of the atmospheric window region, the spectral resolution is more important for PFC-14 than for other compounds. When using a 10 cm<sup>-1</sup> resolution instead of 1 cm<sup>-1</sup> in our calculations, the RE of PFC-14 is underestimated by ~8%, as shown in Figure 6 and briefly discussed in section 3.3.1. For PFC-14 we have carried out explicit simulations using the Oslo LBL model and derived a 10.5% increase to account for stratospheric temperature adjustment (see section 3.3.3 for details), and this value has been used (rather than the generic 10% increase) in the calculation of the RE value of 0.09 W m<sup>-2</sup> ppb<sup>-1</sup>. 

## **PFC-116** $(C_2F_6)$

Previous reports of RE of PFC-116 are in the range 0.25 - 0.35 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.27 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Bravo et al.*, 2010b; *Highwood and Shine*, 2000; *Myhre and Stordal*, 1997; *Roehl et al.*, 1995; *Sihra et al.*, 2001; *Zhang et al.*, 2011a]. *Bravo et al.* [2010b] report a value for RE of 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> (instantaneous RE) from their B3LYP/6-31G\*\* calculations, but it should be noted that C<sub>2</sub>F<sub>6</sub> was part the training set used to determine corrections to band positions. *Papasavva et al.* [1997] obtained an *ab initio* RE value of 0.33 W m<sup>-2</sup> ppb<sup>-1</sup> using the MP2 with a wavenumber scaling factor of 0.9427. In AR4 a RE value of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> was used and is taken from *Highwood and Shine* [2000]. We calculate a mean RE value of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.24 - 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>), which is in good agreement with AR4, and we have used absorption cross-sections from three sources [*Bravo et al.*, 2010b; *Sihra et al.*, 2001; *Zou et al.*, 2004] (Tables 12-13). It should be noted here that as both *Bravo et al.* [2010b] and *Highwood and Shine* [2000] present absorption data from M.S.F./R.A.L., we here choose the most recent spectrum measurement from *Bravo et al.* [2010b]. Also note that

2505 the *Zou et al.* [2004] spectrum does not include the absorption band located at 715 cm<sup>-1</sup> but 2506 this had negligible impact on the RE, thus we keep this spectrum in our calculation.

2507

2508

## **PFC-c216** (c- $C_3F_6$ )

- 2509 Assessments since WMO [1999] have used a RE for PFC-c216 of 0.42 W m<sup>-2</sup> ppb<sup>-1</sup> which is
- reported to have been taken from *Papasavva et al.* [1997]. However, *Papasavva et al.* [1997]
- 2511 did not report a RE for this compound and so the origin of the value used in AR4 is unclear.
- 2512 The only estimate of the RE for c-C<sub>3</sub>F<sub>6</sub> that we are aware of is from a calculation (B3LYP/6-
- 2513 31G\*\*), which gives an instantaneous RE of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> [Bravo et al., 2010b]. An
- 2514 updated RE (assuming a 10% increase to account for stratospheric temperature adjustment)
- and GWP values for PFC-c216 are given in Table 13.

2516

2517

#### $PFC-218 (C_3F_8)$

- 2518 Previous reports of RE of PFC-218 are in the range 0.26 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.27 W m<sup>-2</sup>
- <sup>2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010b; Roehl et al., 1995; Sihra et al., 2001]. Bravo et al. [2010b] also
- 2520 report an instantaneous RE value of 0.27 W m<sup>-2</sup> ppb<sup>-1</sup> from their B3LYP/6-31G\*\*
- 2521 calculations consistent with their instantaneous RE derived from experimental cross-
- sections. AR4 reports a RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Roehl et al.* [1995]. We
- 2523 calculate a slightly higher mean RE value of 0.28 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.27 0.28 W m<sup>-2</sup> ppb<sup>-1</sup>
- 2524 1) using experimental absorption cross-sections from two sources [Bravo et al., 2010b; Sihra
- 2525 et al., 2001] (Tables 12-13). The higher RE calculated here can be explained by the much
- lower integrated absorption cross-section in the PFC-218 spectrum of *Roehl et al.* [1995]
- compared to other studies (see Table 12).

2528

2529

# PFC-318 (c- $C_4F_8$ )

- 2530 Previous reports of RE of PFC-318 based on experimentally measured absorption spectra are
- 2531 in the range 0.31 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.31 W m<sup>-2</sup> ppb<sup>-1</sup>) [Highwood and Shine, 2000;
- 2532 Sihra et al., 2001; Vasekova et al., 2006] while Bravo et al. [2010b] report a value for RE of
- 2533 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> from their B3LYP/6-31G\*\* calculations, in good agreement with the values
- derived from the experimentally measured spectra. AR4 reports a RE of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup>

taken from *Highwood and Shine* [2000]. We have used the absorption spectrum from the same study and our calculations give a RE value of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> which is in agreement with AR4 (Tables 12-13).

#### PFC-31-10 ( $C_4F_{10}$ )

Previous estimates of the RE for PFC-31-10 based on experimentally measured absorption spectra are in the range 0.33 - 0.37 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.36 W m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010b; Roehl et al., 1995; Sihra et al., 2001]. Bravo et al. [2010b] also report an instantaneous RE of  $0.34~W~m^{-2}~ppb^{-1}$  from their  $B3LYP/6-31G^{**}$  calculations – consistent with their instantaneous RE derived from experimental cross-sections. AR4 report a RE of 0.33 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Roehl et al.* [1995]. We calculate a higher RE value of 0.36 W m<sup>-2</sup> ppb<sup>-1</sup> when using the experimental absorption cross-section from *Bravo et al.* [2010b] (Tables 12-13). As for PFC-218, the higher RE calculated here can be explained by the lower integrated absorption cross-section in Roehl et al. [1995] compared to Bravo et al. [2010b]. Updated values of recommended RE and GWP for PFC-31-10 are given in Table 13. 

#### Perfluorocyclopentene (c-C<sub>5</sub>F<sub>8</sub>)

Previous reports of RE of perfluorocyclopentene are in the range 0.22 - 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.27 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Bravo et al.*, 2010b; *Vasekova et al.*, 2006]. Part of the reason for the large difference between these two studies is that *Vasekova et al.* [2006] applied a factor of 0.8 to account for non-homogeneous vertical profile, while *Bravo et al.* [2010b] assumed a constant vertical profile. No new calculations have been carried out here for this compound and to provide recommended RE we therefore use the average of the instantaneous REs reported in the literature (0.30 W m<sup>-2</sup> ppb<sup>-1</sup>) and account for stratospheric temperature adjustment as well as non-homogeneous mixing (see sections 3.3.2 and 3.3.4) and end up with a RE value of 0.08 W m<sup>-2</sup> ppb<sup>-1</sup>. The only lifetime reported in the literature for this compound is 1.0 year from *Vasekova et al.* [2006] who refer to a non-traceable source. Considering that *Cometto et al.* [2010] estimated a lifetime of only 31 days for CF<sub>3</sub>CF=CFCF<sub>3</sub>, we think that the lifetime from *Vasekova et al.* [2006] may be too long and instead use a value of 31 days when applying the lifetime correction and calculating the GWP value.

### 2566 **PFC-41-12** $(n-C_5F_{12})$

Previous reports of RE of PFC-41-12 are in the range 0.40 - 0.41 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.41 W 2567 m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010b; Roehl et al., 1995]. Bravo et al. [2010b] also report an 2568 instantaneous RE of 0.40 W m<sup>-2</sup> ppb<sup>-1</sup> from their B3LYP/6-31G\*\* calculations – in agreement 2569 with their instantaneous RE estimate based on experimental absorption cross-sections (it 2570 2571 should be noted that C<sub>5</sub>F<sub>12</sub> was part the training set used to determine corrections to band positions). AR4 has used a value of 0.41 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Roehl et al.* [1995], 2572 2573 and we calculate the exact same RE value when using the experimental absorption cross-2574 section from Bravo et al. [2010b] (Tables 12-13).

2575

2576

## PFC-51-14 $(n-C_6F_{14})$

Previous reports of RE of PFC-51-14 are in the range 0.43 - 0.49 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.46 W 2577 m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010b; Roehl et al., 1995]. Bravo et al. [2010b] also report an 2578 instantaneous RE of 0.42 W m<sup>-2</sup> ppb<sup>-1</sup> from their B3LYP/6-31G\*\* calculations, but it should 2579 2580 be noted that C<sub>6</sub>F<sub>14</sub> was part of the training set used to determine corrections to band positions. AR4 report a RE of 0.49 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Roehl et al.* [1995]. We 2581 calculate a RE value of 0.44 W m<sup>-2</sup> ppb<sup>-1</sup> when using the experimental absorption cross-2582 2583 section from Bravo et al. [2010b] (Tables 12-13). The lower RE value calculated here is presumably due to the lower integrated absorption cross-section in Bravo et al. [2010b] than 2584 in Roehl et al. [1995] (Table 12). 2585

2586

2587

## PFC-61-16 $(n-C_7F_{16})$

Ivy et al. [2012] calculated the RE of PFC-61-16 using experimental absorption data and derived a value of 0.48 W m<sup>-2</sup> ppb<sup>-1</sup>. Bravo et al. [2010b] reported a value of 0.45 W m<sup>-2</sup> ppb<sup>-1</sup> using absorption data from B3LYP/6-31G\*\* calculations, in reasonable agreement with the result obtained using experimental absorption data. We have used the absorption spectrum from Ivy et al. [2012] and calculated a RE value of 0.50 W m<sup>-2</sup> ppb<sup>-1</sup> (Tables 12-13).

2593

2594

#### $PFC-71-18 (C_8F_{18})$

Previous experimental results for RE of PFC-71-18 are in the range 0.50 - 0.57 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.53 W m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010b; Ivy et al., 2012]. We calculate a mean RE value of 0.55 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.51 - 0.59 W m<sup>-2</sup> ppb<sup>-1</sup>) when using absorption cross-sections from both of these studies (Tables 12-13). The large range in our calculations is caused by the large difference in the integrated absorption cross-sections of Bravo et al. [2010b] and Ivy et al. [2012] (Table 12). The lifetime of 3,000 years is taken from Bravo et al. [2010b], who also report a value for RE of 0.50 W m<sup>-2</sup> ppb<sup>-1</sup> from their B3LYP/6-31G\*\* calculations, but it should be noted that PFC-71-18 was part of the training set used to determine corrections to band positions.

# Perfluorodecalin (mixed $C_{10}F_{18}$ , Z- $C_{10}F_{18}$ , E- $C_{10}F_{18}$ )

The RE of perfluorodecalin has been reported to be  $0.56 \text{ W m}^{-2} \text{ ppb}^{-1}$  [*Shine et al.*, 2005b] and this value was adopted by AR4. We calculate a RE value of  $0.55 \text{ W m}^{-2} \text{ ppb}^{-1}$  using the absorption cross-section from *Shine et al.* [2005b] (Tables 12-13), which was derived experimentally in the wavenumber range  $600 - 1500 \text{ cm}^{-1}$  while the absorption bands were calculated in the lower wavenumber range  $0 - 600 \text{ cm}^{-1}$ . Our calculations for the isomers Z- $C_{10}F_{18}$  and E- $C_{10}F_{18}$  yield REs (in the wavenumber range  $600 - 1500 \text{ cm}^{-1}$ ) of  $0.56 \text{ and } 0.48 \text{ W m}^{-2} \text{ ppb}^{-1}$ , respectively. *Bravo et al.* [2010b] report instantaneous RE values of 0.58,  $0.60 \text{ and } 0.56 \text{ W m}^{-2} \text{ ppb}^{-1}$  for  $C_{10}F_{18}$  (mixed), Z- $C_{10}F_{18}$ , E- $C_{10}F_{18}$ , respectively, from their B3LYP/6-31G\*\* calculations.

## $PFC-1114 (CF_2=CF_2)$

Previous results for RE of PFC-1114 are in the range 0.01 - 0.11 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.06 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Acerboni et al.*, 2001; *Drage et al.*, 2006]. (*Acerboni et al.* [2001] used vertical profiles from a CTM distribution while *Drage et al.* [2006] assumed a constant profile.) Due to the short lifetime of 1.1 days, we calculate a RE value which rounds to 0.00 W m<sup>-2</sup> ppb<sup>-1</sup> when using the absorption cross-section from *Acerboni et al.* [2001] (Tables 12-13) and the correction factor for non-uniform mixing discussed in section 3.3.4.

## **PFC-1216** (**CF**<sub>3</sub>**CF**=**CF**<sub>2</sub>)

Only one study has estimated RE due to PFC-1216, with a value 0.04 W m<sup>-2</sup> ppb<sup>-1</sup> [Acerboni 2625 et al., 20011 (vertical profiles from a CTM distribution were used). We have used their 2626 spectrum and calculated a RE value of 0.01 W m<sup>-2</sup> ppb<sup>-1</sup> when accounting for the non-2627 homogeneous vertical profile (Tables 12-13). 2628 2629 **Perfluorobuta-1,3-diene** (CF<sub>2</sub>=CFCF=CF<sub>2</sub>) 2630 Previous reports of RE of Perfluorobuta-1,3-diene are in the range 0.01 - 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> 2631 (mean: 0.11 W m<sup>-2</sup> ppb<sup>-1</sup>) [Acerboni et al., 2001; Bravo et al., 2010b]. (Acerboni et al. [2001] 2632 used vertical profiles from a CTM distribution while Bravo et al. [2010b] assumed a constant 2633 profile.) We calculate a RE value which rounds to 0.00 W m<sup>-2</sup> ppb<sup>-1</sup> when using the 2634 absorption cross-section from Acerboni et al. [2001] (Tables 12-13). 2635 2636 **Perfluorobut-1-ene** (CF<sub>3</sub>CF<sub>2</sub>CF=CF<sub>2</sub>) 2637 Only one study has estimated RE due to perfluorobut-1-ene, with a value 0.29 W m<sup>-2</sup> ppb<sup>-1</sup> 2638 Young et al. [2009a]. We calculate a RE value of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> when using their 2639 absorption cross-section, and account for stratospheric temperature adjustment and non-2640 homogeneous distribution. A lifetime of 6 days has been used in the RE and GWP calculation 2641 for this compound, assuming that its lifetime is comparable to the lifetime of PFC-1216. 2642 2643 **Perfluorobut-2-ene** (CF<sub>3</sub>CF=CFCF<sub>3</sub>) 2644 Previous reports of RE of perfluorobut-2-ene are in the range 0.30 - 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 2645 0.31 W m<sup>-2</sup> ppb<sup>-1</sup>) [Cometto et al., 2010; Young et al., 2009a]. We calculate a RE value of 2646 0.07 W m<sup>-2</sup> ppb<sup>-1</sup> when using the absorption spectra and lifetime estimate (31 days) from 2647 Cometto et al. [2010], and accounting for stratospheric temperature adjustment and non-2648 2649 homogeneous distribution.

# 2651 Other PFCs

2650

In the sections above, recommended values of RE have been presented for the range of fully fluorinated compounds considered in AR4, along with a small number of others, where

experimental data are available. In addition, *Bravo et al.* [2010b] report estimates of RE for a range of other PFCs, based on theoretical calculations.

## 4.1.7 Halogenated Alcohols and Ethers

This is a very broad range of compounds with lifetimes stretching from days to centuries. The generally complex structure, compared to other compounds considered here, leads to a rich infrared absorption spectrum – Figure 17 shows the spectrum of isoflurane (CHF<sub>2</sub>OCHClCF) a molecule used as an inhalation anesthetic, which has absorption bands stretching across much of the infrared.

Previously published absorption cross-sections are listed in Table 14, while updated atmospheric lifetimes, radiative efficiencies, and 100-year GWP values for halogenated alcohols and ethers are presented in Table 15 and discussed below. In contrast to sections 4.1.1-4.1.6, not all compounds have their own individual piece of text in this section. For the purpose of presentation quality and brevity, some compounds are grouped together where we found it appropriate. However, all the information about previously published estimates (both based on experimental and *ab initio* absorption spectra) and results from our calculations can be found in Tables 14-15, and in Table S7 in the supplementary material. With the exception of PFPMIE, which is lost by photolysis in the upper atmosphere [*Young et al.*, 2006], the *S*-shaped fit from section 3.3.4 (Equation (2) and dark blue curve in Figure 9) has been used to account for a non-uniform vertical profile and geographic distribution for all compounds presented in this subsection.

In what follows, we focus particularly on the experimental studies. There have been *ab initio* studies from three groups [*Blowers et al.*, 2007; 2008b; *Bravo et al.*, 2011a; *Good et al.*, 1998]. We can make the following general observations about these studies. The work from the group of Blowers tends to calculate REs that are significantly higher than those obtained from experimentally determined values. Differences are around 25%, but can be as high as 40%. This group does not adjust for atmospheric lifetimes, so the differences can appear greater. The calculations from *Bravo et al.* [2011a] tend to agree with experimental values within about 10-15%, although the more sophisticated lifetime adjustment applied here can make the differences appear larger. However, REs calculated for the HG' HFPEs are some 35% higher than experimental values, although it should be noted that only one group has

studied these compounds experimentally [Stevenson et al., 2004]. Good et al. [1998] examined only three compounds using a narrow band model; they obtain values that are somewhat higher than those using experimentally determined cross-sections. In the text below, we do not discuss the *ab initio* calculations except where they provide the only RE values, or are of special note. Whenever RE values based on *ab initio* calculations are presented, this has been clearly marked in the text.

A large number of the compounds in this section were examined by *Imasu et al.* [1995], who reported both laboratory spectroscopy measurements and REs, calculated for a clear-sky mid-latitude atmosphere. In *WMO* [1999] (which became a source for REs used in many subsequent IPCC and WMO Ozone assessments), these were approximately converted to global-mean all-sky adjusted RE by taking their RE relative to *Imasu et al's* [1995] own CFC-11 calculation and then multiplying by the CFC-11 RE (0.25 W m<sup>-2</sup> ppb<sup>-1</sup>) used in *WMO* [1999] (see footnote i of Table 10-6 of *WMO* [1999]). Henceforth in this section, we refer to these forcings as "*Imasu et al.* [1995] as modified by *WMO* [1999]". When referring to the *Imasu et al.* [1995] REs we renormalize the *WMO* [1999] forcings to account for our recommended 4% increase in the CFC-11 RE (see section 4.1.1).

### **HFE-125 (CHF<sub>2</sub>OCF<sub>3</sub>)**

- 2703 Previous reports of RE due to HFE-125 are in the range 0.41 0.44 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.42
- W m<sup>-2</sup> ppb<sup>-1</sup>) [Christidis et al., 1997; Heathfield et al., 1998; Sihra et al., 2001]. IPCC AR4
- uses a RE of 0.44 W m<sup>-2</sup> ppb<sup>-1</sup> taken from Christidis et al. [1997], Good et al. [1998] and
- 2706 Heathfield et al. [1998] (the latter two after rescaling as reported in WMO [1999]). We have
- used the absorption cross-sections from Sihra et al. [2001] and calculated a RE of 0.41 W m<sup>-2</sup>
- $ppb^{-1} 8\%$  lower than that in AR4.

### HFE-134 (HG-00) (CHF<sub>2</sub>OCHF<sub>2</sub>)

- 2711 Previous reports of RE of HFE-134 (HG-00) are in the range 0.40 0.44 W m<sup>-2</sup> ppb<sup>-1</sup> (mean:
- 2712 0.43 W m<sup>-2</sup> ppb<sup>-1</sup>) [Andersen et al., 2010a; Heathfield et al., 1998; Imasu et al., 1995; Myhre
- 2713 et al., 1999]. IPCC AR4 used a RE value of 0.45 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from Good et al.
- 2714 [1998] and Heathfield et al. [1998] after rescaling in WMO [1999]. Here we have used the
- 2715 absorption cross-section from *Imasu et al.* [1995] and calculated a RE value of 0.44 W m<sup>-2</sup>

- 2716 ppb<sup>-1</sup>, which is in good agreement with AR4. Due to an update in the lifetime for this
- 2717 compound (24.4 years in WMO [2011] compared to 26 years in AR4), and a higher AGWP<sub>CO2</sub>
- value, the GWP(100) value is significantly lower than that in AR4 (see Table 15).

- 2720 HFE-143a (CH<sub>3</sub>OCF<sub>3</sub>)
- 2721 Previous reports of RE of HFE-143a are in the range 0.17 0.19 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.18 W
- 2722 m<sup>-2</sup> ppb<sup>-1</sup>) [Christensen et al., 1999; Sihra et al., 2001]. IPCC AR4 reports a RE of 0.27 W m<sup>-2</sup>
- <sup>2</sup> ppb<sup>-1</sup> which is taken from the *ab initio* study of *Good et al.* [1998] after rescaling assuming
- 2724 CFC-11 RE =  $0.25 \text{ W m}^{-2} \text{ ppb}^{-1} \text{ in } WMO [1999]$ . We calculate a RE value of  $0.18 \text{ W m}^{-2} \text{ ppb}^{-1}$
- using absorption cross-section from Sihra et al. [2001]. Our estimate is much lower (34%)
- lower) than the AR4 value, which is based on an ab initio study, but in good agreement with
- 2727 experimental studies.

2728

- 2729 **HFE-227ea** (**CF<sub>3</sub>CHFOCF<sub>3</sub>**)
- 2730 Previous reports of RE of HFE-227ea are in the range 0.31 0.42 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.37 W
- 2731 m<sup>-2</sup> ppb<sup>-1</sup>) [*Imasu et al.*, 1995; *Jain et al.*, 2001; *Oyaro et al.*, 2005; *Takahashi et al.*, 2002].
- 2732 IPCC AR4 reports a RE of 0.40 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Imasu et al.* [1995] as
- 2733 modified by WMO [1999]. We calculate a RE value of 0.44 W m<sup>-2</sup> ppb<sup>-1</sup> both when using
- 2734 absorption cross-sections from Oyaro et al. [2005] and Imasu et al. [1995]. Our estimate is
- 2735 10% higher than in AR4.

2736

- 2737 HCFE-235ca2 (enflurane) (CHF<sub>2</sub>OCF<sub>2</sub>CHFCl)
- 2738 Previous studies of RE due to HCFE-235ca2 (enflurane) are in the range 0.42 0.45 W m<sup>-2</sup>
- 2739 ppb<sup>-1</sup> (mean: 0.43 W m<sup>-2</sup> ppb<sup>-1</sup>) [Andersen et al., 2012b; Dalmasso et al., 2006]. We have
- 2740 used the absorption cross-sections from these two studies and calculated a mean RE value of
- 2741 0.41 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.39 0.42 W m<sup>-2</sup> ppb<sup>-1</sup>).

- 2743 HCFE-235da2 (isoflurane) (CHF<sub>2</sub>OCHClCF<sub>3</sub>)
- 2744 Previous reports of RE due to HCFE-235da2 (isoflurane) are in the range 0.37 0.48 W m<sup>-2</sup>
- 2745 ppb<sup>-1</sup> (mean: 0.44 W m<sup>-2</sup> ppb<sup>-1</sup>) [Andersen et al., 2010b; Christidis et al., 1997; Ryan and

Nielsen, 2010; Sihra et al., 2001]. IPCC AR4 accounted for stratospheric decay and reports a RE of 0.38 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Christidis et al.* [1997]. We calculate a RE value

of 0.42 W m<sup>-2</sup> ppb<sup>-1</sup> both when using absorption cross-sections from *Andersen et al.* [2010c]

and from Ryan and Nielsen [2010]. Our estimate is about 10% higher than in AR4.

2750

2751

2749

### HFEs studied theoretically by *Blowers et al.* [2007] and *Blowers et al.* [2008a]

- 2752 For some HFE compounds, no RE estimates based on experimental absorption cross-sections
- exist, and the *ab initio* studies of *Blowers et al.* [2007] and *Blowers et al.* [2008a] provide the
- only RE estimates of these HFEs. These compounds are:
- 2755 HFE-236ca (CHF<sub>2</sub>OCF<sub>2</sub>CHF<sub>2</sub>)
- 2756 Fluoro(methoxy)methane (CH<sub>3</sub>OCH<sub>2</sub>F)
- 2757 Difluoro(methoxy)methane (CH<sub>3</sub>OCHF<sub>2</sub>)
- 2758 Fluoro(fluoromethoxy)methane (CH<sub>2</sub>FOCH<sub>2</sub>F)
- 2759 Difluoro(fluoromethoxy)methane (CH<sub>2</sub>FOCHF<sub>2</sub>)
- 2760 Trifluoro(fluoromethoxy)methane (CH<sub>2</sub>FOCF<sub>3</sub>)
- 2761 Trifluoro(trifluoromethoxy)methane (CF<sub>3</sub>OCF<sub>3</sub>)

2762

2763

2764

2765

2766

2767

2768

2769

2770

2771

2772

2773

2774

Note that *Blowers et al.* [2007] estimated REs for some hydrofluoroethers not listed in this section. *Blowers et al.* [2007] and *Blowers et al.* [2008a] calculated instantaneous REs by using the theoretical procedure described by *Papasavva et al.* [1997] combined with the *Pinnock et al.* [1995] method (their RE estimates are listed in Table S7 in the supplementary material). Since absorption spectra were unavailable for the seven compounds listed above, no new calculations have been carried out here. Thus, we use the REs from *Blowers et al.* [2007] and *Blowers et al.* [2008a], accounting for stratospheric temperature adjustment and lifetime correction (see sections 3.3.2 and 3.3.4, respectively), and present new best estimate RE and GWP values in Table 15. The lifetime of HFE-236ca is from *WMO* [2011], the lifetime of fluoro(methoxy)methane is from *Urata et al.* [2003], while a lifetime estimate could not be found for trifluoro(trifluoromethoxy)methane and thus we only present RE assuming a uniform distribution for this compound. The lifetimes of the remaining compounds are taken

- 2775 from *Blowers et al.* [2008a]. The resulting REs are 0.56, 0.07, 0.17, 0.19, 0.30, 0.33 and 0.53
- 2776 W m<sup>-2</sup> ppb<sup>-1</sup> for HFE-236ca, fluoro(methoxy)methane, difluoro(methoxy)methane,
- 2777 fluoro(fluoromethoxy)methane, difluoro(fluoromethoxy)methane,
- 2778 trifluoro(fluoromethoxy)methane and trifluoro(trifluoromethoxy)methane, respectively.
- 2779 However, it should be stressed that these REs are based on ab initio studies, and the
- 2780 uncertainties are therefore larger than for REs based on experimental absorption spectra, as
- discussed in section 3.6.1.

- 2783 HFE-236ea2 (desflurane) (CHF<sub>2</sub>OCHFCF<sub>3</sub>)
- 2784 Previous studies of RE of HFE-236ea2 (desflurane) are in the range 0.45 0.47 W m<sup>-2</sup> ppb<sup>-1</sup>
- 2785 (mean: 0.46 W m<sup>-2</sup> ppb<sup>-1</sup>) [Andersen et al., 2010b; Imasu et al., 1995; Oyaro et al., 2005].
- 2786 IPCC AR4 used a RE of 0.44 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Imasu et al.* [1995] as
- 2787 modified by WMO [1999]. We calculate a mean RE value of 0.45 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.45 -
- 2788 0.46 W m<sup>-2</sup> ppb<sup>-1</sup>) using absorption cross-sections from three sources [Andersen et al., 2010c;
- 2789 Imasu et al., 1995; Oyaro et al., 2005]. Our RE estimate is in good agreement with AR4, but
- 2790 due to an updated lifetime estimate (10.8 years in WMO [2011] compared to 5.8 years in
- AR4), our GWP(100) value is much higher, despite the higher AGWP<sub>CO2</sub> value used here.

- 2793 HFEs studied by *Imasu et al.* [1995]
- For a number of HFE compounds, *Imasu et al.* [1995] is the only study providing REs based
- on experimental absorption cross-sections:
- 2796 HFE-236fa (CF<sub>3</sub>CH<sub>2</sub>OCF<sub>3</sub>)
- 2797 HFE-245cb2 (CF<sub>3</sub>CF<sub>2</sub>OCH<sub>3</sub>)
- 2798 HFE-245fa1 (CHF<sub>2</sub>CH<sub>2</sub>OCF<sub>3</sub>)
- 2799 HFE-329mcc2 (CHF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>3</sub>)
- 2800 HFE-338mmz1 ((CF<sub>3</sub>)<sub>2</sub>CHOCHF<sub>2</sub>)
- 2801 HFE-338mcf2 (CF<sub>3</sub>CH<sub>2</sub>OCF<sub>2</sub>CF<sub>3</sub>)
- 2802 HFE-347mcf2 (CHF<sub>2</sub>CH<sub>2</sub>OCF<sub>2</sub>CF<sub>3</sub>)

```
2803 HFE-347mmy1 ((CF<sub>3</sub>)<sub>2</sub>CFOCH<sub>3</sub>)
```

- 2804 HFE-356mec3 (CH<sub>3</sub>OCF<sub>2</sub>CHFCF<sub>3</sub>)
- 2805 HFE-356pcf2 (CHF<sub>2</sub>CH<sub>2</sub>OCF<sub>2</sub>CHF<sub>2</sub>)
- 2806 HFE-356pcf3 (CHF<sub>2</sub>OCH<sub>2</sub>CF<sub>2</sub>CHF<sub>2</sub>)
- 2807 HFE-356pcc3 (CH<sub>3</sub>OCF<sub>2</sub>CF<sub>2</sub>CHF<sub>2</sub>)
- 2808 1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)-2-propanol ((CF<sub>3</sub>)<sub>3</sub>COH)
- 2809 2,2,3,3,4,4,5,5-Octafluorocyclopentanol (-(CF<sub>2</sub>)<sub>4</sub>CH(OH)-)
- 2810 1,1,1,3,3,3-Hexafluoropropan-2-ol ((CF<sub>3</sub>)<sub>2</sub>CHOH)

2812

2813

2814

2815

2816

2817

2818

2819

2820

2821

2822

2823

2824

2825

2826

2827

2828

2829

2830

2831

2832

Many of the compounds listed above have also been studied using *ab initio* methods in Blowers et al. [2007] and Bravo et al. [2011a] (see Table 14). As previously mentioned, the uncertainties are larger for theoretical studies and we choose to focus on the experimental studies when these are available. With the exception of 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-2-propanol, for which no lifetime estimate is available in the literature, all the 15 compounds listed above, and their REs, have been reported in AR4 based on Imasu et al. [1995] as modified by WMO [1999]. We have used the Imasu et al. [1995] cross-sections to calculate new estimates of RE, taking into account both stratospheric temperature adjustment (by increasing the instantaneous RE by 10% as described in section 3.3.2) and fractional correction (by using the method described in section 3.3.4). Table 15 presents the results of our calculations and highlights the best estimate RE and GWP(100) values for each compound. For 5 of the 14 compounds which are listed above and included in AR4, our calculation of RE differed by more than 5% compared to AR4. The differences in RE between our calculation and AR4 were larger for compounds which were not well-mixed in the atmosphere (with lifetimes typically less than a few years), because lifetime corrections were not considered in AR4 (recall from the introduction to section 4.1.7 that the Imasu et al. [1995] results were scaled to a CFC-11 value of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> as explained in WMO [1999]). In many of the cases the REs in our calculation were in good agreement with AR4, but the updated lifetimes, which we take from WMO [2011], led to a change in the GWP(100) compared to AR4 (note also that the updated AGWP<sub>CO2</sub> lead to ~5% lower GWP(100) for all compounds compared to AR4).

## HFE-245fa2 (CHF<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub>)

Previous calculations of RE of HFE-245fa2 are in the range 0.33 - 0.39 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.37 W m<sup>-2</sup> ppb<sup>-1</sup>) [Christidis et al., 1997; Imasu et al., 1995; Oyaro et al., 2005; Sihra et al., 2001]. IPCC AR4 reports a RE of 0.31 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Christidis et al.* [1997], but modified to approximately account for stratospheric decay as described in WMO [1999]. We have used absorption cross-sections from Oyaro et al. [2005], Sihra et al. [2001] and Imasu et al. [1995] and calculated a RE value of 0.36 W m<sup>-2</sup> ppb<sup>-1</sup> for all three absorption spectra. The reason for the 16% higher RE value calculated here compared to AR4 is related to the different factors to account for the non-uniform distribution in the atmosphere. AR4 used a crude factor of 0.8 from Freckleton et al. [1998] while our method (see section 3.3.4) yields a factor of 0.93 for a lifetime of 5.5 years. 

### 2,2,3,3,3-Pentafluoropropan-1-ol (CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>OH)

Previous studies of RE due to 2,2,3,3,3-pentafluoropropan-1-ol are in the range 0.25 - 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.25 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Antiñolo et al.*, 2012b; *Imasu et al.*, 1995; *Sellevåg et al.*, 2007]. IPCC AR4 reports a RE of 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Imasu et al.* [1995] as modified by *WMO* [1999]. We calculate a mean RE value of 0.14 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.13 - 0.15 W m<sup>-2</sup> ppb<sup>-1</sup>) using absorption cross-sections from three sources [*Antiñolo et al.*, 2012b; *Imasu et al.*, 1995; *Sellevåg et al.*, 2007]. Our estimate is much lower (42% different) than that in AR4. The short lifetime of 0.3 years [*Antiñolo et al.*, 2012b] for this compound leads to a strong effect of the fractional correction factor which has been applied to account for non-uniform mixing (vertical and horizontal). It should be noted here that the uncertainties associated with this correction factor are very large on a percentage basis for such short-lived species (see Figure 9 and associated discussion in section 3.3.4), and we further note that our calculated instantaneous RE (i.e., without applying corrections for stratospheric temperature adjustment and lifetime correction) is in good agreement with the published instantaneous RE estimates (Table 7 in supplementary material).

### HFE-254cb1 (CH<sub>3</sub>OCF<sub>2</sub>CHF<sub>2</sub>)

- 2863 Previous calculations of RE of HFE-254cb1 are in the range 0.29 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> (mean:
- 2864 0.29 W m<sup>-2</sup> ppb<sup>-1</sup>) [Heathfield et al., 1998; Imasu et al., 1995]. IPCC AR4 used a RE of 0.28
- 2865 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Imasu et al.* [1995] as modified by *WMO* [1999]. We
- 2866 calculate an 8% lower RE value of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup> using absorption cross-section from
- 2867 *Imasu et al.* [1995].

2869

### HFE-263fb1 (CF<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub>)

- 2870 Previous reports of RE of HFE-263fb2 are in the range 0.19 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.20
- 2871 W m<sup>-2</sup> ppb<sup>-1</sup>) [Imasu et al., 1995; Osterstrom et al., 2012; Oyaro et al., 2005]. IPCC AR4
- 2872 gives a RE of 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Imasu et al.* [1995] as modified by *WMO*
- 2873 [1999]. Using absorption cross-sections from three studies [Imasu et al., 1995; Osterstrom et
- 2874 al., 2012; Oyaro et al., 2005] that give the same results we calculate a much lower (81%)
- 2875 mean RE value of 0.04 W m<sup>-2</sup> ppb<sup>-1</sup>. The reason for the large differences between our estimate
- and the AR4 is the lifetime correction factor of 0.18 (for a lifetime of 23 days [WMO, 2011])
- 2877 which has been applied here to account for non-uniform distribution (vertical and horizontal).
- 2878 It should be noted here that the uncertainties associated with this correction factor are very
- 2879 large on a percentage basis for such short-lived species (see Figure 9 and associated
- 2880 discussion in section 3.3.4). Our calculated RE is, however, in good agreement with the
- results from Imasu et al. [1995], and hence AR4, if we compare instantaneous RE (i.e.,
- 2882 without applying corrections for stratospheric temperature adjustment and lifetime correction)
- 2883 (Table 7 in supplementary material).

2884

2885

#### HFEs studied by Oyaro et al. [2005]

- For the following HFE compounds, Oyaro et al. [2005] is the only study providing REs based
- on experimental absorption cross-sections:
- 2888 HFE-263m1 (CF<sub>3</sub>OCH<sub>2</sub>CH<sub>3</sub>)
- 2889 1,1,2-Trifluoro-2-(trifluoromethoxy)-ethane (CHF<sub>2</sub>CHFOCF<sub>3</sub>)
- 2890 1-Ethoxy-1,1,2,3,3,3-hexafluoropropane (CF<sub>3</sub>CHFCF<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>)
- 2891 1,1,1,2,2,3,3-Heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)-propane (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OCHFCF<sub>3</sub>)

Ab initio studies are available for these compounds [Blowers et al., 2007; Bravo et al., 2011a] (Table 14), but we focus here on the experimental data from Oyaro et al. [2005]. They used the Pinnock et al. [1995] method to estimate instantaneous REs of 0.21, 0.35, 0.33 and 0.56 W m<sup>-2</sup> ppb<sup>-1</sup> for HFE-263m1, 1,1,2-Trifluoro-2-(trifluoromethoxy)-ethane, 1-Ethoxy-1,1,2,3,3,3-hexafluoropropane, and1,1,1,2,2,3,3-Heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)-propane, respectively. The corresponding RE estimates from our calculations (now taking into account stratospheric temperature adjustment and inhomogeneous distribution in the troposphere) are 0.13, 0.35, 0.33 and 0.58 W m<sup>-2</sup> ppb<sup>-1</sup>, respectively, when using absorption cross-sections from Oyaro et al. [2005] and lifetime estimates of 0.4 [Bravo et al., 2011a], 9.8, 0.4 and 67.0 years [Oyaro et al., 2005], respectively. None of these compounds are included in AR4, thus we provide new best estimates of RE and GWP for all these compounds.

## 3,3,3-Trifluoropropan-1-ol (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH)

Previous experimental studies of 3,3,3-trifluoropropan-1-ol have reported values for RE in the range 0.17 - 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.19 W m<sup>-2</sup> ppb<sup>-1</sup>) [Jimenez et al., 2010; Sellevåg et al., 2007]. We have used absorption cross-sections from Jimenez et al. [2010]. Sellevåg et al. [2007] and Waterland et al. [2005] and calculated the same RE of 0.02 W m<sup>-2</sup> ppb<sup>-1</sup> for all three spectra. Our calculated instantaneous REs of 0.21 W m<sup>-2</sup> ppb<sup>-1</sup> and 0.17 W m<sup>-2</sup> ppb<sup>-1</sup> using spectra from Jimenez et al. [2010] and Sellevåg et al. [2007], respectively, compare well with the previously published REs (which did not account for stratospheric temperature adjustment and lifetime correction). The lifetime of 12.0 days is taken from Jimenez et al. [2010].

## Sevoflurane, HFE-347mmz1 ((CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>2</sub>F)

Experimental studies have reported RE values for sevoflurane in the range 0.35 - 0.37 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.36 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Andersen et al.*, 2010c; *Ryan and Nielsen*, 2010]. We have used the absorption cross-sections from these two studies and calculated a RE value of 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> for both spectra. It should be noted here that *Andersen et al.* [2010c] and *Ryan and Nielsen* [2010] calculated the instantaneous RE using the *Pinnock et al.* [1995] method

while we have accounted for stratospheric temperature adjustment and non-uniform distribution in the troposphere.

2925

2926

### HFE-347mcc3 (HFE-7000) (CH<sub>3</sub>OCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)

- 2927 Previous experimental studies of HFE-347mcc3 (HFE-7000) have reported values for RE in
- 2928 the range 0.32 0.35 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.34 W m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010a; Imasu et al.,
- 2929 1995; *Ninomiya et al.*, 2000]. We have used the absorption cross-sections from all these three
- 2930 studies and calculated a mean RE value of 0.35 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.33 0.36 W m<sup>-2</sup> ppb<sup>-1</sup>).
- 2931 Our estimate is in reasonable agreement with the RE of 0.34 W m<sup>-2</sup> ppb<sup>-1</sup> in AR4 (which
- originated from *Imasu et al.* [1995] as modified by *WMO* [1999]).

2933

2934

## HFE-347pcf2 (CHF<sub>2</sub>CF<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub>)

- One experimental study has reported a value of RE for this HFE-347pcf2 [Heathfield et al.,
- 2936 1998]. The original value (0.47 W m<sup>-2</sup> ppb<sup>-1</sup>) was determined using the *Pinnock et al.* [1995]
- 2937 method. There is some confusion regarding the RE of this molecule. WMO [1999] (where it is
- referred to as HFE-347mfc2) use the *Heathfield et al.* [1998] value this molecule then does
- 2939 not seem to appear in IPCC or WMO/UNEP ozone assessments tabulations until IPCC [2007]
- 2940 which recommends a value of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> this is perhaps a lifetime-corrected version
- of the earlier value, although no reference is given. We recommend instead, using the original
- 2942 Heathfield et al. [1998] value, applying our generic correction of a 10% increase to account
- 2943 for stratospheric temperature adjustment and applying the lifetime correction (assuming a
- 2944 lifetime of 6 years) from section 3.3.4 of 0.93. This yields our recommended value of 0.48 W
- $2945 m^{-2} ppbv^{-1}$ .

2946

2947

#### HFE-356mff2 (CF<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub>)

- 2948 Previous experimental studies of HFE-356mff2 have reported values for RE in the range 0.33
- 2949 0.35 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.35 W m<sup>-2</sup> ppb<sup>-1</sup>) [Oyaro et al., 2004; Sihra et al., 2001;
- 2950 Wallington et al., 1998]. We calculate a mean RE value of 0.17 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.17 -
- 2951 0.18 W m<sup>-2</sup> ppb<sup>-1</sup>) using absorption cross-sections from two sources [Oyaro et al., 2004; Sihra
- 2952 et al., 2001]. The non-homogeneous mixing of this short-lived compound was not accounted

for in the three previous studies; our estimate of RE is consistent with the published values if we assume uniform mixing.

#### HFE-356mmz1 ((CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub>)

Previous experimental studies of HFE-356mmz1 have both reported values for RE of 0.31 W m<sup>-2</sup> ppb<sup>-1</sup> [*Imasu et al.*, 1995; *Oyaro et al.*, 2004] (note that the *Imasu et al.* [1995] value is here scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). The *Imasu et al.* [1995] value (as modified by *WMO* [1999]) of 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> was used by IPCC AR4. We have used the absorption cross-sections from *Imasu et al.* [1995] and *Oyaro et al.* [2004] and calculated a RE value of 0.15 W m<sup>-2</sup> ppb<sup>-1</sup> for both of these spectra. Our estimate is 50% lower than AR4, and this is almost entirely due to the factor applied here to account for non-homogeneous mixing for this short-lived species (lifetime of 97.1 days [*Oyaro et al.*, 2004]). The best estimate RE and GWP values are shown in Table 15.

## HFE-365mcf3 (CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)

Previous experimental studies of HFE-365mcf3 have reported values for RE in the range 0.28 - 0.33 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.30 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Imasu et al.*, 1995; *Oyaro et al.*, 2004; *Thomsen et al.*, 2011] (note that the *Imasu et al.* [1995] value is here scaled to our recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). The *Imasu et al.* [1995] value (as modified by *WMO* [1999]) of 0.27 W m<sup>-2</sup> ppb<sup>-1</sup> was used by IPCC AR4. In contrast to the published values we have accounted for stratospheric temperature adjustment and non-homogeneous mixing in the troposphere (assuming a lifetime of 19.3 days [*Oyaro et al.*, 2004]), and calculated a RE value of 0.05 W m<sup>-2</sup> ppb<sup>-1</sup> when using absorption cross-sections from both *Oyaro et al.* [2004] and *Imasu et al.* [1995]. Our estimate is ~80% lower than that in AR4, but it should be noted here that the uncertainties associated with the lifetime correction factors are very large on a percentage basis for such short-lived species (see Figure 9 and associated discussion in section 3.3.4), and we further note that our calculated instantaneous RE is consistent with the published estimates.

## HFEs studied theoretically by Bravo et al. [2011a]

- 2983 For a number of HFE compounds, no RE estimates based on experimental absorption cross-
- sections exist and the *ab initio* study of *Bravo et al.* [2011a] provides the only RE estimate of
- these HFEs. These compounds are:
- 2986 HFE-365mcf2 (CF<sub>3</sub>CF<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>)
- 2987 HG-02 (HF<sub>2</sub>C-(OCF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>-OCF<sub>2</sub>H)
- 2988  $HG-03 (HF_2C-(OCF_2CF_2)_3-OCF_2H)$
- 2989 HG-20 (HF<sub>2</sub>C–(OCF<sub>2</sub>)<sub>2</sub>–OCF<sub>2</sub>H)
- 2990 HG-21 (HF<sub>2</sub>C–OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>O–CF<sub>2</sub>H)
- 2991  $HG-30 (HF_2C-(OCF_2)_3-OCF_2H)$
- 2992 1-Ethoxy-1,1,2,2,3,3,3-heptafluoropropane (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>)
- 2993 Fluoroxene (CF<sub>3</sub>CH<sub>2</sub>OCH=CH<sub>2</sub>)
- 2994 1,1,2,2-Tetrafluoro-1-(fluoromethoxy)ethane (CH<sub>2</sub>FOCF<sub>2</sub>CF<sub>2</sub>H)
- 2995 HG'-10 (CH<sub>3</sub>OCF<sub>2</sub>OCH<sub>3</sub>)
- 2996 HG'-20 (CH<sub>3</sub>O(CF<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub>)
- 2997 HG'-30 (CH<sub>3</sub>O(CF<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)

2999

3000

3001

3002

3003

3004

3005

3006

3007

3008

3009

3010

3011

For all of the compounds listed above we have used the theoretical absorption cross-sections from *Bravo et al.* [2011a] to calculate estimates of RE, taking into account both stratospheric temperature adjustment (by increasing the instantaneous RE by 10% as described in section 3.3.2) and fractional correction (by using the method described in section 3.3.4). For three of these compounds (HG'-10, HG'-20, HG'-30), no lifetime estimates were found in the literature, and hence the RE estimates for these compounds assumes a uniform vertical and horizontal distribution in the atmosphere. Lifetimes for the remaining nine compounds were taken from *Bravo et al.* [2011a]. The study of *Bravo et al.* [2011a] used the *Pinnock et al.* [1995] method to estimate instantaneous REs, and accounted for non-homogeneous mixing by applying the exponential function from *Sihra et al.* [2001] (see section 3.3.4) for compounds where lifetime estimates were known. The RE estimates of *Bravo et al.* [2011a] are listed in Table S7 in the supplementary material, while our results are presented in Table 15. In general, differences are small but reflect the use of an updated

Pinnock et al. [1995] curve in this study, and that the stratospheric temperature adjustment was not taken into account in *Bravo et al.* [2011a]. None of the compounds listed above are included in AR4, thus we provide new best estimates of RE and GWP for all these compounds. It should, however, be kept in mind that RE estimates based on *ab initio* calculations are associated with larger uncertainties than estimates based on experimental cross-sections, as discussed in section 3.6.1 (see also Table 1).

3018

3019

## HFE-374pc2 (CHF<sub>2</sub>CF<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>)

- Previous experimental studies of HFE-374pc2 have reported values for RE in the range 0.31 0.32 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.31 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Heathfield et al.*, 1998; *Imasu et al.*, 1995]. AR4 uses a RE of 0.25 W m<sup>-2</sup> ppb<sup>-1</sup> taken from *Heathfield et al.* [1998], but modified in *WMO* [1999] to crudely account for non-homogeneous mixing by applying a factor of 0.8 based on *Freckleton et al.* [1998]. We calculate a RE value of 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> using absorption cross-sections from *Imasu et al.* [1995]. Due to the different methods used to account for non-homogeneous mixing, our estimate is 19% higher than in AR4. The lifetime of 5.0 years is
- 3026 homogeneous mixing, our estimate is 19% higher than in AR4. The lifetime of 5.0 years is

taken from AR4.

3028

3029

## 4,4,4-Trifluorobutan-1-ol (CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH)

Jimenez et al. [2010] used the *Pinnock et al.* [1995] method and report an instantaneous RE value for 4,4,4-trifluorobutan-1-ol of 0.11 W m<sup>-2</sup> ppb<sup>-1</sup>. We have used their absorption cross-section and calculated the same instantaneous RE. When taking into account stratospheric temperature adjustment and non-homogeneous mixing in the troposphere (assuming a lifetime of 4.0 days [*Jimenez et al.*, 2010]), our calculation yield a RE value of 0.01 W m<sup>-2</sup> ppb<sup>-1</sup>.

3035

3036

#### HFE-43-10pccc124 (H-Galden 1040x, HG-11) (CHF<sub>2</sub>OCF<sub>2</sub>OC<sub>2</sub>F<sub>4</sub>OCHF<sub>2</sub>)

Previous experimental studies of HFE-43-10pccc124 (H-Galden 1040x, HG-11) have reported values for RE in the range 0.99 – 1.37 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 1.12 W m<sup>-2</sup> ppb<sup>-1</sup>)

[Christidis et al., 1997; Myhre et al., 1999; Sihra et al., 2001; Wallington et al., 2009]. IPCC AR4 use a RE of 1.37 W m<sup>-2</sup> ppb<sup>-1</sup> taken from Myhre et al. [1999]. We have used the absorption cross-section from Wallington et al. [2009] and calculated a 26% lower RE value

of 1.02 W m<sup>-2</sup> ppb<sup>-1</sup>, which is the same as the estimate in *Wallington et al.* [2009]. It should be noted here that the spectrum from *Wallington et al.* [2009] supersedes previous Ford measurements of HG-11 [*Christidis et al.*, 1997; *Sihra et al.*, 2001] and that the cross-section from *Cavalli et al.* [1998], which has been used in *Myhre et al.* [1999], is an overestimate [*Wallington et al.*, 2009].

3047

3048

### HFE-449s1 (HFE-7100) ( $C_4F_9OCH_3$ )

- Previous studies of RE due to HFE-449s1 (HFE-7100) are in the range 0.31 0.37 W m<sup>-2</sup> ppb<sup>-1</sup>
- 3050 (mean: 0.34 W m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010a; Sihra et al., 2001; Wallington et al., 1997].
- 3051 IPCC AR4 report a RE of 0.31 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from Wallington et al. [1997] as
- modified by WMO [1999]. We estimate a 17% higher RE of 0.36 W m<sup>-2</sup> ppb<sup>-1</sup> using the
- 3053 absorption cross-sections from two sources [Bravo et al., 2010a; Sihra et al., 2001] and
- 3054 applying our lifetime correction. The main reason for the higher estimate is due to lower
- 3055 lifetime correction with a factor of 0.92 instead of 0.8 applied in WMO [1999].

3056

3057

#### HFEs studied by Sihra et al. [2001]

- For the following HFE compounds, Sihra et al. [2001] is the only study providing REs based
- on experimental absorption cross-sections:
- 3060 n-HFE-7100 (n-C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>)
- 3061 i-HFE-7100 (i-C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>)
- i-HFE-7200 (i-C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>)

3063

3064

3065

3066

3067

3068

3069

3070

3071

Ab initio studies are available for these compounds [Blowers et al., 2007; Bravo et al., 2011a] (Table 14), but we focus here on the experimental data from Sihra et al. [2001]. They assumed homogeneous distribution in the atmosphere and estimated REs of 0.47, 0.37 and 0.34 W m<sup>-2</sup> ppb<sup>-1</sup> for *n*-HFE-7100, *i*-HFE-7100 and *i*-HFE-7200, respectively. Our calculations are consistent with the Sihra et al. [2001] results if we make the same assumption and use their absorption cross-sections. When accounting for non-homogeneous vertical and horizontal distribution, our calculations yield lower REs with values of 0.42, 0.35 and 0.24 W m<sup>-2</sup> ppb<sup>-1</sup> for *n*-HFE-7100, *i*-HFE-7100 and *i*-HFE-7200, respectively. We have then assumed

- 3072 that the lifetime of n-HFE-7100 and i-HFE-7100 are the same as for HFE-7100 (4.7 years
- 3073 [WMO, 2011]), and that i-HFE-7200 has the same lifetime as HFE-7200 (0.8 years [WMO,
- 3074 2011]). None of these compounds are included in AR4, thus we provide new best estimates of
- 3075 RE and GWP for all these compounds.

- 3077 HFE-569sf2 (HFE-7200) ( $C_4F_9OC_2H_5$ )
- Previous studies of RE due to HFE-569sf2 (HFE-7200) are in the range 0.30 0.39 W m<sup>-2</sup>
- 3079 ppb<sup>-1</sup> (mean: 0.33 W m<sup>-2</sup> ppb<sup>-1</sup>) [Bravo et al., 2010a; Christensen et al., 1998; Sihra et al.,
- 3080 2001]. IPCC AR4 report a RE of 0.30 W m<sup>-2</sup> ppb<sup>-1</sup> which is taken from *Christensen et al.*
- 3081 [1998] as modified by WMO [1999]. We have used absorption cross-sections from two
- 3082 sources [Bravo et al., 2010a; Sihra et al., 2001] and calculated a mean RE value of 0.30 W m
- $^{2}$  ppb<sup>-1</sup> (range: 0.29 0.32 W m<sup>-2</sup> ppb<sup>-1</sup>) in agreement with AR4.

3084

3085

- n-HFE-7200 (n-C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>)
- 3086 The only estimates of the RE of *n*-HFE-7200 are from the *ab initio* studies of *Bravo et al*.
- 3087 [2011a] and Blowers et al. [2007] who both used the Pinnock et al. [1995] method to
- 3088 calculate instantaneous REs of 0.47 and 0.55 W m<sup>-2</sup> ppb<sup>-1</sup>, respectively. We have used the
- 3089 theoretical absorption spectrum from Bravo et al. [2011a] and calculated a similar
- 3090 instantaneous RE (0.45 W m<sup>-2</sup> ppb<sup>-1</sup>). When accounting for stratospheric temperature
- adjustment and non-homogeneous tropospheric distribution, our RE estimate is 0.35 W m<sup>-2</sup>
- 3092 ppb<sup>-1</sup>. We have then assumed that n-HFE-7200 has the same lifetime as HFE-7200 (0.8 years
- 3093 [*WMO*, 2011]).

3094

- HFE-236ca12 (HG-10) (CHF<sub>2</sub>OCF<sub>2</sub>OCHF<sub>2</sub>)
- The RE of HFE-236ca12 (HG-10) has been estimated to be 0.66 W m<sup>-2</sup> ppb<sup>-1</sup> in *Myhre et al*.
- 3097 [1999], and this value was used in the AR4 report. We have used the absorption cross-section
- from the same study and calculated a RE value of 0.65 W m<sup>-2</sup> ppb<sup>-1</sup> in good agreement with
- 3099 AR4. Due to an updated lifetime for this compound, from 12.1 years in AR4 to 25.0 years in
- 3100 WMO [2011], our calculated GWP(100) value is considerably higher than in AR4, despite the
- 3101 higher AGWP<sub>CO2</sub> value used here.

3102	
3103	HFE-338pcc13 (HG-01) (CHF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCHF <sub>2</sub> )
3104	Myhre et al. [1999] have estimated a RE due to HFE-338pcc13 (HG-01) of 0.87 W m <sup>-2</sup> ppb <sup>-1</sup>
3105	which is the value adopted by AR4. We have used the Myhre et al. [1999] absorption cross-
3106	section and calculated a similar RE value of 0.86 W m <sup>-2</sup> ppb <sup>-1</sup> . We use an updated lifetime of
3107	12.9 years [WMO, 2011], compared to 6.2 years in AR4, and this leads to a GWP(100) value
3108	which is about a factor 2 higher than in AR4.
3109	
3110	2-Ethoxy-3,3,4,4,5-pentafluorotetrahydro-2,5-bis[1,2,2,2-tetrafluoro-1-
3111	$(trifluoromethyl)ethyl]\hbox{-}furan\;(C_{12}H_5F_{19}O_2)$
3112	Javadi et al. [2007] used the Pinnock et al. [1995] method to estimate an instantaneous RE
3113	due to 2-ethoxy-3,3,4,4,5-pentafluorotetrahydro-2,5-bis[1,2,2,2-tetrafluoro-1-
3114	(trifluoromethyl)ethyl]-furan of 0.60 W m <sup>-2</sup> ppb <sup>-1</sup> . Since no new calculations have been
3115	carried out here for this compound, we apply our generic correction of a 10% increase to
3116	account for stratospheric temperature adjustment, and our lifetime correction factor (assuming
3117	a lifetime of 1.0 year [Javadi et al., 2007]) from section 3.3.4 of 0.74, and recommend a RE
3118	value of 0.49 W m <sup>-2</sup> ppbv <sup>-1</sup> .
3119	
3120	HFEs studied by Andersen et al. [2004]
3121	For the following HFE compounds, Andersen et al. [2004] is the only study providing REs
3122	based on experimental absorption cross-sections:
3123	HG'-01 (CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub> )
3124	HG'-02 (CH <sub>3</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>2</sub> CH <sub>3</sub> )
3125	HG'-03 (CH <sub>3</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>3</sub> CH <sub>3</sub> )
3126	
3127	RE estimates using ab initio calculations are available for these compounds [Bravo e
3128	al., 2011a] (Table S7 in the supplementary material), but we focus here on the experimental
3129	data from Andersen et al. [2004]. They used the Pinnock et al. [1995] method to estimate
3130	instantaneous REs of 0.32, 0.61 and 0.83 W m <sup>-2</sup> ppb <sup>-1</sup> for HG'-01, HG'-02 and HG'-03

respectively. The corresponding RE estimates from our calculations (now taking into account stratospheric temperature adjustment and inhomogeneous distribution in the troposphere) are 0.29, 0.56 and 0.76 W m<sup>-2</sup> ppb<sup>-1</sup>, respectively, when using absorption cross-sections and lifetimes from *Andersen et al.* [2004]. None of these compounds are included in AR4, thus we provide new best estimates of RE and GWP for all these compounds.

3136

- 3137 **HFE-329me3** (**CF<sub>3</sub>CFHCF<sub>2</sub>OCF<sub>3</sub>**)
- 3138 Wallington et al. [2004] have calculated an instantaneous RE value of HFE-329me3 of 0.48
- W m<sup>-2</sup> ppb<sup>-1</sup> by using experimental absorption cross-section and the *Pinnock et al.* [1995]
- 3140 method. We have used the absorption spectrum from the same study and calculated the same
- 3141 RE value when accounting for stratospheric temperature adjustment. Due to the relatively
- 3142 long lifetime of 40 years [Wallington et al., 2004], the compound is well-mixed in the
- 3143 troposphere and the lifetime correction factor does not impact the RE value.

3144

- 3145 HFE-338mec3 (CF<sub>3</sub>CFHCF<sub>2</sub>OCF<sub>2</sub>H)
- Previous experimental studies of RE due to HFE-338mec3 are in the range 0.49 0.51 W m<sup>-2</sup>
- 3147 ppb<sup>-1</sup> (mean: 0.50 W m<sup>-2</sup> ppb<sup>-1</sup>) [Oyaro et al., 2005; Wallington et al., 2004]. We have used
- 3148 the absorption cross-sections from both these studies and calculated a mean RE value of 0.51
- 3149 W m<sup>-2</sup> ppb<sup>-1</sup> (range: 0.51 0.52 W m<sup>-2</sup> ppb<sup>-1</sup>) when assuming a uniform distribution in the
- 3150 atmosphere. This is probably an upper estimate as no fractional correction factor has been
- 3151 applied because of the large disagreement found in the literature of the lifetime for this
- 3152 compound [Oyaro et al., 2005; Wallington et al., 2004].

3153

- HFEs studied by Waterland et al. [2005]
- 3155 For the following HFE compounds, Waterland et al. [2005] is the only study providing
- 3156 experimental absorption cross-sections:
- 3157 3,3,4,4,5,5,6,6,7,7,7-Undecafluoroheptan-1-ol (CF<sub>3</sub>(CF<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>OH)
- 3158 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluorononan-1-ol (CF<sub>3</sub>(CF<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>OH)

3159	3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Nonadecafluoroundecan-1-ol
3160	$(CF_3(CF_2)_8CH_2CH_2OH)$
3161	
3162	Waterland et al. [2005] did not estimate REs of the compounds listed above, but we
3163	have used their absorption cross-sections to calculate REs of 0.06, 0.07 and 0.05 W m <sup>-2</sup> ppb <sup>-1</sup>
3164	for 3,3,4,4,5,5,6,6,7,7,7-undecafluoroheptan-1-ol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-
3165	pentadecafluorononan-1-ol and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-
3166	nonadecafluoroundecan-1-ol, respectively. The lifetimes for all three compounds were
3167	assumed to be 20 days based on Ellis et al. [2003].
3168	
3169	2-Chloro-1,1,2-trifluoro-1-methoxyethane (CH <sub>3</sub> OCF <sub>2</sub> CHFCl)
3170	One experimental study has used the Pinnock et al. [1995] method to estimate an
3171	instantaneous RE due to 2-chloro-1,1,2-trifluoro-1-methoxyethane of 0.26 W m <sup>-2</sup> ppb <sup>-1</sup>
3172	[Dalmasso et al., 2006]. We have used their absorption cross-section to calculate a slightly
3173	lower RE value of 0.21 W m <sup>-2</sup> ppb <sup>-1</sup> (now taking into account stratospheric temperature
3174	adjustment and inhomogeneous distribution in the troposphere). The lifetime of 1.4 years is
3175	taken from Dalmasso et al. [2006].
3176	
3177	$PFPMIE\ (perfluor opolymethylis opropyl)\ (CF_3OCF(CF_3)CF_2OCF_2OCF_3)$
3178	One experimental study has estimated RE due to PFPMIE (perfluoropolymethylisopropyl),
3179	with a value 0.65 W m <sup>-2</sup> ppb <sup>-1</sup> [Young et al., 2006] which is used in IPCC AR4. We have used
3180	the same absorption cross-section and calculated the same RE value. In contrast to the other
3181	compounds listed in this section, PFPMIE is lost by photolysis in the upper atmosphere and
3182	this results in a long lifetime of approximately 800 years [Young et al., 2006]. Hence, we have
3183	used the exponential fit from section 3.3.4 (Equation (1) and red curve in Figure 9) rather than
3184	the S-shaped fit to account for a non-uniform vertical profile, although this has almost a
3185	negligible impact on the RE because such long-lived compounds are relatively well-mixed
3186	throughout the atmosphere.

HFE-216 (CF<sub>3</sub>OCF=CF<sub>2</sub>)

3189	Mashino et al. [2000] have estimated the instantaneous RE of HFE-216 by using the Pinnock
3190	et al. [1995] method and report a value of 0.28 W m <sup>-2</sup> ppb <sup>-1</sup> . We have used their absorption
3191	cross-section, accounted for stratospheric temperature adjustment and lifetime correction, and
3192	calculated a much lower RE value of 0.02 W m <sup>-2</sup> ppb <sup>-1</sup> . The reason for the large difference is
3193	the short lifetime of 8.4 days [Mashino et al., 2000] which leads to a strong correction when
3194	accounting for non-homogeneous horizontal and vertical distribution in the troposphere. It
3195	should be noted here that the uncertainties associated with the lifetime correction factors are
3196	very large on a percentage basis for such short-lived species (see Figure 9 and associated
3197	discussion in section 3.3.4).
3198	
3199	HFEs studied theoretically by Bravo et al. [2011b]
3200	For a number of HFE compounds, no RE estimates based on experimental absorption cross-
3201	sections exist and the ab initio study of Bravo et al. [2011b] provides the only RE estimate of
3202	these HFEs. These compounds are:
3203	Trifluoromethyl formate (HCOOCF <sub>3</sub> )
3204	Perfluoroethyl formate (HCOOCF <sub>2</sub> CF <sub>3</sub> )
3205	Perfluoropropyl formate (HCOOCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> )
3206	Perfluorobutyl formate (HCOOCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> )
3207	2,2,2-Trifluoroethyl formate (HCOOCH <sub>2</sub> CF <sub>3</sub> )
3208	3,3,3-Trifluoropropyl formate (HCOOCH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub> )
3209	1,2,2,2-Tetrafluoroethyl formate (HCOOCHFCF <sub>3</sub> )
3210	1,1,1,3,3,3-Hexafluoropropan-2-yl formate (HCOOCH(CF <sub>3</sub> ) <sub>2</sub> )
3211	Perfluorobutyl acetate (CH <sub>3</sub> COOCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> )
3212	Perfluoropropyl acetate (CH <sub>3</sub> COOCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> )
3213	Perfluoroethyl acetate (CH <sub>3</sub> COOCF <sub>2</sub> CF <sub>3</sub> )
3214	Trifluoromethyl acetate (CH <sub>3</sub> COOCF <sub>3</sub> )
3215	Methyl carbonofluoridate (FCOOCH <sub>3</sub> )
3216	Fluoromethyl carbonofluoridate (FCOOCFH <sub>2</sub> )

3218	Trifluoromethyl carbonofluoridate (FCOOCF <sub>3</sub> )
3219	Perfluoroethyl carbonofluoridate (FCOOCF <sub>2</sub> CF <sub>3</sub> )
3220	2,2,2-Trifluoroethyl carbonofluoridate (FCOOCH <sub>2</sub> CF <sub>3</sub> )
3221	1,1-Difluoroethyl carbonofluoridate (FCOOCF <sub>2</sub> CH <sub>3</sub> )
3222	Perfluoropropyl carbonofluoridate (FCOOCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> )
3223	Trifluoromethyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCF <sub>3</sub> )
3224	Perfluoroethyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCF <sub>2</sub> CF <sub>3</sub> )
3225	1,1-Difluoroethyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCF <sub>2</sub> CH <sub>3</sub> )
3226	$1,1,1,3,3,3-Hexafluoropropan-2-yl\ 2,2,2-trifluoroacetate\ (CF_3COOCH(CF_3)_2)$
3227	Vinyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCH=CH <sub>2</sub> )
3228	Ethyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub> )
3229	2,2,2-Trifluoroethyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCH <sub>2</sub> CF <sub>3</sub> )
3230	Allyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCH <sub>2</sub> CHCH <sub>2</sub> )
3231	Methyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCH <sub>3</sub> )
3232	Phenyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOPh)
3233	Methyl 2-fluoroacetate (H <sub>2</sub> CFCOOCH <sub>3</sub> )
3234	Difluoromethyl 2,2-difluoroacetate (HCF <sub>2</sub> COOCHF <sub>2</sub> )
3235	Methyl 2,2-difluoroacetate (HCF <sub>2</sub> COOCH <sub>3</sub> )
3236	Difluoromethyl 2,2,2-trifluoroacetate (CF <sub>3</sub> COOCHF <sub>2</sub> )
3237	
3238	For all of the compounds listed above we have used the theoretical absorption cross-
3239	sections from Bravo et al. [2011b] to calculate estimates of RE, taking into account both
3240	stratospheric temperature adjustment (by increasing the instantaneous RE by 10% as
3241	described in section 3.3.2) and the fractional correction (by using the method described in
3242	section 3.3.4). For 14 of the 34 compounds listed above, no lifetime estimates were found in
3243	the literature, hence the RE estimates for these compounds assume a uniform vertical and

 $Diffluoromethyl\ carbonofluoridate\ (FCOOCF_2H)$ 

3244 horizontal distribution in the atmosphere. Lifetimes for the remaining 20 compounds were 3245 taken from various sources [Blanco and Teruel, 2007; Bravo et al., 2011b; Chen et al., 2006; Christensen et al., 1998; Oyaro et al., 2004; Wallington et al., 1988; Wallington et al., 1997; 3246 3247 WMO, 2011] (see Table S7 in the supplementary material for details). The Bravo et al. 3248 [2011b] study used the *Pinnock et al.* [1995] method to estimate instantaneous REs, but they 3249 did not account for non-homogeneous mixing. The RE estimates of Bravo et al. [2011b] are 3250 listed in Table S7 in the supplementary material, while our results are presented in Table 15. 3251 In general, differences reflect the use of an updated *Pinnock et al.* [1995] curve in this study, 3252 and that stratospheric temperature adjustment and lifetime correction were not taken into 3253 account in Bravo et al. [2011b]. None of the compounds listed above are included in AR4, 3254 thus we provide new best estimates of RE and GWP for all these compounds. It should, 3255 however, be kept in mind that RE estimates based on ab initio calculations are associated with 3256 larger uncertainties than estimates based on experimental cross-sections, as discussed in 3257 section 3.6.1 (see also Table 1).

3258

3259

#### 2,2,3,3,4,4,4-Heptafluorobutan-1-ol ( $C_3F_7CH_2OH$ )

One experimental study has estimated the instantaneous lifetime-corrected RE due to 2,2,3,3,4,4,4-heptafluorobutan-1-ol with a value 0.20 W m<sup>-2</sup> ppb<sup>-1</sup> [*Bravo et al.*, 2010a]. We have used their absorption cross-section and calculated the same RE value when also taking into account stratospheric temperature adjustment and when using our own lifetime correction method (*Bravo et al.* [2010a] used the exponential function of *Sihra et al.* [2001]). The lifetime of 0.6 years is taken from *Bravo et al.* [2010a].

3266

3267

#### 2,2,3,3-Tetrafluoro-1-propanol (CHF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH)

Previous experimental studies of RE due to 2,2,3,3-tetrafluoro-1-propanol are in the range 0.20 - 0.23 W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.22 W m<sup>-2</sup> ppb<sup>-1</sup>) [*Antiñolo et al.*, 2012b; *Sellevåg et al.*, 2007]. We have used the absorption cross-sections from these two studies and calculated a RE value of 0.11 W m<sup>-2</sup> ppb<sup>-1</sup> for both sources. The lifetime correction applied here is the main reason for the lower value compared to earlier work where the instantaneous RE assuming constant distribution was estimated. The lifetime of 91.2 days is taken from *Antiñolo et al.* [2012b].

3275	
3276	2,2,3,4,4,4-Hexafluoro-1-butanol (CF <sub>3</sub> CHFCF <sub>2</sub> CH <sub>2</sub> OH)
3277	The experimental study of Sellevåg et al. [2007] has used the Pinnock et al. [1995] method to
3278	estimate an instantaneous RE due to 2,2,3,4,4,4-hexafluoro-1-butanol of 0.37 W m <sup>-2</sup> ppb <sup>-1</sup> .
3279	We have used their absorption cross-section and calculated a RE value of 0.19 W m <sup>-2</sup> ppb <sup>-1</sup>
3280	when taking into account stratospheric temperature adjustment and lifetime correction. The
3281	lifetime of 94.9 days is taken from Sellevåg et al. [2007].
3282	
3283	$2,2,3,3,4,4,4-Heptafluoro-1-butanol\ (CF_3CF_2CF_2CH_2OH)$
3284	One experimental study has estimated the instantaneous RE due to 2,2,3,3,4,4,4-heptafluoro-
3285	1-butanol, with a value 0.30 W m <sup>-2</sup> ppb <sup>-1</sup> [Sellevåg et al., 2007]. We calculate a RE value of
3286	0.16 W m <sup>-2</sup> ppb <sup>-1</sup> using the absorption cross-section from the same study. Our RE estimate
3287	accounts for stratospheric temperature adjustment and lifetime correction; the latter factor
3288	explains the lower RE calculated here. The lifetime of 0.3 years is taken from Sellevåg et al.
3289	[2007].
3290	
3291	$1,1,2,2\text{-}Tetrafluoro-3\text{-}methoxy-propane} \ (CHF_2CF_2CH_2OCH_3)$
3292	One experimental study has estimated the instantaneous RE due to 1,1,2,2-tetrafluoro-3-
3293	methoxy-propane with a value 0.24 W m <sup>-2</sup> ppb <sup>-1</sup> [Oyaro et al., 2004]. We have used their
3294	absorption cross-section and calculated a much lower RE value of 0.04 W m <sup>-2</sup> ppb <sup>-1</sup> when
3295	taking into account stratospheric temperature adjustment and non-homogeneous distribution
3296	in the troposphere (these factors were not taken into account in the published RE estimate).
3297	The lifetime of 14.2 days is taken from Oyaro et al. [2004], and it should be noted here that
3298	the uncertainties associated with the lifetime correction factor are very large on a percentage
3299	basis for such short-lived species (see Figure 9 and associated discussion in section 3.3.4),
3300	
3301	Perfluoro-2-methyl-3-pentanone (CF <sub>3</sub> CF <sub>2</sub> C(O)CF(CF <sub>3</sub> ) <sub>2</sub> )

3303

3304

No RE estimates of perfluoro-2-methyl-3-pentanone exist in the literature. Here we have used the absorption cross-section from  $D'Anna\ et\ al.\ [2005]$  and calculate a RE value of 0.03 W m  $^{-}$ <sup>2</sup> ppb<sup>-1</sup> assuming a lifetime of 7.0 days [D'Anna et al., 2005].

3306

3307

3308

3309

3310

3311

3312

3313

3314

### 3,3,3-Trifluoro-propanal (CF<sub>3</sub>CH<sub>2</sub>CHO)

No RE estimates of 3,3,3-trifluoro-propanal can be found in the literature, but here we have calculated its RE by using the absorption cross-sections of *Antiñolo et al.* [2011] and *Sellevag et al.* [2004a]. Due to the very short lifetime of only 2.0 days for this compound [*Antiñolo et al.*, 2011], our calculated RE rounds to 0.00 W m<sup>-2</sup> ppb<sup>-1</sup> when applying the lifetime correction (section 3.3.4). Uncertainties related to the fractional correction are large for compounds with such short lifetimes. The mean RE calculated here when assuming a uniform horizontal and vertical distribution is 0.16 W m<sup>-2</sup> ppb<sup>-1</sup>, and should be considered an upper estimate.

3315

3316

### 4,4,4-Trifluorobutanal (CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CHO)

- No RE or lifetime estimates of 4,4,4-trifluorobutanal can be found in the literature. Here we have used the absorption cross-section from *Antiñolo et al.* [2012a] and calculated a RE value of 0.16 W m<sup>-2</sup> ppb<sup>-1</sup> assuming a constant horizontal and vertical distribution in the
- troposphere. Hence, this RE value should be considered an upper estimate.

3321

3322

#### 2-Fluoroethanol (CH<sub>2</sub>FCH<sub>2</sub>OH)

- In the experimental study of *Sellevag et al.* [2004b] a broadband model and a CTM were used to estimate the RE due to 2-fluoroethanol with a value 0.02 W m<sup>-2</sup> ppb<sup>-1</sup>. We have used their absorption cross-section and calculated the same RE value. The lifetime of 20.4 days is taken
- 3326 from *Sellevag et al.* [2004b].

3327

3328

#### 2,2-Difluoroethanol (CHF<sub>2</sub>CH<sub>2</sub>OH)

- One experimental study has estimated RE due to 2,2-difluoroethanol, with a value 0.02 W m<sup>-2</sup>
- ppb<sup>-1</sup> [Sellevag et al., 2004b]. We used their absorption cross-section and calculated a higher
- RE value of 0.04 W m<sup>-2</sup> ppb<sup>-1</sup>. As discussed in section 3.3.4 and illustrated in Figure 9, the
- 3332 uncertainties when applying lifetime corrections are large for such short-lived compounds
- 3333 (lifetime of 40.0 days [*Sellevag et al.*, 2004b]).

$\boldsymbol{\gamma}$	$^{\circ}$	$\sim$	4
4	٠.	٠.	4
J	J	J	т.

### 2,2,2-Trifluoroethanol (CF<sub>3</sub>CH<sub>2</sub>OH)

- Previous experimental studies of RE due to 2,2,2-trifluoroethanol are in the range 0.09 0.19
- W m<sup>-2</sup> ppb<sup>-1</sup> (mean: 0.14 W m<sup>-2</sup> ppb<sup>-1</sup>) and stem from the work of *Sellevag et al.* [2004b] and
- 3338 Imasu et al. [1995] (note that the RE from the latter study has been scaled to our
- recommended CFC-11 RE of 0.26 W m<sup>-2</sup> ppb<sup>-1</sup>). We calculate a RE value of 0.10 W m<sup>-2</sup> ppb<sup>-1</sup>
- 3340 when using the absorption cross-sections from both these sources. Our value is close to the
- RE of 0.09 W m<sup>-2</sup> ppb<sup>-1</sup> from *Sellevag et al.* [2004b] who used a CTM to account for the non-
- homogeneous tropospheric distribution. The lifetime of 0.3 years is taken from Sellevag et al.
- 3343 [2004b].

3344

3345

### HFEs studied by Andersen et al. [2010b]

- For the following HFE compounds, *Andersen et al.* [2010b] is the only study providing REs
- based on experimental absorption cross-sections:
- 3348 1,1'-Oxybis[2-(difluoromethoxy)-1,1,2,2-tetrafluoroethane (HCF<sub>2</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>2</sub>CF<sub>2</sub>H)
- 3349 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12-hexadecafluoro-2,5,8,11-Tetraoxadodecane
- 3350  $(HCF_2O(CF_2CF_2O)_3CF_2H)$
- 3351 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15-eicosafluoro-2,5,8,11,14-
- Pentaoxapentadecane (HCF<sub>2</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>4</sub>CF<sub>2</sub>H)

- Andersen et al. [2010b] used the Pinnock et al. [1995] method to estimate
- instantaneous REs of these compounds. Since absorption spectra were unavailable for the
- three compounds listed above, no new calculations have been carried out here. Thus, we use
- 3357 the REs from Andersen et al. [2010b], accounting for stratospheric temperature adjustment
- and lifetime correction (see sections 3.3.2 and 3.3.4, respectively), and present new best
- estimate REs of 1.15, 1.43 and 1.46 W m<sup>-2</sup> ppb<sup>-1</sup> for 1,1'-oxybis[2-(difluoromethoxy)-1,1,2,2-
- 3360 tetrafluoroethane, 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12-hexadecafluoro-2,5,8,11-
- 3361 tetraoxadodecane and 1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15-eicosafluoro-
- 3362 2,5,8,11,14-pentaoxapentadecane, respectively. We have used the same assumption as in
- 3363 Andersen et al. [2010b] of a lifetime for all three compounds of 26 years.

# 4.2 Additional metrics for most important gases: GTPs and GWPs for other time horizons

While we have used a time horizon of 100 years in the main tables we also show GWP values for 20 and 500 years for a selection of gases together with GTP values for the same gases in Table 16. The GTP values vary with time horizon in a way that depends on adjustment time and how this compares with the time scale for the response of CO<sub>2</sub>. For gases with short and medium lifetimes (e.g., HFC-152a and HCFC-22), the GTP falls rapidly with time horizon from 20 to 100 years. By contrast, the longer-lived gases, such as HFC-23 and CFC-12, show GTPs that increase from time horizons of 20 to 50 years, before decreasing, while for the very long-lived gases (SF<sub>6</sub> and PFC-14), the GTP values continue to increase out to 100 years. The contrast between the GWP and GTP values in Table 16 is particularly noticeable for gases with short and medium lifetimes – for example, for HCFC-22, the GWP drops by an about a factor of 3 between time horizons of 20 and 100 years, whereas the GTP drops by more than an order of magnitude. This reflects the fact that the integral nature of the GWP means that it keeps the memory of the strong short-lived forcing, while the GTP, being an end-point metric, retains less of a memory, and the impact of the forcing pulse on temperature has largely disappeared after 100 years.

Compared to *Fuglestvedt et al.* [2010], the GWP and GTPs for CCl<sub>4</sub> are higher due to the higher RE calculated in this study compared to the recommended RE in AR4 (see discussion of CCl<sub>4</sub> in section 4.1.4 for details). The metric values for SF<sub>6</sub> have also increased (except for GWP 500-yr) due to the increase of the best estimate RE for this compound (see section 4.1.6).

It should be noted that while the impulse response function for CO<sub>2</sub> includes climate-carbon cycle feedbacks, no feedbacks are included for the non-CO<sub>2</sub> gases. The magnitude of this bias has not been assessed for the gases addressed here. However, *Gillett and Matthews* [2010] found that for N<sub>2</sub>O and CH<sub>4</sub> the GWP-100 values increased by 20% when climate-carbon feedbacks were included; which gives some indication of the bias in the GWP values presented here.

## 3394 5 Summary and conclusions

- We present a comprehensive assessment of the radiative efficiencies (REs) for a large number of halocarbons and related radiatively-active compounds including CFCs, HCFCs, bromofluorocarbons and bromochlorofluorocarbons (halons), HFCs, PFCs, SF<sub>6</sub>, NF<sub>3</sub>, and related halogen containing compounds. A consistent method for calculating RE has been used for all compounds ruling out any differences related to the radiative transfer method. Further, our results have been compared with previously published literature and new best estimates have been presented for lifetimes, REs, and GWPs. A total of 223 compounds were included in this study. Here we summarize our main findings:
  - 1. Absorption cross-sections have been collected from various sources including freely-available databases and requests to authors of individual studies. The absorption cross-section data used include experimental data and *ab initio* calculations. For most of the important halocarbons, several independent sources are available for absorption cross sections. However, we find insufficient data available (and hence encourage further studies) for HFC-23, HFC-236ea, HFC-245ca, CCl<sub>4</sub>, and several HFEs.
  - 2. An updated version of the simplified method presented in *Pinnock et al.* [1995] to calculate REs was developed and is presented. In the updated version an improved representation of clouds and the spatial distribution of temperature and water vapor leads to changes in the estimated REs of up to 10% from those estimated using the values given by *Pinnock et al.* [1995]. For most compounds we apply a generic correction to account for the effect of stratospheric temperature adjustment. The simulations by the simplified method are performed with a LBL model and results are presented on a 1 cm<sup>-1</sup> resolution. There was very little (1-2%) difference between REs calculated using 1 cm<sup>-1</sup> or 10 cm<sup>-1</sup> resolution, but it is greater for some compounds, most notably CF<sub>4</sub> where the difference is 8%.
  - 3. Simulations using a chemical transport model and results from the existing literature were used to develop simple lifetime-dependent correction factors to account for inhomogeneous mixing in the atmosphere. Application of these correction factors is shown to be particularly important for very short-lived compounds and leads to substantially lower REs than generally reported in the literature.
  - 4. We estimate that the uncertainty (5-95% confidence range) in RE of compounds for which we have experimental absorption cross-sections is approximately 13% for gases with atmospheric lifetimes greater than 5 years, and approximately 23% for gases with lifetimes less than 5 years. For compounds for which only *ab initio* cross-sections are available, the estimated uncertainties are 16% and 25% for compounds with lifetimes greater and less than 5 years, respectively. These estimates assume that empirical corrections based on knowledge of the spectra of related compounds have been applied to the *ab initio* cross-sections to account for systematic errors in the

- calculation of the wavenumbers of the vibrational modes. Where more generic corrections have been made, the errors can be somewhat larger. Our estimated uncertainties are larger than the value of 10% given in IPCC AR4 for the RE of the long-lived greenhouse gases. The uncertainty in GWP<sub>HFC-134a</sub> is estimated to 24%, 34% and 37% for a 20, 100, and 500 year time horizon. For CFC-11 the GWP uncertainties are 23%, 38% and 47% for a 20, 100, and 500 year time horizon.
- 5. Compared to AR4, the REs presented here differed significantly (by more than 5%) for 49 compounds, while 42 compounds had similar (<5% difference) RE as in AR4. For 7 of the compounds included in AR4 we have not carried out calculations because spectrally-resolved absorption cross-section data were not available, but for 2 of these compounds we have updated the recommended RE based on values from the literature. Best estimate REs and GWPs have also been presented for 112 compounds which were not included in AR4. For 20 additional compounds we have only presented new REs and not GWPs due to missing lifetime estimates.
  - 6. Substantial updates in REs are made for several important gases: CFC-11, CFC-115, HCFC-124, HCFC-225cb, HFC-143a, HFC-245fa, CCl<sub>4</sub>, CHCl<sub>3</sub>, and SF<sub>6</sub>.

- 7. As shown in Figure 18, where there are substantial differences between the REs evaluated in the present work and those given in AR4, the values evaluated here tend to be lower than those given in AR4. This trend largely reflects an improvement in the methodology used to correct for the inhomogeneous mixing of shorter lived species (see section 3.3.4).
- 8. SF<sub>6</sub> has the highest GWP(100) with a value of 23,500 (relative to CO<sub>2</sub>) as a result of its high RE and very long lifetime. A majority of the compounds considered here have a GWP(100) below 1,000 and almost half of the compounds have a GWP(100) below 100. (See Figure 19 showing GWP(100) values in ordered ranking for all the compounds investigated in this study.) The AGWPs for CO<sub>2</sub> have been updated and this leads to a lowering of the GWP(100) values of approximately 6% compared to AR4.
- 9. We have calculated GWPs for 20, 100, and 500 year time horizons and Global Temperature change Potentials (GTP) for 20, 50 and 100 years. The contrast between the GWP and GTP values is particularly noticeable for gases with short and medium lifetimes and reflects the integral nature of the GWP which retains memory of the strong short-lived forcing, while the GTP, being an end-point metric, has less of a memory.
  - The GWP and GTP values are expected to change in the future, reflecting changes related to the reference gas CO<sub>2</sub> (i.e., AGWP<sub>CO2</sub> and AGTP<sub>CO2</sub> will be updated as background conditions change and models improve) and as our understanding of the RE and lifetimes of the compounds improve. In future reviews it will be important to distinguish between changes

in GWP and GTP values that are due to changes in RE and/or lifetime of the non- $CO_2$  gas and those that are due to the changes related to the reference gas  $CO_2$  (i.e.,  $AGWP_{CO2}$  and  $AGTP_{CO2}$ ). Updated GWPs and GTPs can be obtained by multiplying old values with the ratio between old and new  $AGWP_{CO2}$  and  $AGTP_{CO2}$  values, respectively.

Our main focus has been on providing a comprehensive and self-consistent set of new calculations of REs. A follow up study could be a detailed assessment of lifetimes with calculations of how uncertainties in lifetimes together with uncertainties in RE propagate to GWPs and GTPs.

There are several important impacts of our new results. First of all, the large number of compounds included in the review, and the high degree of consistency in the method of calculating REs of each compound, make it a lot easier for researchers, industry and others to compare the potential climate impacts (i.e., the GWPs and GTPs) of molecules, and this may be helpful in choosing compounds that are more climate-friendly. Such a consistent set of RE values may also be relevant for future assessment reports and could in turn have policy implications. Second, the contribution from halocarbons to the present-day total radiative forcing of anthropogenic greenhouse gases is also expected to change slightly as a result of our updated RE numbers. In particular, carbon tetrachloride (CCl<sub>4</sub>) has a high atmospheric concentration and the RE for this compound is much higher in our study (0.17 W m<sup>-2</sup> ppb<sup>-1</sup>) than in AR4 (0.13 W m<sup>-2</sup> ppb<sup>-1</sup>). Finally, we provide the research community with an improved tool for calculating the RE, GWP and GTP of a compound in a relatively simple manner.

#### Supplementary Material

Supplementary Material is available and includes additional tables, the updated Pinnock et al. curve, and a large number of absorption cross-sections (see SM\_Readme.txt for more information).

#### Acknowledgments

Ø. Hodnebrog, G. Myhre and J. S. Fuglestvedt acknowledge funding from the Norwegian
 Climate and Pollution Agency (Klif), and the Research Council of Norway within the project
 "Climate and health impacts of Short-Lived Atmospheric Components (SLAC)". The authors

would like to thank Lars Hoffmann for providing the MIPAS CFC-11 dataset, and several people for kindly providing absorption cross sections: Andrea Pietropolli Charmet, Vladimir L. Orkin, Silvia Lane, Mads P. Sulbaek Andersen, Freja Østerstrøm, Elena Jiménez, Maria Antiñolo, and Ryoichi Imasu. We thank Borgar Aamaas for making Figure 10, and Glen Peters and Amund Søvde for useful discussions. The Reading authors acknowledge the help of Ivan Bravo for his early work on updating the Pinnock method, and for many useful discussions. G. Marston and K. P. Shine acknowledge the RAL Molecular Spectroscopy Facility for their role in facilitating halocarbon absorption cross-section measurements, including those under grants from the UK Natural Environment Research Council (NMSF/0506/06 and NMSF/1112/01).

#### References

- Acerboni, G., J. A. Beukes, N. R. Jensen, J. Hjorth, G. Myhre, C. J. Nielsen, and J. K. Sundet
- 3518 (2001), Atmospheric degradation and global warming potentials of three perfluoroalkenes,
- 3519 *Atmospheric Environment*, *35*(24), 4113-4123.
- Anastasi, C., A. E. Heathfield, G. P. Knight, and F. Nicolaisen (1994), Integrated absorption-
- 3521 coefficients of CHClF<sub>2</sub> (HCFC-22) and CH<sub>3</sub>Br in the atmospheric infrared window region,
- 3522 Spectroc. Acta Pt. A-Molec. Biomolec. Spectr., 50(10), 1791-1798.
- Andersen, M. P. S., D. R. Blake, F. S. Rowland, M. D. Hurley, and T. J. Wallington (2009),
- 3524 Atmospheric Chemistry of Sulfuryl Fluoride: Reaction with OH Radicals, CI Atoms and O<sub>3</sub>,
- 3525 Atmospheric Lifetime, IR Spectrum, and Global Warming Potential, *Environmental Science*
- 3526 & Technology, 43(4), 1067-1070.
- Andersen, M. P. S., M. D. Hurley, V. F. Andersen, O. J. Nielsen, and T. J. Wallington
- 3528 (2010a), CHF<sub>2</sub>OCHF<sub>2</sub> (HFE-134): IR Spectrum and Kinetics and Products of the Chlorine-
- 3529 Atom-Initiated Oxidation, *J. Phys. Chem. A*, 114(14), 4963-4967.
- Andersen, M. P. S., V. F. Andersen, O. J. Nielsen, S. P. Sander, and T. J. Wallington (2010b),
- 3531 Atmospheric Chemistry of HCF<sub>2</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>x</sub>CF<sub>2</sub>H (x=2-4): Kinetics and Mechanisms of the
- 3532 Chlorine-Atom-Initiated Oxidation, ChemPhysChem, 11(18), 4035-4041.
- Andersen, M. P. S., R. L. Waterland, S. P. Sander, O. J. Nielsen, and T. J. Wallington
- 3534 (2012a), Atmospheric chemistry of CxF2x+1CH=CH2 (x=1, 2, 4, 6 and 8): Radiative
- efficiencies and global warming potentials, *J. Photochem. Photobiol. A-Chem.*, 233, 50-52.
- Andersen, M. P. S., O. J. Nielsen, T. J. Wallington, B. Karpichev, and S. P. Sander (2012b),
- 3537 Assessing the Impact on Global Climate from General Anesthetic Gases, Anesth. Analg.,
- 3538 114(5), 1081-1085.
- Andersen, M. P. S., E. J. K. Nilsson, O. J. Nielsen, M. S. Johnson, M. D. Hurley, and T. J.
- Wallington (2008), Atmospheric chemistry of trans-CF<sub>3</sub>CHCHCl: Kinetics of the gas-phase
- reactions with Cl atoms, OH radicals, and O<sub>3</sub>, Journal of Photochemistry and Photobiology A:
- 3542 *Chemistry*, 199(1), 92-97.
- Andersen, M. P. S., S. P. Sander, O. J. Nielsen, D. S. Wagner, T. J. Sanford, and T. J.
- Wallington (2010c), Inhalation anaesthetics and climate change, Br. J. Anaesth., 105(6), 760-
- 3545 766.
- Andersen, M. P. S., M. D. Hurley, T. J. Wallington, F. Blandini, N. R. Jensen, V. Librando,
- and J. Hjorth (2004), Atmospheric chemistry of CH<sub>3</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub> (n=1-3): Kinetics and
- mechanism of oxidation initiated by Cl atoms and OH radicals, IR spectra, and global warmin
- 3549 potentials, J. Phys. Chem. A, 108(11), 1964-1972.
- Andersen, M. P. S., O. J. Nielsen, A. Toft, T. Nakayama, Y. Matsumi, R. L. Waterland, R. C.
- Buck, M. D. Hurley, and T. J. Wallington (2005), Atmospheric chemistry of C<sub>x</sub>F<sub>2x+1</sub>CH=CH<sub>2</sub>
- 3552 (x=1, 2, 4, 6, and 8): Kinetics of gas-phase reactions with Cl atoms, OH radicals, and O<sub>3</sub>, J.
- 3553 Photochem. Photobiol. A-Chem., 176(1-3), 124-128.
- Andrews, T., and P. M. Forster (2008), CO<sub>2</sub> forcing induces semi-direct effects with
- 3555 consequences for climate feedback interpretations, *Geophys. Res. Lett.*, 35(4), 5.

- Antiñolo, M., E. Jimenez, and J. Albaladejo (2011), UV absorption cross sections between
- 3557 230 and 350 nm and pressure dependence of the photolysis quantum yield at 308 nm of
- 3558 CF<sub>3</sub>CH<sub>2</sub>CHO, Physical Chemistry Chemical Physics, 13(35), 15936-15946.
- Antiñolo, M., E. Jimenez, and J. Albaladejo (2012a), Photochemistry of CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CHO in
- air: UV absorption cross sections between 230 and 340 nm and photolysis quantum yields at
- 3561 308 nm, J. Photochem. Photobiol. A-Chem., 231(1), 33-40.
- Antiñolo, M., S. González, B. Ballesteros, J. Albaladejo, and E. Jiménez (2012b), Laboratory
- 3563 Studies of CHF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH and CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>OH: UV and IR Absorption Cross Sections and
- 3564 OH Rate Coefficients between 263 and 358 K, The Journal of Physical Chemistry A.
- Anttila, R., C. Betrencourtstirnemann, and J. Dupre (1983), The infrared bands nu-2 and nu-5
- of CH<sub>3</sub>Br with coriolis interaction, *J. Mol. Spectrosc.*, 100(1), 54-74.
- 3567 Atkins, P. W., and R. S. Friedman (2010), Molecular quantum mechanics, Fifth Edition,
- 3568 Oxford University Press.
- 3569 Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E.
- 3570 Jenkin, M. J. Rossi, J. Troe, and T. J. Wallington (2008), Evaluated kinetic and
- 3571 photochemical data for atmospheric chemistry: Volume IV gas phase reactions of organic
- halogen species, *Atmospheric Chemistry and Physics*, 8(15), 4141-4496.
- Baasandori, M., A. R. Ravishankara, and J. B. Burkholder (2011), Atmospheric Chemistry of
- 3574 (Z)-CF<sub>3</sub>CH=CHCF<sub>3</sub>: OH Radical Reaction Rate Coefficient and Global Warming Potential, *J.*
- 3575 Phys. Chem. A, 115(38), 10539-10549.
- Baasandorj, M., G. Knight, V. C. Papadimitriou, R. K. Talukdar, A. R. Ravishankara, and J.
- 3577 B. Burkholder (2010), Rate Coefficients for the Gas-Phase Reaction of the Hydroxyl Radical
- 3578 with CH<sub>2</sub>=CHF and CH<sub>2</sub>= CF<sub>2</sub>, J. Phys. Chem. A, 114(13), 4619-4633.
- Ballard, J., R. J. Knight, and D. A. Newnham (2000a), Infrared absorption cross-sections and
- integrated absorption intensities of perfluoroethane and cis-perfluorocyclobutane, J. Quant.
- 3581 Spectrosc. Radiat. Transf., 66(2), 199-212.
- Ballard, J., R. J. Knight, D. A. Newnham, J. Vander Auwera, M. Herman, G. Di Lonardo, G.
- 3583 Masciarelli, F. M. Nicolaisen, J. A. Beukes, L. K. Christensen, R. McPheat, G. Duxbury, R.
- 3584 Freckleton, and K. P. Shine (2000b), An intercomparison of laboratory measurements of
- absorption cross-sections and integrated absorption intensities for HCFC-22, J. Quant.
- 3586 Spectrosc. Radiat. Transf., 66(2), 109-128.
- Ballard, J., R. J. Knight, D. A. Newnham, J. Vander Auwera, M. Herman, G. DiLonardo, G.
- 3588 Masciarelli, F. M. Nicolaisen, J. A. Buekes, L. K. Christiansen, G. Duxbury, R. McPheat, K.
- P. Shine, E. J. Highwood, R. Freckleton, C. Bruning, and Swagg (2000c), SWAGG Project -
- 3590 Introduction, J. Quant. Spectrosc. Radiat. Transf., 66(2), 107-108.
- Barry, J., G. Locke, D. Scollard, H. Sidebottom, J. Treacy, C. Clerbaux, R. Colin, and J.
- Franklin (1997), 1,1,1,3,3,-pentafluorobutane (HFC-365mfc): Atmospheric degradation and
- 3593 contribution to radiative forcing, *Int. J. Chem. Kinet.*, 29(8), 607-617.
- 3594 Bera, P. P., J. S. Francisco, and T. J. Lee (2009), Identifying the Molecular Origin of Global
- 3595 Warming, J. Phys. Chem. A, 113(45), 12694-12699.
- 3596 Bera, P. P., J. S. Francisco, and T. J. Lee (2010), Design strategies to minimize the radiative
- efficiency of global warming molecules, *Proc. Natl. Acad. Sci. U. S. A.*, 107(20), 9049-9054.

- Berglen, T. F., T. K. Berntsen, I. S. A. Isaksen, and J. K. Sundet (2004), A global model of
- 3599 the coupled sulfur/oxidant chemistry in the troposphere: The sulfur cycle, J. Geophys. Res.-
- 3600 Atmos., 109(D19).
- Blanco, M. B., and M. A. Teruel (2007), Atmospheric degradation of fluoroesters (FESs):
- Gas-phase reactivity study towards OH radicals at 298 K, Atmospheric Environment, 41(34),
- 3603 7330-7338.
- 3604 Blowers, P., and K. Hollingshead (2009), Estimations of Global Warming Potentials from
- 3605 Computational Chemistry Calculations for CH<sub>2</sub>F<sub>2</sub> and Other Fluorinated Methyl Species
- Verified by Comparison to Experiment, J. Phys. Chem. A, 113(20), 5942-5950.
- 3607 Blowers, P., K. F. Tetrault, and Y. Trujillo-Morehead (2008a), Global warming potential
- predictions for hydrofluoroethers with two carbon atoms, Theor. Chem. Acc., 119(4), 369-
- 3609 381.
- 3610 Blowers, P., D. M. Moline, K. F. Tetrault, R. R. Wheeler, and S. L. Tuchawena (2007),
- Prediction of radiative forcing values for hydrofluoroethers using density functional theory
- 3612 methods, *J. Geophys. Res.-Atmos.*, *112*(D15).
- Blowers, P., D. M. Moline, K. F. Tetrault, R. R. Wheeler, and S. L. Tuchawena (2008b),
- 3614 Global warming potentials of hydrofluoroethers, *Environmental Science & Technology*, 42(4),
- 3615 1301-1307.
- 3616 Bolin, B., and H. Rodhe (1973), Note on concepts of age distribution and transit-time in
- 3617 natural reservoirs, *Tellus*, 25(1), 58-62.
- 3618 Bond, T. C., D. G. Streets, K. F. Yarber, S. M. Nelson, J. H. Woo, and Z. Klimont (2004), A
- 3619 technology-based global inventory of black and organic carbon emissions from combustion,
- 3620 *J. Geophys. Res.-Atmos.*, 109(D14).
- Boucher, O. (2012), Comparison of physically- and economically-based CO<sub>2</sub>-equivalences for
- methane, Earth Syst. Dynam. Discuss., 3(1), 1-29.
- Boucher, O., and M. S. Reddy (2008), Climate trade-off between black carbon and carbon
- 3624 dioxide emissions, *Energy Policy*, 193-200.
- 3625 Bravo, I., G. Marston, D. R. Nutt, and K. P. Shine (2011a), Radiative efficiencies and global
- 3626 warming potentials using theoretically determined absorption cross-sections for several
- 3627 hydrofluoroethers (HFEs) and hydrofluoropolyethers (HFPEs), Journal of Quantitative
- 3628 Spectroscopy and Radiative Transfer, 112(12), 1967-1977.
- Bravo, I., Y. Diaz-de-Mera, A. Aranda, K. Smith, K. P. Shine, and G. Marston (2010a),
- 3630 Atmospheric chemistry of C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub> (HFE-7200), C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub> (HFE-7100), C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>
- 3631 (HFE-7000) and C<sub>3</sub>F<sub>7</sub>CH<sub>2</sub>OH: temperature dependence of the kinetics of their reactions with
- 3632 OH radicals, atmospheric lifetimes and global warming potentials, *Physical Chemistry*
- 3633 *Chemical Physics*, *12*(19), 5115-5125.
- Bravo, I., Y. Diaz-de-Mera, A. Aranda, E. Moreno, D. R. Nutt, and G. Marston (2011b),
- 3635 Radiative efficiencies for fluorinated esters: indirect global warming potentials of
- 3636 hydrofluoroethers, *Physical Chemistry Chemical Physics*, 13(38), 17185-17193.
- Bravo, I., A. Aranda, M. D. Hurley, G. Marston, D. R. Nutt, K. P. Shine, K. Smith, and T. J.
- Wallington (2010b), Infrared absorption spectra, radiative efficiencies, and global warming
- potentials of perfluorocarbons: Comparison between experiment and theory, J. Geophys. Res.-
- 3640 Atmos., 115.

- Brodbeck, C., I. Rossi, H. Strapelias, and J. P. Bouanich (1980), Infrared spectral absorption
- intensities in the  $v_3$  and  $v_4$  regions of SF<sub>6</sub>, Chem. Phys., 54(1), 1-7.
- Brown, L. R., C. B. Farmer, C. P. Rinsland, and R. A. Toth (1987), Molecular line parameters
- 3644 for the atmospheric trace molecule spectroscopy experiment, Appl. Optics, 26(23), 5154-
- 3645 5182.
- 3646 Calvert, J. G., R. G. Derwent, J. J. Orlando, G. S. Tyndall, and T. J. Wallington (2008),
- 3647 Atmospheric Oxidation of the Alkanes, ISBN 978-0-19-536581-8, Oxford University Press.
- 3648 Cappellani, F., and G. Restelli (1992), Infrared band strengths and their temperature-
- 3649 dependence of the hydrohalocarbons HFC-134a, HFC-152a, HCFC-22, HCFC-123 and
- 3650 HCFC-142b, Spectroc. Acta Pt. A-Molec. Biomolec. Spectr., 48(8), 1127-1131.
- 3651 Cavalli, F., M. Glasius, J. Hjorth, B. Rindone, and N. R. Jensen (1998), Atmospheric
- 3652 lifetimes, infrared spectra and degradation products of a series of hydrofluoroethers,
- 3653 *Atmospheric Environment*, *32*(21), 3767-3773.
- Chapados, C. (1988), Infrared-absorption of SF<sub>6</sub> from 32-cm<sup>-1</sup> to 3000-cm<sup>-1</sup> in the gaseous
- 3655 and liquid states, *J. Mol. Spectrosc.*, 132(2), 323-351.
- 3656 Charmet, A. P., N. Tasinato, P. Stoppa, A. Baldacci, and S. Giorgianni (2008), Jet-cooled
- 3657 diode laser spectrum and FTIR integrated band intensities of CF<sub>3</sub>Br: rovibrational analysis of
- 3658  $2v_5$  and  $v_2+v_3$  bands near 9 µm and cross-section measurements in the 450-2500 cm<sup>-1</sup> region,
- 3659 Mol. Phys., 106(9-10), 1171-1179.
- 3660 Charmet, A. P., P. Stoppa, N. Tasinato, A. Baldan, S. Giorgianni, and A. Gambi (2010),
- 3661 Spectroscopic study of CHBrF<sub>2</sub> up to 9500 cm<sup>-1</sup>: Vibrational analysis, integrated band
- intensities, and ab initio calculations, *J. Chem. Phys.*, 133(4).
- 3663 Chen, L., S. Kutsuna, K. Tokuhashi, and A. Sekiya (2006), Kinetics and mechanisms of
- 3664 CF3CHFOCH3, CF3CHFOC(O)H, and FC(O)OCH3 reactions with OH radicals, J. Phys.
- 3665 *Chem. A*, 110(47), 12845-12851.
- 3666 Christensen, L. K., T. J. Wallington, A. Guschin, and M. D. Hurley (1999), Atmospheric
- 3667 degradation mechanism of CF<sub>3</sub>OCH<sub>3</sub>, *J. Phys. Chem. A*, 103(21), 4202-4208.
- 3668 Christensen, L. K., J. Sehested, O. J. Nielsen, M. Bilde, T. J. Wallington, A. Guschin, L. T.
- 3669 Molina, and M. J. Molina (1998), Atmospheric chemistry of HFE-7200 (C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>):
- Reaction with OH radicals and fate of C<sub>4</sub>F<sub>9</sub>OCH<sub>2</sub>CH<sub>2</sub>O(•) and C<sub>4</sub>F<sub>9</sub>OCHO(•)CH<sub>3</sub> radicals, J.
- 3671 *Phys. Chem. A*, 102(25), 4839-4845.
- 3672 Christidis, N., M. D. Hurley, S. Pinnock, K. P. Shine, and T. J. Wallington (1997), Radiative
- 3673 forcing of climate change by CFC-11 and possible CFC-replacements, J. Geophys. Res.-
- 3674 Atmos., 102(D16), 19597-19609.
- 3675 Clerbaux, C., and R. Colin (1994), Determination of the infrared cross-sections and global
- warming potentials of 1,1,2-trifluoroethane (HFC-143), Geophys. Res. Lett., 21(22), 2377-
- 3677 2380.
- 3678 Clerbaux, C., R. Colin, P. C. Simon, and C. Granier (1993), Infrared cross-sections and global
- warming potentials of 10 alternative hydrohalocarbons, J. Geophys. Res.-Atmos., 98(D6),
- 3680 10491-10497.
- 3681 Collins, W. D., V. Ramaswamy, M. D. Schwarzkopf, Y. Sun, R. W. Portmann, Q. Fu, S. E. B.
- Casanova, J. L. Dufresne, D. W. Fillmore, P. M. D. Forster, V. Y. Galin, L. K. Gohar, W. J.
- Ingram, D. P. Kratz, M. P. Lefebvre, J. Li, P. Marquet, V. Oinas, Y. Tsushima, T. Uchiyama,

- and W. Y. Zhong (2006), Radiative forcing by well-mixed greenhouse gases: Estimates from
- 3685 climate models in the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment
- 3686 Report (AR4), *J. Geophys. Res.-Atmos.*, 111(D14).
- 3687 Cometto, P. M., R. A. Taccone, J. D. Nieto, P. R. Dalmasso, and S. I. Lane (2010), Kinetic
- 3688 Study of OH Radical Reactions with CF<sub>3</sub>CCl=CCl<sub>2</sub>, CF<sub>3</sub>CCl=CClCF<sub>3</sub> and CF<sub>3</sub>CF=CFCF<sub>3</sub>,
- 3689 *ChemPhysChem*, 11(18), 4053-4059.
- Cunnold, D. M., R. F. Weiss, R. G. Prinn, D. Hartley, P. G. Simmonds, P. J. Fraser, B. Miller,
- 3691 F. N. Alyea, and L. Porter (1997), GAGE/AGAGE measurements indicating reductions in
- 3692 global emissions of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> in 1992-1994, J. Geophys. Res.-Atmos., 102(D1),
- 3693 1259-1269.
- D'Anna, B., S. R. Sellevag, K. Wirtz, and C. J. Nielsen (2005), Photolysis study of perfluoro-
- 3695 2-methyl-3-pentanone under natural sunlight conditions, Environmental Science &
- 3696 *Technology*, 39(22), 8708-8711.
- 3697 Dalmasso, P. R., R. A. Taccone, J. D. Nieto, M. A. Teruel, and S. I. Lane (2006),
- 3698 CH<sub>3</sub>OCF<sub>2</sub>CHFCl and CHF<sub>2</sub>OCF<sub>2</sub>CHFCl: Reaction with Cl atoms, atmospheric lifetimes,
- 3699 ozone depletion and global warming potentials, Atmospheric Environment, 40(38), 7298-
- 3700 7307.
- 3701 Daniel, J. S., S. Solomon, and D. L. Albritton (1995), On the evaluation of halocarbon
- 3702 radiative forcing and global warming potentials, J. Geophys. Res.-Atmos., 100(D1), 1271-
- 3703 1285.
- 3704 Derwent, R. G. (1990), Trace gases and their relative contribution to the greenhouse
- 3705 effectRep., Atomic Energy Research Establishment Harwell Oxon UK. Report AERE-
- 3706 R13716.
- 3707 Di Lonardo, G., and G. Masciarelli (2000), Infrared absorption cross-sections and integrated
- 3708 absorption intensities of HFC-125 and HFC-143a, J. Quant. Spectrosc. Radiat. Transf., 66(2),
- 3709 129-142.
- Dillon, T. J., A. Horowitz, and J. N. Crowley (2008), The atmospheric chemistry of sulphuryl
- 3711 fluoride, SO<sub>2</sub>F<sub>2</sub>, Atmospheric Chemistry and Physics, 8(6), 1547-1557.
- Douglass, A. R., R. S. Stolarski, M. R. Schoeberl, C. H. Jackman, M. L. Gupta, P. A.
- Newman, J. E. Nielsen, and E. L. Fleming (2008), Relationship of loss, mean age of air and
- 3714 the distribution of CFCs to stratospheric circulation and implications for atmospheric
- 3715 lifetimes, J. Geophys. Res.-Atmos., 113(D14).
- 3716 Drage, E. A., D. Jaksch, K. M. Smith, R. A. McPheat, E. Vasekova, and N. J. Mason (2006),
- 3717 FTIR spectroscopy and estimation of the global warming potential of CF<sub>3</sub>Br and C<sub>2</sub>F<sub>4</sub>, J.
- 3718 *Quant. Spectrosc. Radiat. Transf.*, 98(1), 44-56.
- Dunn, D. S., K. Scanlon, and J. Overend (1982), The absolute intensities of the binary
- 3720 combination bands in the infrared-spectrum of SF<sub>6</sub>, Spectroc. Acta Pt. A-Molec. Biomolec.
- 3721 *Spectr.*, 38(8), 841-847.
- Ellingson, R. G., and Y. Fouquart (1991), The intercomparison of radiation codes in climate
- 3723 models an overview, *J. Geophys. Res.-Atmos.*, 96(D5), 8925-8927.
- Ellis, D. A., J. W. Martin, S. A. Mabury, M. D. Hurley, M. P. S. Andersen, and T. J.
- Wallington (2003), Atmospheric lifetime of fluorotelomer alcohols, *Environmental Science &*
- 3726 *Technology*, *37*(17), 3816-3820.

- Farman, J. C., B. G. Gardiner, and J. D. Shanklin (1985), Large losses of total ozone in
- 3728 Antarctica reveal seasonal ClO<sub>X</sub>/NO<sub>X</sub> interaction, *Nature*, *315*(6016), 207-210.
- 3729 Fisher, D. A., C. H. Hales, W. C. Wang, M. K. W. Ko, and N. D. Sze (1990), Model-
- 3730 calculations of the relative effects of CFCs and their replacements on global warming, *Nature*,
- *3731 344*(6266), 513-516.
- Forster, P. M., and M. Joshi (2005), The role of halocarbons in the climate change of the
- troposphere and stratosphere, *Climatic Change*, 71(1-2), 249-266.
- Forster, P. M., R. S. Freckleton, and K. P. Shine (1997), On aspects of the concept of
- 3735 radiative forcing, *Clim. Dyn.*, *13*(7-8), 547-560.
- Forster, P. M., J. B. Burkholder, C. Clerbaux, P. F. Coheur, M. Dutta, L. K. Gohar, M. D.
- Hurley, G. Myhre, R. W. Portmann, K. P. Shine, T. J. Wallington, and D. Wuebbles (2005),
- 3738 Resolution of the uncertainties in the radiative forcing of HFC-134a, J. Quant. Spectrosc.
- 3739 *Radiat. Transf.*, 93(4), 447-460.
- Forster, P. M., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D. W. Fahey, J. Haywood, J.
- Lean, D. C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz, and R. Van Dorland
- 3742 (2007), Changes in Atmospheric Constituents and in Radiative Forcing, In: Climate Change
- 3743 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment
- Report of the Intergovernmental Panel on Climate Change eds. Solomon, S., D. Qin, M.
- 3745 Manning, Z. Chen, M. Marquis et al. Rep., 129-234 pp, Cambridge, United Kingdom and
- New York, NY, USA.
- Forster, P. M., V. I. Fomichev, E. Rozanov, C. Cagnazzo, A. I. Jonsson, U. Langematz, B.
- Fomin, M. J. Iacono, B. Mayer, E. Mlawer, G. Myhre, R. W. Portmann, H. Akiyoshi, V.
- Falaleeva, N. Gillett, A. Karpechko, J. N. Li, P. Lemennais, O. Morgenstern, S. Oberlander,
- 3750 M. Sigmond, and K. Shibata (2011), Evaluation of radiation scheme performance within
- 3751 chemistry climate models, J. Geophys. Res.-Atmos., 116.
- Freckleton, R. S., E. J. Highwood, K. P. Shine, O. Wild, K. S. Law, and M. G. Sanderson
- 3753 (1998), Greenhouse gas radiative forcing: Effects of averaging and inhomogeneities in trace
- 3754 gas distribution, Q. J. R. Meteorol. Soc., 124(550), 2099-2127.
- Fuglestvedt, J. S., T. K. Berntsen, O. Godal, R. Sausen, K. P. Shine, and T. Skodvin (2003),
- 3756 Metrics of climate change: Assessing radiative forcing and emission indices, Climatic
- 3757 *Change*, 58(3), 267-331.
- Fuglestvedt, J. S., K. P. Shine, T. Berntsen, J. Cook, D. S. Lee, A. Stenke, R. B. Skeie, G. J.
- 3759 M. Velders, and I. A. Waitz (2010), Transport impacts on atmosphere and climate: Metrics,
- 3760 *Atmospheric Environment*, 44(37), 4648-4677.
- 3761 Garland, N. L., L. J. Medhurst, and H. H. Nelson (1993), Potential chlorofluorocarbon
- 3762 replacements OH reaction-rate constants between 250 and 315-K and infrared-absorption
- 3763 spectra, J. Geophys. Res.-Atmos., 98(D12), 23107-23111.
- 3764 Gierczak, T., R. K. Talukdar, J. B. Burkholder, R. W. Portmann, J. S. Daniel, S. Solomon,
- and A. R. Ravishankara (1996), Atmospheric fate and greenhouse warming potentials of HFC
- 3766 236fa and HFC 236ea, *J. Geophys. Res.-Atmos.*, 101(D8), 12905-12911.
- 3767 Gillett, N., and H. Matthews (2010), Accounting for carbon cycle feedbacks in a comparison
- 3768 of the global warming effects of greenhouse gases, Environmental Research Letters, 5,
- 3769 034011.

- 3770 Gohar, L. K., G. Myhre, and K. P. Shine (2004), Updated radiative forcing estimates of four
- 3771 halocarbons, J. Geophys. Res.-Atmos., 109(D1).
- 3772 Golden, W. G., D. A. Horner, and J. Overend (1978), Intensities of binary overtone and
- 3773 combination bands in IR-spectrum of CCIF<sub>3</sub>, J. Chem. Phys., 68(3), 964-969.
- 3774 Good, D. A., J. S. Francisco, A. K. Jain, and D. J. Wuebbles (1998), Lifetimes and global
- warming potentials for dimethyl ether and for fluorinated ethers: CH<sub>3</sub>OCF<sub>3</sub> (E143a),
- 3776 CHF<sub>2</sub>OCHF<sub>2</sub> (E134), CHF<sub>2</sub>OCF<sub>3</sub> (E125), *J. Geophys. Res.-Atmos.*, 103(D21), 28181-28186.
- 3777 Graner, G. (1981), The methyl-bromide molecule a critical consideration of perturbations in
- 3778 spectra, J. Mol. Spectrosc., 90(2), 394-438.
- 3779 Graner, G., and W. E. Blass (1975), Vibration-rotation bands  $v_2$  and  $v_5$  of methyl-bromide,
- 3780 *Journal De Physique*, *36*(9), 769-771.
- 3781 Gregory, J. M., W. J. Ingram, M. A. Palmer, G. S. Jones, P. A. Stott, R. B. Thorpe, J. A.
- Lowe, T. C. Johns, and K. D. Williams (2004), A new method for diagnosing radiative
- 3783 forcing and climate sensitivity, *Geophys. Res. Lett.*, 31(3).
- 3784 Grossman, A. S., K. E. Grant, W. E. Blass, and D. J. Wuebbles (1997), Radiative forcing
- 3785 calculations for CH<sub>3</sub>Cl and CH<sub>3</sub>Br, *J. Geophys. Res.-Atmos.*, 102(D12), 13651-13656.
- Hansen, J., A. Lacis, and M. Prather (1989), Greenhouse-effect of chlorofluorocarbons and
- 3787 other trace gases, *J. Geophys. Res.-Atmos.*, 94(D13), 16417-16421.
- 3788 Hansen, J., M. Sato, and R. Ruedy (1997), Radiative forcing and climate response, J.
- 3789 Geophys. Res.-Atmos., 102(D6), 6831-6864.
- Hansen, J., M. Sato, R. Ruedy, L. Nazarenko, A. Lacis, G. A. Schmidt, G. Russell, I. Aleinov,
- 3791 M. Bauer, S. Bauer, N. Bell, B. Cairns, V. Canuto, M. Chandler, Y. Cheng, A. Del Genio, G.
- Faluvegi, E. Fleming, A. Friend, T. Hall, C. Jackman, M. Kelley, N. Kiang, D. Koch, J. Lean,
- J. Lerner, K. Lo, S. Menon, R. Miller, P. Minnis, T. Novakov, V. Oinas, J. Perlwitz, D. Rind,
- A. Romanou, D. Shindell, P. Stone, S. Sun, N. Tausnev, D. Thresher, B. Wielicki, T. Wong,
- 3795 M. Yao, and S. Zhang (2005), Efficacy of climate forcings, J. Geophys. Res.-Atmos.,
- 3796 110(D18).
- 3797 Heathfield, A. E., C. Anastasi, A. McCulloch, and F. M. Nicolaisen (1998), Integrated
- infrared absorption coefficients of several partially fluorinated ether compounds: CF<sub>3</sub>OCF<sub>2</sub>H,
- 3799 CF<sub>2</sub>HOCF<sub>2</sub>H, CH<sub>3</sub>OCF<sub>2</sub>CF<sub>2</sub>H, CH<sub>3</sub>OCF<sub>2</sub>CFCIH, CH<sub>3</sub>CH<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>H, CF<sub>3</sub>CH<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>H
- and CH<sub>2</sub>=CHCH<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>H, Atmospheric Environment, 32(16), 2825-2833.
- Highwood, E. J., and K. P. Shine (2000), Radiative forcing and global warming potentials of
- 3802 11 halogenated compounds, J. Quant. Spectrosc. Radiat. Transf., 66(2), 169-183.
- Highwood, E. J., K. P. Shine, M. D. Hurley, and T. J. Wallington (1999), Estimation of direct
- radiative forcing due to non-methane hydrocarbons, Atmospheric Environment, 33(5), 759-
- 3805 767.
- Hoffmann, L., M. Kaufmann, R. Spang, R. Muller, J. J. Remedios, D. P. Moore, C. M. Volk,
- 3807 T. von Clarmann, and M. Riese (2008), Envisat MIPAS measurements of CFC-11: retrieval,
- validation, and climatology, *Atmospheric Chemistry and Physics*, 8(13), 3671-3688.
- 3809 Hollas, J. M. (2004), *Modern Spectroscopy (4th edition)* John Wiley & Sons, Chichester.
- 3810 Hurley, M. D., J. C. Ball, and T. J. Wallington (2007), Atmospheric chemistry of the Z and E
- isomers of CF<sub>3</sub>CF=CHF; Kinetics, mechanisms, and products of gas-phase reactions with Cl
- 3812 atoms, OH radicals, and O<sub>3</sub>, J. Phys. Chem. A, 111(39), 9789-9795.

- 3813 Hurley, M. D., T. Wallington, G. Buchanan, L. Gohar, G. Marston, and K. Shine (2005), IR
- 3814 spectrum and radiative forcing of CF<sub>4</sub> revisited, J. Geophys. Res.-Atmos., 110(D2).
- 3815 Imasu, R., A. Suga, and T. Matsuno (1995), Radiative effects and halocarbon global warming
- 3816 potentials of replacement compounds for chlorofluorocarbons, J. Meteorol. Soc. Jpn., 73(6),
- 3817 1123-1136.
- Inoue, Y., M. Kawasaki, T. J. Wallington, and M. D. Hurley (2008), Atmospheric chemistry 3818
- 3819 of CF<sub>3</sub>CH<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub> (HFC-365mfc): Kinetics and mechanism of chlorine atom initiated
- 3820 oxidation, infrared spectrum, and global warming potential, Chemical Physics Letters, 462(4-
- 3821 6), 164-168.
- 3822 IPCC (1990), Climate Change: The IPCC Scientific Assessment, edited by J. T. Houghton, G.
- 3823 J. Jenkins and J. J. Ephraums, p. 410, Cambridge University Press, Cambridge.
- 3824 IPCC (1994), Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation
- 3825 of the IPCC IS92 Emission Scenarios, edited by: J.T. Houghton, L.G. Meira Filho, J. Bruce,
- 3826 Hoesung Lee, B.A. Callander, E.F. Haites, N. Harris and K. Maskell. Rep., Cambridge
- 3827 University Press, Cambridge, United Kingdom.
- 3828 IPCC (1995), Climate Change 1995, the science of climate change, edited by J. T. Houghton,
- 3829 L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg and K. Maskell, Cambridge.
- 3830 IPCC (2001), Climate Change 2001: The Scientific Basis. Contribution of Working Group I
- 3831 to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by:
- 3832 Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P. J., Dai, X., Maskell,
- 3833 K., and Johnson, C.A. Rep., 881 pp, Cambridge University Press, Cambridge, United
- 3834 Kingdom and New York, NY, USA.
- 3835 IPCC (2007), Climate Change 2007: The Physical Science Basis. Contribution of Working
- Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate 3836
- 3837 Change Rep., Cambridge University Press, Cambridge, United Kingdom and New York, NY,
- 3838 USA.
- 3839 Ivy, D. J., M. Rigby, M. Baasandorj, J. B. Burkholder, and R. G. Prinn (2012), Global
- 3840 emission estimates and radiative impact of C<sub>4</sub>F<sub>10</sub>, C<sub>5</sub>F<sub>12</sub>, C<sub>6</sub>F<sub>14</sub>, C<sub>7</sub>F<sub>16</sub> and C<sub>8</sub>F<sub>18</sub>, Atmos.
- 3841 Chem. Phys., 12, 7635-7645.
- 3842 Jacquinet-Husson, N., L. Crepeau, R. Armante, C. Boutammine, A. Chedin, N. A. Scott, C.
- 3843 Crevoisier, V. Capelle, C. Boone, N. Poulet-Crovisier, A. Barbe, A. Campargue, D. C.
- 3844 Benner, Y. Benilan, B. Bezard, V. Boudon, L. R. Brown, L. H. Coudert, A. Coustenis, V.
- 3845 Dana, V. M. Devi, S. Fally, A. Fayt, J. M. Flaud, A. Goldman, M. Herman, G. J. Harris, D.
- Jacquemart, A. Jolly, I. Kleiner, A. Kleinbohl, F. Kwabia-Tchana, N. Lavrentieva, N. 3846
- 3847 Lacome, L. H. Xu, O. M. Lyulin, J. Y. Mandin, A. Maki, S. Mikhailenko, C. E. Miller, T.
- 3848 Mishina, N. Moazzen-Ahmadi, H. S. P. Muller, A. Nikitin, J. Orphal, V. Perevalov, A. Perrin,
- 3849 D. T. Petkie, A. Predoi-Cross, C. P. Rinsland, J. J. Remedios, M. Rotger, M. A. H. Smith, K.
- 3850 Sung, S. Tashkun, J. Tennyson, R. A. Toth, A. C. Vandaele, and J. Vander Auwera (2011),
- 3851 The 2009 edition of the GEISA spectroscopic database, J. Quant. Spectrosc. Radiat. Transf.,
- 3852 112(15), 2395-2445.
- 3853 Jain, A. K., B. P. Briegleb, K. Minschwaner, and D. J. Wuebbles (2000), Radiative forcings
- 3854 and global warming potentials of 39 greenhouse gases, J. Geophys. Res.-Atmos., 105(D16),
- 3855 20773-20790.

- Jain, A. K., Z. J. Li, V. Naik, D. J. Wuebbles, D. A. Good, J. C. Hansen, and J. S. Francisco
- 3857 (2001), Evaluation of the atmospheric lifetime and radiative forcing on climate for 1,2,2,2-
- Tetrafluoroethyl Trifluoromethyl Ether (CF<sub>3</sub>OCHFCF<sub>3</sub>), J. Geophys. Res.-Atmos., 106(D12),
- 3859 12615-12618.
- Javadi, M. S., O. J. Nielsen, T. J. Wallington, M. D. Hurley, and J. G. Owens (2007),
- 3861 Atmospheric chemistry of 2-ethoxy-3,3,4,4,5-pentafluorotetra-hydro-2,5-bis 1,2,2,2
- 3862 tetrafluoro-1- (trifluoromethyl)ethyl -furan: Kinetics, mechanisms, and products of Cl atom
- and OH radical initiated oxidation, *Environmental Science & Technology*, 41(21), 7389-7395.
- Jimenez, E., M. Antinolo, B. Ballesteros, E. Martinez, and J. Albaladejo (2010), Atmospheric
- 3865 Lifetimes and Global Warming Potentials of CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH and CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH,
- 3866 *ChemPhysChem*, 11(18), 4079-4087.
- Johansson, D. J. A. (2012), Economics- and physical-based metrics for comparing greenhouse
- 3868 gases, Climatic Change, 110(1-2), 123-141.
- Joos, F., R. Roth, J. S. Fuglestvedt, G. P. Peters, I. G. Enting, W. von Bloh, V. Brovkin, E. J.
- Burke, M. Eby, N. R. Edwards, T. Friedrich, T. L. Frölicher, P. R. Halloran, P. B. Holden, C.
- Jones, T. Kleinen, F. Mackenzie, K. Matsumoto, M. Meinshausen, G. K. Plattner, A.
- Reisinger, J. Segschneider, G. Shaffer, M. Steinacher, K. Strassmann, K. Tanaka, A.
- 3873 Timmermann, and A. J. Weaver (2013), Carbon dioxide and climate impulse response
- 3874 functions for the computation of greenhouse gas metrics: a multi-model analysis, Atmos.
- 3875 Chem. Phys., 13, 2793-2825.
- Joshi, M., K. Shine, M. Ponater, N. Stuber, R. Sausen, and L. Li (2003), A comparison of
- 3877 climate response to different radiative forcings in three general circulation models: towards an
- improved metric of climate change, Clim. Dyn., 20(7-8), 843-854.
- Kagann, R. H., J. W. Elkins, and R. L. Sams (1983), Absolute band strengths of halocarbons
- F-11 and F-12 in the 8-mu-mu to 16-mu-m region, Journal of Geophysical Research-Oceans
- 3881 *and Atmospheres*, 88(NC2), 1427-1432.
- Kiehl, J. T., and K. E. Trenberth (1997), Earth's annual global mean energy budget, Bull.
- 3883 Amer. Meteorol. Soc., 78(2), 197-208.
- 3884 Kim, K., R. S. McDowell, and W. T. King (1980), Integrated infrared intensities and
- 3885 transition moments in SF<sub>6</sub>, *J. Chem. Phys.*, 73(1), 36-41.
- 3886 Ko, M., R. L. Shia, N. D. Sze, H. Magid, and R. G. Bray (1999), Atmospheric lifetime and
- 3887 global warming potential of HFC-245fa, J. Geophys. Res.-Atmos., 104(D7), 8173-8181.
- 3888 Ko, M., N. D. Sze, W. C. Wang, G. Shia, A. Goldman, F. J. Murcray, D. G. Murcray, and C.
- 3889 P. Rinsland (1993), Atmospheric sulfur-hexafluoride sources, sinks and greenhouse
- 3890 warming, J. Geophys. Res.-Atmos., 98(D6), 10499-10507.
- 3891 Kratz, D. P. (2008), The sensitivity of radiative transfer calculations to the changes in the
- 3892 HITRAN database from 1982 to 2004, J. Quant. Spectrosc. Radiat. Transf., 109(6), 1060-
- 3893 1080.
- Kunde, V. G., B. J. Conrath, R. A. Hanel, W. C. Maguire, Prabhaka.C, and Salomons.Vv
- 3895 (1974), NIMBUS-4 infrared spectroscopy experiment .2. Comparison of observed and
- theoretical radiances from 425-1450 cm-1, *Journal of Geophysical Research*, 79(6), 777-784.
- 3897 Kutsuna, S., L. Chen, T. Abe, J. Mizukado, T. Uchimaru, K. Tokuhashi, and A. Sekiya
- 3898 (2005), Henry's law constants of 2,2,2-trifluoroethyl formate, ethyl trifluoro acetate, and non-
- fluorinated analogous esters, *Atmospheric Environment*, 39(32), 5884-5892.

- Lashof, D. A., and D. R. Ahuja (1990), Relative contributions of greenhouse gas emissions to
- 3901 global warming, *Nature*, *344*(6266), 529-531.
- Laube, J. C., A. Keil, H. Bönisch, A. Engel, T. Röckmann, C. M. Volk, and W. T. Sturges
- 3903 (2012), Observation-based assessment of stratospheric fractional release, lifetimes, and ozone
- depletion potentials of ten important source gases, *Atmos. Chem. Phys.*, 13, 2779-2791.
- 3905 Le Bris, K., and K. Strong (2010), Temperature-dependent absorption cross-sections of
- 3906 HCFC-142b, J. Quant. Spectrosc. Radiat. Transf., 111(3), 364-371.
- 3907 Le Bris, K., R. Pandharpurkar, and K. Strong (2011), Mid-infrared absorption cross-sections
- 3908 and temperature dependence of CFC-113, J. Quant. Spectrosc. Radiat. Transf., 112(8), 1280-
- 3909 1285.
- 3910 Le Bris, K., J. McDowell, and K. Strong (2012), Measurements of the infrared absorption
- 3911 cross-sections of HCFC-141b (CH3CFCl2), J. Quant. Spectrosc. Radiat. Transf., 113(15),
- 3912 1913-1919.
- 3913 Li, Z. H., and P. Varanasi (1994), Measurement of the absorption cross-sections of CFC-11 at
- 3914 conditions representing various model atmospheres, J. Quant. Spectrosc. Radiat. Transf.,
- 3915 *52*(2), 137-144.
- 3916 Lovelock, J. E., and R. J. Maggs (1973), Halogenated hydrocarbons in and over Atlantic,
- 3917 Nature, 241(5386), 194-196.
- 3918 M.S.F./R.A.L. Molecular Spectroscopy Facility / Rutherford Appleton Laboratory,
- 3919 <a href="http://www.msf.rl.ac.uk">http://www.msf.rl.ac.uk</a>, edited.
- Manne, A. S., and R. G. Richels (2001), An alternative approach to establishing trade-offs
- 3921 among greenhouse gases, *Nature*, 410(6829), 675-677.
- 3922 Mashino, M., M. Kawasaki, T. J. Wallington, and M. D. Hurley (2000), Atmospheric
- 3923 degradation of CF<sub>3</sub>OCF=CF<sub>2</sub>: Kinetics and mechanism of its reaction with OH radicals and Cl
- 3924 atoms, J. Phys. Chem. A, 104(13), 2925-2930.
- 3925 Massie, S. T., A. Goldman, D. G. Murcray, and J. C. Gille (1985), Approximate absorption
- 3926 cross-sections of F12, F11, C10NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, CCl<sub>4</sub>, CF<sub>4</sub>, F21, F113, F114, and HNO<sub>4</sub>,
- 3927 Appl. Optics, 24(21), 3426-3427.
- Maycock, A. C., and K. P. Shine (2012), Stratospheric water vapor and climate: Sensitivity to
- 3929 the representation in radiation codes, *J. Geophys. Res.*, in press.
- 3930 McCulloch, A., P. M. Midgley, and D. A. Fisher (1994), Distribution of emissions of
- 3931 chlorofluorocarbons (CFCs) 11, 12, 113, 114 and 115 among reporting and non-reporting
- 3932 countries in 1986, *Atmospheric Environment*, 28(16), 2567-2582.
- 3933 McDaniel, A. H., C. A. Cantrell, J. A. Davidson, R. E. Shetter, and J. G. Calvert (1991), The
- 3934 temperature-dependent, infrared-absorption cross-sections for the chlorofluorocarbons CFC-
- 3935 11, CFC-12, CFC-13, CFC-14, CFC-22, CFC-113, CFC-114, and CFC-115, J. Atmos. Chem.,
- 3936 *12*(3), 211-227.
- 3937 McDowell, R. S., B. J. Krohn, H. Flicker, and M. C. Vasquez (1986), Vibrational levels and
- anharmonicity in SF<sub>6</sub> .1. Vibrational band analysis, Spectroc. Acta Pt. A-Molec. Biomolec.
- 3939 *Spectr.*, 42(2-3), 351-369.
- 3940 McPheat, R., and G. Duxbury (2000), Infrared absorption cross-sections and integrated
- 3941 absorption intensities of chloroform and fluoroform vapour, J. Quant. Spectrosc. Radiat.
- 3942 *Transf.*, 66(2), 153-167.

- 3943 Mills, I. M., W. B. Person, J. R. Scherer, and B. Crawford (1958), Vibrational intensities .9.
- 3944  $C_2F_6$  extension and revision, *J. Chem. Phys.*, 28(5), 851-853.
- 3945 Minschwaner, K., L. Hoffmann, A. Brown, M. Riese, R. Müller, and P. F. Bernath (2012),
- 3946 Stratospheric loss and atmospheric lifetimes of CFC-11 and CFC-12 derived from satellite
- 3947 observations, *Atmos. Chem. Phys. Discuss.*, *12*(11), 28733-28764.
- 3948 Molina, M. J., and F. S. Rowland (1974), Stratospheric Sink for Chlorofluoromethanes -
- 3949 Chlorine Atomic-Catalysed Destruction of Ozone, *Nature*, 249(5460), 810-812.
- Montzka, S. A., M. Krol, E. Dlugokencky, B. Hall, P. Jöckel, and J. Lelieveld (2011), Small
- 3951 Interannual Variability of Global Atmospheric Hydroxyl, *Science*, 331(6013), 67-69.
- Morcillo, J., L. J. Zamorano, and J. M. V. Heredia (1966), Infra-red intensities in CH<sub>2</sub>F<sub>2</sub>,
- 3953 CH<sub>2</sub>Cl<sub>2</sub> and CF<sub>2</sub>Cl<sub>2</sub>, *Spectrochimica Acta*, 22(12), 1969-1980.
- Myhre, G., and F. Stordal (1997), Role of spatial and temporal variations in the computation
- 3955 of radiative forcing and GWP, *J. Geophys. Res.-Atmos.*, 102(D10), 11181-11200.
- 3956 Myhre, G., E. J. Highwood, K. P. Shine, and F. Stordal (1998), New estimates of radiative
- forcing due to well mixed greenhouse gases, *Geophys. Res. Lett.*, 25(14), 2715-2718.
- 3958 Myhre, G., C. J. Nielsen, D. L. Powell, and F. Stordal (1999), Infrared absorption cross
- 3959 section, radiative forcing, and GWP of four hydrofluoro(poly)ethers, Atmospheric
- 3960 Environment, 33(27), 4447-4458.
- 3961 Myhre, G., F. Stordal, I. Gausemel, C. J. Nielsen, and E. Mahieu (2006), Line-by-line
- 3962 calculations of thermal infrared radiation representative for global condition: CFC-12 as an
- 3963 example, *J. Quant. Spectrosc. Radiat. Transf.*, 97(3), 317-331.
- Naik, V., A. K. Jain, K. O. Patten, and D. J. Wuebbles (2000), Consistent sets of atmospheric
- 3965 lifetimes and radiative forcings on climate for CFC replacements: HCFCs and HFCs, J.
- 3966 Geophys. Res.-Atmos., 105(D5), 6903-6914.
- Nanes, R., P. M. Silvaggio, and R. W. Boese (1980), Temperature-dependence of intensities
- 3968 of the 8-12 μm bands of CFCl<sub>3</sub>, J. Quant. Spectrosc. Radiat. Transf., 23(2), 211-220.
- Nemtchinov, V., and P. Varanasi (2003), Thermal infrared absorption cross-sections of CCl<sub>4</sub>
- needed for atmospheric remote sensing, J. Quant. Spectrosc. Radiat. Transf., 82(1-4), 473-
- 3971 481.
- Nemtchinov, V., and P. Varanasi (2004), Absorption cross-sections of HFC-134a in the
- spectral region between 7 and 12 μm, J. Quant. Spectrosc. Radiat. Transf., 83(3-4), 285-294.
- Newnham, D., J. Ballard, and M. Page (1996), Infrared band strengths of HFC-134a vapour,
- 3975 *J. Quant. Spectrosc. Radiat. Transf.*, *55*(3), 373-381.
- Nielsen, O. J., F. M. Nicolaisen, C. Bacher, M. D. Hurley, T. J. Wallington, and K. P. Shine
- 3977 (2002), Infrared spectrum and global warming potential of SF<sub>5</sub>CF<sub>3</sub>, Atmospheric
- 3978 Environment, 36(7), 1237-1240.
- Nielsen, O. J., M. S. Javadi, M. P. S. Andersen, M. D. Hurley, T. J. Wallington, and R. Singh
- 3980 (2007), Atmospheric chemistry of CF<sub>3</sub>CF=CH<sub>2</sub>: Kinetics and mechanisms of gas-phase
- reactions with Cl atoms, OH radicals, and O<sub>3</sub>, Chemical Physics Letters, 439(1-3), 18-22.
- Nilsson, E. J. K., O. J. Nielsen, M. S. Johnson, M. D. Hurley, and T. J. Wallington (2009),
- 3983 Atmospheric chemistry of cis-CF<sub>3</sub>CHCHF: Kinetics of reactions with OH radicals and O<sub>3</sub> and
- 3984 products of OH radical initiated oxidation, *Chemical Physics Letters*, 473(4-6), 233-237.

- Ninomiya, Y., M. Kawasaki, A. Guschin, L. T. Molina, M. J. Molina, and T. J. Wallington
- 3986 (2000), Atmospheric chemistry of n-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>: Reaction with OH radicals and Cl atoms and
- 3987 atmospheric fate of n-C<sub>3</sub>F<sub>7</sub>OCH<sub>2</sub>O( $\bullet$ ) radicals, *Environmental Science & Technology*, 34(14),
- 3988 2973-2978.
- 3989 O'Neill, B. C. (2000), The jury is still out on global warming potentials, *Climatic Change*,
- 3990 44(4), 427-443.
- 3991 Olivié, D. J. L., and G. P. Peters (2012), The impact of model variation in CO2 and
- 3992 temperature impulse response functions on emission metrics, Earth Syst. Dynam. Discuss.,
- 3993 *3*(2), 935-977.
- 3994 Olliff, M. P., and G. Fischer (1994), Integrated absorption intensities of haloethanes and
- 3995 halopropanes, Spectroc. Acta Pt. A-Molec. Biomolec. Spectr., 50(13), 2223-2237.
- 3996 Oreopoulos, L., E. Mlawer, J. Delamere, T. Shippert, J. Cole, B. Fomin, M. Iacono, Z. H. Jin,
- 3997 J. N. Li, J. Manners, P. Raisanen, F. Rose, Y. C. Zhang, M. J. Wilson, and W. B. Rossow
- 3998 (2012), The Continual Intercomparison of Radiation Codes: Results from Phase I, *J. Geophys.*
- 3999 Res.-Atmos., 117.
- 4000 Orkin, V. L., L. E. Martynova, and A. N. Ilichev (2010), High-Accuracy Measurements of
- 4001 OH Reaction Rate Constants and IR Absorption Spectra: CH<sub>2</sub>=CF-CF<sub>3</sub> and trans-CHF=CH-
- 4002 CF<sub>3</sub>, J. Phys. Chem. A, 114(19), 5967-5979.
- 4003 Orkin, V. L., E. Villenave, R. E. Huie, and M. J. Kurylo (1999), Atmospheric lifetimes and
- 4004 global warming potentials of hydrofluoroethers: Reactivity toward OH, UV spectra, and IR
- 4005 absorption cross sections, *J. Phys. Chem. A*, *103*(48), 9770-9779.
- 4006 Orkin, V. L., A. G. Guschin, I. K. Larin, R. E. Huie, and M. J. Kurylo (2003), Measurements
- 4007 of the infrared absorption cross-sections of haloalkanes and their use in a simplified
- 4008 calculational approach for estimating direct global warming potentials, J. Photochem.
- 4009 Photobiol. A-Chem., 157(2-3), 211-222.
- 4010 Orlando, J. J., G. S. Tyndall, A. Huang, and J. G. Calvert (1992), Temperature-dependence of
- 4011 the infrared-absorption cross-sections of carbon-tetrachloride, Geophys. Res. Lett., 19(10),
- 4012 1005-1008.
- 4013 Osterstrom, F. F., O. J. Nielsen, M. P. S. Andersen, and T. J. Wallington (2012), Atmospheric
- 4014 chemistry of CF<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub>: Reaction with chlorine atoms and OH radicals, kinetics,
- degradation mechanism and global warming potential, *Chemical Physics Letters*, 524, 32-37.
- 4016 Oyaro, N., S. R. Sellevag, and C. J. Nielsen (2004), Study of the OH and Cl-initiated
- 4017 oxidation, IR absorption cross-section, radiative forcing, and global warming potential of four
- 4018 C<sub>4</sub>-hydrofluoroethers, *Environmental Science & Technology*, 38(21), 5567-5576.
- 4019 Oyaro, N., S. R. Sellevag, and C. J. Nielsen (2005), Atmospheric chemistry of
- 4020 hydrofluoroethers: Reaction of a series of hydrofluoro ethers with OH radicals and Cl atoms,
- atmospheric lifetimes, and global warming potentials, *J. Phys. Chem. A*, 109(2), 337-346.
- 4022 Papadimitriou, V. C., R. K. Talukdar, R. W. Portmann, A. R. Ravishankara, and J. B.
- 4023 Burkholder (2008a), CF<sub>3</sub>CF=CH<sub>2</sub> and (Z)-CF<sub>3</sub>CF=CHF: temperature dependent OH rate
- 4024 coefficients and global warming potentials, *Physical Chemistry Chemical Physics*, 10(6), 808-
- 4025 820.
- 4026 Papadimitriou, V. C., M. R. McGillen, E. L. Fleming, C. H. Jackman, and J. B. Burkholder
- 4027 (2013), NF<sub>3</sub>: UV absorption spectrum temperature dependence and the atmospheric and
- 4028 climate forcing implications, *Geophys. Res. Lett.*, 40(2), 440-445.

- 4029 Papadimitriou, V. C., R. W. Portmann, D. W. Fahey, J. Muhle, R. F. Weiss, and J. B.
- 4030 Burkholder (2008b), Experimental and Theoretical Study of the Atmospheric Chemistry and
- 4031 Global Warming Potential of SO<sub>2</sub>F<sub>2</sub>, *J. Phys. Chem. A*, 112(49), 12657-12666.
- 4032 Papanastasiou, D. K., N. R. Carlon, J. A. Neuman, E. L. Fleming, C. H. Jackman, and J. B.
- 4033 Burkholder (2013), Revised UV absorption spectra, ozone depletion potentials, and global
- 4034 warming potentials for the ozone-depleting substances CF2Br2, CF2ClBr, and CF2BrCF2Br,
- 4035 Geophys. Res. Lett., 40(2), 464-469.
- 4036 Papasavva, S., S. Tai, K. H. Illinger, and J. E. Kenny (1997), Infrared radiative forcing of
- 4037 CFC substitutes and their atmospheric reaction products, J. Geophys. Res.-Atmos., 102(D12),
- 4038 13643-13650.
- 4039 Person, W. B., and S. R. Polo (1961), Infrared intensities of the fundamental frequencies of
- 4040 CF<sub>3</sub>Br, *Spectrochimica Acta*, *17*(1), 101-111.
- 4041 Peters, G. P., B. Aamaas, T. Berntsen, and J. S. Fuglestvedt (2011), The integrated global
- 4042 temperature change potential (iGTP) and relationships between emission metrics,
- 4043 Environmental Research Letters, 6(4).
- 4044 Petty, G. W. (2006), A first course in atmospheric radiation. Second Edition. Sundog
- 4045 Publishing.
- 4046 Pinnock, S., and K. P. Shine (1998), The effects of changes in HITRAN and uncertainties in
- the spectroscopy on infrared irradiance calculations, *J. Atmos. Sci.*, 55(11), 1950-1964.
- 4048 Pinnock, S., M. D. Hurley, K. P. Shine, T. J. Wallington, and T. J. Smyth (1995), Radiative
- 4049 forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons, J. Geophys. Res.-
- 4050 Atmos., 100(D11), 23227-23238.
- Plattner, G.-K., T. M. Stocker, P., and M. Tignor (2009), IPCC Expert Meeting on the Science
- 4052 of Alternative Metrics: Meeting Report., IPCC Working Group I, Technical Support
- 4053 UnitRep., Bern, Switzerland.
- 4054 Prather, M. J. (1996), Time scales in atmospheric chemistry: Theory, GWPs for CH<sub>4</sub> and CO,
- 4055 and runaway growth, *Geophys. Res. Lett.*, 23(19), 2597-2600.
- 4056 Prather, M. J. (2007), Lifetimes and time scales in atmospheric chemistry, *Philos. Trans. R.*
- 4057 Soc. A-Math. Phys. Eng. Sci., 365(1856), 1705-1726.
- 4058 Prather, M. J., and C. M. Spivakovsky (1990), Tropospheric OH and the lifetimes of
- 4059 hydrochlorofluorocarbons, J. Geophys. Res.-Atmos., 95(D11), 18723-18729.
- 4060 Prather, M. J., and J. Hsu (2008), NF<sub>3</sub>, the greenhouse gas missing from Kyoto, *Geophys. Res.*
- 4061 Lett., 35(12).
- 4062 Prather, M. J., and J. Hsu (2010), NF<sub>3</sub>, the greenhouse gas missing from Kyoto (vol 37,
- 4063 L11807, 2010), Geophys. Res. Lett., 37.
- 4064 Prather, M. J., C. D. Holmes, and J. Hsu (2012), Reactive greenhouse gas scenarios:
- Systematic exploration of uncertainties and the role of atmospheric chemistry, *Geophys. Res.*
- 4066 *Lett.*, 39.
- 4067 Rajakumar, B., R. W. Portmann, J. B. Burkholder, and A. R. Ravishankara (2006), Rate
- 4068 coefficients for the reactions of OH with CF<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> (HFC-263fb), CF<sub>3</sub>CHFCH<sub>2</sub>F (HFC-
- 4069 245eb), and CHF<sub>2</sub>CHFCHF<sub>2</sub> (HFC-245ea) between 238 and 375 K, J. Phys. Chem. A,
- 4070 *110*(21), 6724-6731.

- 4071 Ramanathan, V. (1975), Greenhouse effect due to chlorofluorocarbons climatic implications,
- 4072 Science, 190(4209), 50-51.
- 4073 Ramanathan, V., R. J. Cicerone, H. B. Singh, and J. T. Kiehl (1985), Trace gas trends and
- 4074 their potential role in climate change, *J. Geophys. Res.-Atmos.*, 90(ND3), 5547-5566.
- 4075 Ramanathan, V., L. Callis, R. Cess, J. Hansen, I. Isaksen, W. Kuhn, A. Lacis, F. Luther, J.
- 4076 Mahlman, R. Reck, and M. Schlesinger (1987), Climate-Chemical Interactions and Effects of
- 4077 Changing Atmospheric Trace Gases, Rev. Geophys., 25(7), 1441-1482.
- 4078 Ravishankara, A. R., S. Solomon, A. A. Turnipseed, and R. F. Warren (1993), Atmospheric
- 4079 lifetimes of long-lived halogenated species, *Science*, 259(5092), 194-199.
- 4080 Ravishankara, A. R., A. A. Turnipseed, N. R. Jensen, S. Barone, M. Mills, C. J. Howard, and
- 4081 S. Solomon (1994), Do hydrofluorocarbons destroy stratospheric ozone, *Science*, 263(5143),
- 4082 71-75.
- 4083 Reisinger, A., M. Meinshausen, and M. Manning (2011), Future changes in global warming
- 4084 potentials under representative concentration pathways, *Environmental Research Letters*,
- $4085 \quad 6(2).$
- 4086 Reisinger, A., M. Meinshausen, M. Manning, and G. Bodeker (2010), Uncertainties of global
- 4087 warming metrics: CO<sub>2</sub> and CH<sub>4</sub>, Geophys. Res. Lett., 37.
- 4088 RETRO (2006), REanalysis of the TROpospheric chemical composition over the past 40
- 4089 years. <a href="http://retro.enes.org">http://retro.enes.org</a>, accessed 15th of March 2012, edited.
- 4090 Rigby, M., R. G. Prinn, S. O'Doherty, S. A. Montzka, A. McCulloch, C. M. Harth, J. Mühle,
- 4091 P. K. Salameh, R. F. Weiss, D. Young, P. G. Simmonds, B. D. Hall, G. S. Dutton, D. Nance,
- 4092 D. J. Mondeel, J. W. Elkins, P. B. Krummel, L. P. Steele, and P. J. Fraser (2013), Re-
- evaluation of the lifetimes of the major CFCs and CH<sub>3</sub>CCl<sub>3</sub> using atmospheric trends, *Atmos*.
- 4094 Chem. Phys., 13, 2691-2702.
- 4095 Rinsland, C. P., S. W. Sharpe, and R. L. Sams (2003), Temperature-dependent absorption
- 4096 cross-sections in the thermal infrared bands of SF<sub>5</sub>CF<sub>3</sub>, J. Quant. Spectrosc. Radiat. Transf.,
- 4097 82(1-4), 483-490.
- 4098 Robson, J. I., L. K. Gohar, M. D. Hurley, K. P. Shine, and T. J. Wallington (2006), Revised
- 4099 IR spectrum, radiative efficiency and global warming potential of nitrogen trifluoride,
- 4100 Geophys. Res. Lett., 33(10).
- 4101 Roehl, C. M., D. Boglu, C. Bruhl, and G. K. Moortgat (1995), Infrared band intensities and
- global warming potentials of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>10</sub>, C<sub>5</sub>F<sub>12</sub>, and C<sub>6</sub>F<sub>14</sub>, Geophys. Res. Lett.,
- 4103 22(7), 815-818.
- 4104 Rogers, J. D., and R. D. Stephens (1988), Absolute infrared intensities for F-113 and F-114
- 4105 and an assessment of their greenhouse warming potential relative to other
- 4106 chlorofluorocarbons, J. Geophys. Res.-Atmos., 93(D3), 2423-2428.
- 4107 Rothman, L. S., I. E. Gordon, A. Barbe, D. C. Benner, P. E. Bernath, M. Birk, V. Boudon, L.
- 4108 R. Brown, A. Campargue, J. P. Champion, K. Chance, L. H. Coudert, V. Dana, V. M. Devi,
- 4109 S. Fally, J. M. Flaud, R. R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W.
- 4110 J. Lafferty, J. Y. Mandin, S. T. Massie, S. N. Mikhailenko, C. E. Miller, N. Moazzen-Ahmadi,
- 4111 O. V. Naumenko, A. V. Nikitin, J. Orphal, V. I. Perevalov, A. Perrin, A. Predoi-Cross, C. P.
- 4112 Rinsland, M. Rotger, M. Simeckova, M. A. H. Smith, K. Sung, S. A. Tashkun, J. Tennyson,
- 4113 R. A. Toth, A. C. Vandaele, and J. Vander Auwera (2009), The HITRAN 2008 molecular
- 4114 spectroscopic database, J. Quant. Spectrosc. Radiat. Transf., 110(9-10), 533-572.

- 4115 Ryan, S. M., and C. J. Nielsen (2010), Global Warming Potential of Inhaled Anesthetics:
- 4116 Application to Clinical Use, *Anesth. Analg.*, 111(1), 92-98.
- 4117 Sander, S. P., J. P. D. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E.
- 4118 Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin, and P. H. Wine (2010),
- 4119 Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation Number
- 4120 17, JPL Publication 10-6, NASA/JPL, Jet Propulsion Laboratory, California Institute of
- 4121 Technology, Pasadena, California Rep.
- Schatz, P. N., and D. F. Hornig (1953), Bond moments and derivatives in CF<sub>4</sub>, SIF<sub>4</sub>, and SF<sub>6</sub>
- 4123 from infrared intensities, *J. Chem. Phys.*, 21(9), 1516-1530.
- 4124 Scott, A. P., and L. Radom (1996), Harmonic vibrational frequencies: An evaluation of
- Hartree-Fock, Moller-Plesset, quadratic configuration interaction, density functional theory,
- 4126 and semiempirical scale factors, *J. Phys. Chem.*, 100(41), 16502-16513.
- 4127 Sellevag, S. R., T. Kelly, H. Sidebottom, and C. J. Nielsen (2004a), A study of the IR and
- 4128 UV-Vis absorption cross-sections, photolysis and OH-initiated oxidation of CF<sub>3</sub>CHO and
- 4129 CF<sub>3</sub>CH<sub>2</sub>CHO, Physical Chemistry Chemical Physics, 6(6), 1243-1252.
- 4130 Sellevag, S. R., C. J. Nielsen, O. A. Sovde, G. Myhre, J. K. Sundet, F. Stordal, and I. S. A.
- 4131 Isaksen (2004b), Atmospheric gas-phase degradation and global warming potentials of 2-
- 4132 fluoro ethanol, 2,2-difluoroethanol, and 2,2,2-trifluoroethanol, Atmospheric Environment,
- *4133 38*(39), 6725-6735.
- 4134 Sellevåg, S. R., B. D'Anna, and C. J. Nielsen (2007), Infrared Absorption Cross-Sections and
- 4135 Estimated Global Warming Potentials of CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, CHF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH, CF<sub>3</sub>CF<sub>2</sub>CH<sub>2</sub>OH,
- 4136 CF<sub>3</sub>CHFCF<sub>2</sub>CH<sub>2</sub>OH, and CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH, *Asian Chemistry Letters*(11), 33-40.
- Shine, K. P. (2009), The global warming potential-the need for an interdisciplinary retrial,
- 4138 Climatic Change, 96(4), 467-472.
- Shine, K. P., and P. M. D. Forster (1999), The effect of human activity on radiative forcing of
- climate change: a review of recent developments, Glob. Planet. Change, 20(4), 205-225.
- Shine, K. P., J. S. Fuglestvedt, K. Hailemariam, and N. Stuber (2005a), Alternatives to the
- 4142 global warming potential for comparing climate impacts of emissions of greenhouse gases,
- 4143 Climatic Change, 68(3), 281-302.
- Shine, K. P., T. K. Berntsen, J. S. Fuglestvedt, R. B. Skeie, and N. Stuber (2007), Comparing
- 4145 the climate effect of emissions of short- and long-lived climate agents, *Philos. Trans. R. Soc.*
- 4146 A-Math. Phys. Eng. Sci., 365(1856), 1903-1914.
- Shine, K. P., L. K. Gohar, M. D. Hurley, G. Marston, D. Martin, P. G. Simmonds, T. J.
- Wallington, and M. Watkins (2005b), Perfluorodecalin: global warming potential and first
- detection in the atmosphere, *Atmospheric Environment*, 39(9), 1759-1763.
- 4150 Sihra, K., M. D. Hurley, K. P. Shine, and T. J. Wallington (2001), Updated radiative forcing
- estimates of 65 halocarbons and nonmethane hydrocarbons, J. Geophys. Res.-Atmos.,
- 4152 *106*(D17), 20493-20505.
- Smith, K., D. Newnham, M. Page, J. Ballard, and G. Duxbury (1996), Infrared band strengths
- and absorption cross-sections of HFC-32 vapour, J. Quant. Spectrosc. Radiat. Transf., 56(1),
- 4155 73-82.

- Smith, K., D. Newnham, M. Page, J. Ballard, and G. Duxbury (1998), Infrared absorption
- 4157 cross-sections and integrated absorption intensities of HFC-134 and HFC-143a vapour, J.
- 4158 Quant. Spectrosc. Radiat. Transf., 59(3-5), 437-451.
- 4159 Spivakovsky, C. M., J. A. Logan, S. A. Montzka, Y. J. Balkanski, M. Foreman-Fowler, D. B.
- 4160 A. Jones, L. W. Horowitz, A. C. Fusco, C. A. M. Brenninkmeijer, M. J. Prather, S. C. Wofsy,
- and M. B. McElroy (2000), Three-dimensional climatological distribution of tropospheric
- 4162 OH: Update and evaluation, *J. Geophys. Res.-Atmos.*, 105(D7), 8931-8980.
- Stevenson, D. S., R. M. Doherty, M. G. Sanderson, W. J. Collins, C. E. Johnson, and R. G.
- Derwent (2004), Radiative forcing from aircraft NOx emissions: Mechanisms and seasonal
- 4165 dependence, *J. Geophys. Res.-Atmos.*, 109(D17307).
- 4166 Stolarski, R., R. Bojkov, L. Bishop, C. Zerefos, J. Staehelin, and J. Zawodny (1992),
- 4167 Measured trends in stratospheric ozone, *Science*, 256(5055), 342-349.
- 4168 Stoppa, P., A. P. Charmet, N. Tasinato, S. Giorgianni, and A. Gambi (2009), Infrared Spectra,
- 4169 Integrated Band Intensities, and Anharmonic Force Field of H<sub>2</sub>C=CHF, J. Phys. Chem. A,
- 4170 *113*(8), 1497-1504.
- 4171 Stordal, F., I. S. A. Isaksen, and K. Horntveth (1985), A diabatic circulation two-dimensional
- 4172 model with photochemistry simulations of ozone and long-lived tracers with surface
- 4173 sources, *J. Geophys. Res.-Atmos.*, 90(ND3), 5757-5776.
- 4174 Sturges, W. T., T. J. Wallington, M. D. Hurley, K. P. Shine, K. Sihra, A. Engel, D. E. Oram,
- 4175 S. A. Penkett, R. Mulvaney, and C. A. M. Brenninkmeijer (2000), A potent greenhouse gas
- 4176 identified in the atmosphere: SF<sub>5</sub>CF<sub>3</sub>, Science, 289(5479), 611-613.
- 4177 Suga, A., Y. Mochizuki, N. Nagasaki, Y. Gotoh, H. Ito, S. Yamashita, T. Uchimaru, M.
- 4178 Sugie, A. Sekiya, S. Kondo, and M. Aoyagi (1994), Estimation of total infrared intensities of
- 4179 fluorinated ethyl methyl ethers, *Chem. Lett.* (12), 2365-2368.
- 4180 Søndergaard, R., O. J. Nielsen, M. D. Hurley, T. J. Wallington, and R. Singh (2007),
- 4181 Atmospheric chemistry of trans-CF<sub>3</sub>CH = CHF: Kinetics of the gas-phase reactions with Cl
- atoms, OH radicals, and O<sub>3</sub>, Chemical Physics Letters, 443(4-6), 199-204.
- Søvde, O. A., M. Gauss, S. P. Smyshlyaev, and I. S. A. Isaksen (2008), Evaluation of the
- 4184 chemical transport model Oslo CTM2 with focus on arctic winter ozone depletion, J.
- 4185 *Geophys. Res.-Atmos.*, 113(D09304).
- 4186 Søvde, O. A., Y. J. Orsolini, D. R. Jackson, F. Stordal, I. S. A. Isaksen, and B. Rognerud
- 4187 (2011), Estimation of Arctic O-3 loss during winter 2006/2007 using data assimilation and
- 4188 comparison with a chemical transport model, Q. J. R. Meteorol. Soc., 137(654), 118-128.
- 4189 Takahashi, K., Y. Matsumi, T. J. Wallington, and M. D. Hurley (2002), Atmospheric
- 4190 chemistry of CF<sub>3</sub>CFHOCF<sub>3</sub>: Reaction with OH radicals, atmospheric lifetime, and global
- 4191 warming potential, J. Geophys. Res.-Atmos., 107(D21).
- Thomsen, D. L., V. F. Andersen, O. J. Nielsen, and T. J. Wallington (2011), Atmospheric
- 4193 chemistry of C<sub>2</sub>F<sub>5</sub>CH<sub>2</sub>OCH<sub>3</sub> (HFE-365mcf), Physical Chemistry Chemical Physics, 13(7),
- 4194 2758-2764.
- Tjemkes, S. A., T. Patterson, R. Rizzi, M. W. Shephard, S. A. Clough, M. Matricardi, J. D.
- 4196 Haigh, M. Hopfner, S. Payan, A. Trotsenko, N. Scott, P. Rayer, J. P. Taylor, C. Clerbaux, L.
- 4197 L. Strow, S. DeSouza-Machado, D. Tobin, and R. Knuteson (2003), The ISSWG line-by-line
- inter-comparison experiment, J. Quant. Spectrosc. Radiat. Transf., 77(4), 433-453.

- 4199 Tol, R. S. J., T. K. Berntsen, B. C. O'Neill, J. S. Fuglestvedt, and K. P. Shine (2012), A
- 4200 unifying framework for metrics for aggregating the climate effect of different emissions,
- 4201 Environmental Research Letters, 7(044006), 8 pp.
- 4202 Trenberth, K. E., and L. Smith (2005), The Mass of the Atmosphere: A Constraint on Global
- 4203 Analyses, *J. Clim.*, 18(6), 864-875.
- 4204 Trenberth, K. E., J. T. Fasullo, and J. Kiehl (2009), Earth's global energy budget, *Bull. Amer.*
- 4205 *Meteorol. Soc.*, 90(3), 311-323.
- 4206 Urata, S., A. Takada, T. Uchimaru, and A. K. Chandra (2003), Rate constants estimation for
- 4207 the reaction of hydrofluorocarbons and hydrofluoroethers with OH radicals, *Chemical Physics*
- 4208 Letters, 368(1-2), 215-223.
- 4209 van der Werf, G. R., J. T. Randerson, L. Giglio, G. J. Collatz, P. S. Kasibhatla, and A. F.
- 4210 Arellano (2006), Interannual variability in global biomass burning emissions from 1997 to
- 4211 2004, Atmos. Chem. Phys., 6, 3423-3441.
- 4212 Vander Auwera, J. (2000), Infrared absorption cross-sections for two substituted ethanes: 1,1-
- 4213 difluoroethane (HFC-152a) and 1,2-dichloroethane, J. Quant. Spectrosc. Radiat. Transf.,
- 4214 66(2), 143-151.
- 4215 Vanthanh, N., I. Rossi, A. Jeanlouis, and H. Rippel (1986), Infrared band shapes and band
- 4216 strengths of CF<sub>2</sub>Cl<sub>2</sub> from 800 to 1200 cm<sup>-1</sup> at 296 and 200 K, J. Geophys. Res.-Atmos.,
- 4217 *91*(D3), 4056-4062.
- 4218 Varanasi, P., and F. K. Ko (1977), Intensity measurements in freon bands of atmospheric
- 4219 interest, J. Quant. Spectrosc. Radiat. Transf., 17(3), 385-388.
- 4220 Varanasi, P., and S. Chudamani (1988a), Remeasurement of the absolute intensities of CFC-
- 4221 11 (CFCl<sub>3</sub>) and CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>), J. Quant. Spectrosc. Radiat. Transf., 39(3), 193-195.
- 4222 Varanasi, P., and S. Chudamani (1988b), Infrared intensities of some chlorofluorocarbons
- 4223 capable of perturbing the global climate, J. Geophys. Res.-Atmos., 93(D2), 1666-1668.
- 4224 Varanasi, P., and V. Nemtchinov (1994), Thermal infrared-absorption coefficients of CFC-12
- 4225 at atmospheric conditions, J. Quant. Spectrosc. Radiat. Transf., 51(5), 679-687.
- 4226 Varanasi, P., Z. Li, V. Nemtchinov, and A. Cherukuri (1994), Spectral absorption-coefficient
- 4227 data on HCFC-22 and SF<sub>6</sub> for remote-sensing applications, J. Quant. Spectrosc. Radiat.
- 4228 Transf., 52(3-4), 323-332.
- 4229 Vasekova, E., E. A. Drage, K. M. Smith, and N. J. Mason (2006), FTIR spectroscopy and
- 4230 radiative forcing of octafluorocyclobutane and octofluorocyclopentene, J. Quant. Spectrosc.
- 4231 Radiat. Transf., 102(3), 418-424.
- Velders, G. J. M., S. O. Andersen, J. S. Daniel, D. W. Fahey, and M. McFarland (2007), The
- 4233 importance of the Montreal Protocol in protecting climate, *Proc. Natl. Acad. Sci. U. S. A.*,
- 4234 *104*(12), 4814-4819.
- Vlachogiannis, D., A. Sfetsos, A. K. Stubos, R.-E. P. Sotiropoulou, E. Tagaris, C. Pilinis, W.
- 4236 Zhong, J. D. Haigh, D. O. Eriksen, S. K. Hartvig, C. Chatzichristos, J. Muller, R. Kleven, and
- 4237 I. Nielssen (2005), Assessment of the impact of SF<sub>6</sub> and PFC reservoir tracers on global
- warming, the AEOLOS study, *Environmental Sciences*, 2(2-3), 263-272.
- Volk, C. M., J. W. Elkins, D. W. Fahey, G. S. Dutton, J. M. Gilligan, M. Loewenstein, J. R.
- 4240 Podolske, K. R. Chan, and M. R. Gunson (1997), Evaluation of source gas lifetimes from
- 4241 stratospheric observations, J. Geophys. Res.-Atmos., 102(D21), 25543-25564.

- Wallington, T. J., M. D. Hurley, and O. J. Nielsen (2009), The radiative efficiency of
- 4243 HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (H-Galden 1040x) revisited, Atmospheric Environment, 43(27),
- 4244 4247-4249.
- 4245 Wallington, T. J., M. P. S. Andersen, and O. J. Nielsen (2010), Relative integrated IR
- 4246 absorption in the atmospheric window is not the same as relative radiative efficiency, *Proc.*
- 4247 Natl. Acad. Sci. U. S. A., 107(48), E178-E179.
- Wallington, T. J., P. Dagaut, R. H. Liu, and M. J. Kurylo (1988), The gas-phase reactions of
- 4249 hydroxyl radicals with a series of esters over the temperature-range 240-440-K, *Int. J. Chem.*
- 4250 Kinet., 20(2), 177-186.
- Wallington, T. J., W. F. Schneider, J. Sehested, and O. J. Nielsen (1995), Hydrofluorocarbons
- and stratospheric ozone, Faraday Discuss., 100, 55-64.
- Wallington, T. J., M. D. Hurley, O. J. Nielsen, and M. P. S. Andersen (2004), Atmospheric
- 4254 chemistry of CF<sub>3</sub>CFHCF<sub>2</sub>OCF<sub>3</sub> and CF<sub>3</sub>CFHCF<sub>2</sub>OCF<sub>2</sub>H: Reaction with Cl atoms and OH
- radicals, degradation mechanism, and global warming potentials, J. Phys. Chem. A, 108(51),
- 4256 11333-11338.
- Wallington, T. J., M. D. Hurley, J. C. Ball, T. Ellermann, O. J. Nielsen, and J. Sehested
- 4258 (1994a), Atmospheric chemistry of HFC-152 UV absorption-spectrum of CH<sub>2</sub>FCFHO<sub>2</sub>
- radicals, kinetics of the reaction CH<sub>2</sub>FCFHO<sub>2</sub>+NO-> CH<sub>2</sub>FCHFO+NO<sub>2</sub>, and fate of the
- 4260 alkoxy radical CH<sub>2</sub>FCFHO, *J. Phys. Chem.*, 98(21), 5435-5440.
- Wallington, T. J., W. F. Schneider, D. R. Worsnop, O. J. Nielsen, J. Sehested, W. J. Debruyn,
- and J. A. Shorter (1994b), The environmental-impact of CFC replacements HFCs and
- 4263 HCFCs, Environmental Science & Technology, 28(7), A320-A326.
- Wallington, T. J., A. Guschin, T. N. N. Stein, J. Platz, J. Sehested, L. K. Christensen, and O.
- J. Nielsen (1998), Atmospheric chemistry of CF<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CF<sub>3</sub>: UV spectra and kinetic data
- 4266 for CF<sub>3</sub>CH(•)OCH<sub>2</sub>CF<sub>3</sub> and CF<sub>3</sub>CH(OO•)OCH<sub>2</sub>CF<sub>3</sub> radicals and atmospheric fate of
- 4267 CF<sub>3</sub>CH(O•)OCH<sub>2</sub>CF<sub>3</sub> radicals, *J. Phys. Chem. A*, 102(7), 1152-1161.
- Wallington, T. J., W. F. Schneider, J. Sehested, M. Bilde, J. Platz, O. J. Nielsen, L. K.
- 4269 Christensen, M. J. Molina, L. T. Molina, and P. W. Wooldridge (1997), Atmospheric
- 4270 chemistry of HFE-7100 (C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>): Reaction with OH radicals, UV spectra and kinetic data
- for C<sub>4</sub>F<sub>9</sub>OCH<sub>2</sub>• and C<sub>4</sub>F<sub>9</sub>CH<sub>2</sub>O<sub>2</sub>• radicals, and the atmospheric fate of C<sub>4</sub>F<sub>9</sub>OCH<sub>2</sub>O center dot
- 4272 radicals, J. Phys. Chem. A, 101(44), 8264-8274.
- Wang, W. C., Y. L. Yung, A. A. Lacis, T. Mo, and J. E. Hansen (1976), Greenhouse effects
- due to man-made perturbations of trace gases, *Science*, 194(4266), 685-690.
- Waterland, R. L., M. D. Hurley, J. A. Misner, T. J. Wallington, S. M. L. Melo, K. Strong, R.
- 4276 Dumoulin, L. Castera, N. L. Stock, and S. A. Mabury (2005), Gas phase UV and IR
- absorption spectra of CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH and F(CF<sub>2</sub>CF<sub>2</sub>)<sub>x</sub>CH<sub>2</sub>CH<sub>2</sub>OH (x=2, 3, 4), J. Fluor.
- 4278 *Chem.*, 126(9-10), 1288-1296.
- 4279 WMO (1999), Scientific Assessment of Ozone Depletion: 1998, Global Ozone Research and
- 4280 Monitoring Project Report No. 44, World Meteorological Organization, Geneva,
- 4281 Switzerland*Rep*.
- 4282 WMO (2003), Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and
- 4283 Monitoring Project Report No. 47*Rep.*, 498 pp, Geneva
- 4284 WMO (2007), Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and
- 4285 Monitoring Project Report No. 50, edited, p. 572pp, Geneva.

- 4286 WMO (2011), Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and
- 4287 Monitoring Project Report No. 50, 572 pp., World Meteorological Organization, Geneva,
- 4288 Switzerland Rep.
- 4289 WMO/GAW (2011), WMO Greenhouse Gas Bulletin. Number 7, 21 November 2011.
- 4290 <a href="http://www.wmo.int/pages/prog/arep/gaw/ghg/documents/GHGbulletin\_7\_en.pdf">http://www.wmo.int/pages/prog/arep/gaw/ghg/documents/GHGbulletin\_7\_en.pdf</a> Rep.
- 4291 WMO/GAW (2012), WMO Greenhouse Gas Bulletin. Number 8, 19 November 2012.
- 4292 <a href="http://www.wmo.int/pages/prog/arep/gaw/ghg/documents/GHG\_Bulletin\_No.8\_en.pdf">http://www.wmo.int/pages/prog/arep/gaw/ghg/documents/GHG\_Bulletin\_No.8\_en.pdf</a> Rep.
- Wuebbles, D. J. (1989), Beyond CO2—the other greenhouse gases Rep., Lawrence Livermore
- National Laboratory report UCRL-99883; Air and Waste Management Association paper 89-
- 4295 119.4.
- Wuebbles, D. J., A. K. Jain, K. O. Patten, and K. E. Grant (1995), SENSITIVITY OF
- 4297 DIRECT GLOBAL WARMING POTENTIALS TO KEY UNCERTAINTIES, Climatic
- 4298 *Change*, 29(3), 265-297.
- Wuebbles, D. J., D. Youn, K. Patten, D. Wang, and M. Martinez-Aviles (2009), Metrics for
- 4300 Ozone and Climate: Three-Dimensional Modeling Studies of Ozone Depletion Potentials and
- 4301 Indirect Global Warming Potentials, 297-326 pp., Springer, New York.
- 4302 Young, C. J., M. D. Hurley, T. J. Wallington, and S. A. Mabury (2006), Atmospheric lifetime
- and global warming potential of a perfluoropolyether, Environmental Science & Technology,
- 4304 40(7), 2242-2246.
- 4305 Young, C. J., M. D. Hurley, T. J. Wallington, and S. A. Mabury (2009a), Atmospheric
- chemistry of perfluorobutenes (CF<sub>3</sub>CFCFCF<sub>3</sub> and CF<sub>3</sub>CF<sub>2</sub>CFCF<sub>2</sub>): Kinetics and mechanisms
- of reactions with OH radicals and chlorine atoms, IR spectra, global warming potentials, and
- 4308 oxidation to perfluorocarboxylic acids, *Atmospheric Environment*, 43(24), 3717-3724.
- 4309 Young, C. J., M. D. Hurley, T. J. Wallington, and S. A. Mabury (2009b), Atmospheric
- chemistry of CF<sub>3</sub>CF<sub>2</sub>H and CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H: Kinetics and products of gas-phase reactions
- with Cl atoms and OH radicals, infrared spectra, and formation of perfluorocarboxylic acids,
- 4312 *Chemical Physics Letters*, *473*(4-6), 251-256.
- 4313 Zhang, H., J. X. Wu, and Z. P. Shen (2011a), Radiative forcing and global warming potential
- of perfluorocarbons and sulfur hexafluoride, Sci. China-Earth Sci., 54(5), 764-772.
- 2315 Zhang, H., J. X. Wu, and P. Luc (2011b), A study of the radiative forcing and global warming
- potentials of hydrofluorocarbons, J. Quant. Spectrosc. Radiat. Transf., 112(2), 220-229.
- Zou, Q., C. Sun, V. Nemtchinov, and P. Varanasi (2004), Thermal infrared cross-sections of
- 4318 C<sub>2</sub>F<sub>6</sub> at atmospheric temperatures, *J. Quant. Spectrosc. Radiat. Transf.*, 83(2), 215-221.

4322

4323

**Table 1.** Estimated contributions to the total radiative forcing uncertainty.

Source of uncertainty	Estimated contribution to total RF uncertainty	References used as basis for uncertainty estimates
Absorption cross-sections	~5% for experimentally determined spectra,	[Ballard et al., 2000b; Bravo et al., 2010b; Forster et al., 2005]
	~10% for ab initio spectra	
Radiation scheme	~5%	[Collins et al., 2006; Forster et al., 2005; Oreopoulos et al., 2012]
Clouds	~5%	[Forster et al., 2005; Gohar et al., 2004]
Spectral overlap and water vapor distribution	~3%	[Forster et al., 2005; Jain et al., 2000; Pinnock et al., 1995]
Surface temperature and atmospheric temperature	~3%	[Forster et al., 2005]
Tropopause level	~5%	[Forster et al., 2005; Freckleton et al., 1998; Myhre and Stordal, 1997]
Temporal and spatial averaging	~1%	[Freckleton et al., 1998; Myhre and Stordal, 1997]
Stratospheric temperature adjustment	~4%	[Forster et al., 2005; Gohar et al., 2004]
Non-uniform vertical profile	~5% for lifetimes > ~5 years,	[Sihra et al., 2001] + this study
	~20% for lifetimes < ~5 years	
Total (RSS) (experimental)	~13% for lifetimes > ~5 years	
	~23% for lifetimes < ~5 years	
Total (RSS) (ab initio)	~15% for lifetimes > ~5 years	

**Table 2.** Integrated absorption cross-sections (*S*) for chlorofluorocarbons (CFCs) from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Acronym	Formula	Data <sup>1</sup>	T/K	Wn. range /cm <sup>-1</sup>	$S^2$	Reference	Database <sup>3</sup>
Trichlorofluoromethane	75-69-4	CFC-11	CCl <sub>3</sub> F	Е	295	820 - 1120	9.3	[Orkin et al., 2003]	
				E	296	650 - 1500	9.3	[Sihra et al., 2001]	
				E				[Naik et al., 2000]	
				E				[Ninomiya et al., 2000]	
				E	296	810 - 1120	9.5	[Varanasi-priv.com., 2000]	H
				A				[Good et al., 1998]	
				E	298	800 - 1120	9.4	[Heathfield et al., 1998]	G
				E	296	810 - 1120	9.0	[Christidis et al., 1997]	G
				E	296	700 - 1500	9.8	[Imasu et al., 1995]	
				E	296	810 - 1120	9.5	[Li and Varanasi, 1994]	G
				E	293	800 - 1120	9.2	[McDaniel et al., 1991]	
				E		810 - 1120	8.9	[Fisher et al., 1990]	
				E		800 - 1120	9.8	[Varanasi and Chudamani, 1988a]	
				E		800 - 1120	8.4	[ <i>Massie et al.</i> , 1985]	
				E		800 - 1120	10.3	[Kagann et al., 1983]	
				E		800 - 1120	8.9	[Nanes et al., 1980]	
				E		800 - 1120	8.9	[Varanasi and Ko, 1977]	
Dichlorodifluoromethane	75-71-8	CFC-12	$CCl_2F_2$	E	295	850 - 1190	13.5	[Myhre et al., 2006]	
				E	296	640 - 1200	12.2	[Hurley-priv.com., 2003]	G
				E	295	850 - 1190	12.9	[Orkin et al., 2003]	
				E	296	500 - 1500	12.2	[Sihra et al., 2001]	
				E	296	850 - 1200	13.6	[Varanasi-priv.com., 2000]	H
				A				[Good et al., 1998]	
				E	296	850 - 1200	13.6	[Varanasi and Nemtchinov, 1994]	G
				E	287	850 - 1190	13.5	[Clerbaux et al., 1993]	G
				E	293	850 - 1190	12.6	[McDaniel et al., 1991]	
				E	296	850 - 1190	12.1	[Fisher et al., 1990]	
				E	300	850 - 1190	13.4	[Varanasi and Chudamani, 1988a]	
				E	298	800 - 1200	12.7	[Vanthanh et al., 1986]	

				E E E E	296 296 300	850 - 1190 850 - 1190 850 - 1190	13.3 13.6 12.9	[Massie et al., 1985] [Kagann et al., 1983] [Varanasi and Ko, 1977] [Morcillo et al., 1966]	
Chlorotrifluoromethane	75-72-9	CFC-13	CClF <sub>3</sub>	E	293	765 - 1235	14.8	[McDaniel et al., 1991]	Н
				E		1050 - 1291	16.3	[Varanasi and Chudamani, 1988b]	
				E		755 - 1291	16.1	[Golden et al., 1978]	
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	E	283	600 - 1250	13.7	[Le Bris et al., 2011]	
				E	293	780 - 1232	12.7	[McDaniel et al., 1991]	Н
				E		618 - 1397	12.7	[Fisher et al., 1990]	
				E		780 - 1235	19.4	[Rogers and Stephens, 1988]	
				E		780 - 1235	14.1	[Varanasi and Chudamani, 1988b]	
1,2-Dichloro-1,1,2,2- tetrafluoroethane	76-14-2	CFC-114	CClF <sub>2</sub> CClF <sub>2</sub>	E	293	815 - 1285	15.2	[McDaniel et al., 1991]	Н
				E		555 - 1397	15.4	[Fisher et al., 1990]	
				E		820 - 1310	23.9	[Rogers and Stephens, 1988]	
				E		820 - 1310	15.8	[Varanasi and Chudamani, 1988b]	
				E		1025 - 1310	12.0	[ <i>Massie et al.</i> , 1985]	
1-Chloro-1,1,2,2,2-pentafluoroethane	76-15-3	CFC-115	CClF <sub>2</sub> CF <sub>3</sub>	E	293	955 - 1260	12.1	[McDaniel et al., 1991]	H
				Е		618 - 1397	17.4	[Fisher et al., 1990]	

<sup>4331</sup> Type of data: E, Experimental; A, Ab initio.

 $^{2}$  Integrated absorption cross-section in units of  $10^{-17}$  cm $^{2}$  molecule $^{-1}$  cm $^{-1}$  for the wavenumber interval specified.

<sup>4333 &</sup>lt;sup>3</sup> Database: H, HITRAN 2008; G, GEISA 2009

**Table 3.** Lifetimes, radiative efficiencies and direct GWPs (relative to CO<sub>2</sub>) for chlorofluorocarbons (CFCs). Compounds in bold either have significant current atmospheric concentrations or a clear potential for future emissions. Recommended RE and GWP(100) values are indicated in bold. Lifetimes are from *WMO* [2011].

			Radiat	ive Efficiency (V	GWP(100)			
Acronym	Formula	Lifetime (yr)	AR4	This study – const. profile	This study – lifetime corr.	AR4	This study – lifetime corr.	
CFC-11	CCl <sub>3</sub> F	45.0	0.25	0.28	0.26	4,750	4,660	
CFC-12	$CCl_2F_2$	100.0	0.32	0.33	0.32	10,900	10,200	
CFC-13	CClF <sub>3</sub>	640.0	0.25	0.26	0.25	14,400	13,900	
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	85.0	0.30	0.31	0.30	6,130	5,820	
CFC-114	CClF <sub>2</sub> CClF <sub>2</sub>	190.0	0.31	0.32	0.31	10,000	8,590	
CFC-115	CClF <sub>2</sub> CF <sub>3</sub>	1,020.0	0.18	0.21	0.20	7,370	7,670	

Table 4. Integrated absorption cross-sections (*S*) for hydrochlorofluorocarbons (HCFCs) from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Acronym	Formula	Data <sup>1</sup>	T/K	Wn. range /cm <sup>-1</sup>	$S^2$	Reference	Database
Dichlorofluoromethane	75-43-4	HCFC-21	CHCl <sub>2</sub> F	Е	296	600 - 1500	7.4	[Sihra et al., 2001]	
	, , , , , ,		J-1-2-2-	E	296	450 - 2000	6.8	[ <i>Christidis et al.</i> , 1997]	
				E	296	785 - 840	2.7	[ <i>Massie et al.</i> , 1985]	Н
Chlorodifluoromethane	75-45-6	HCFC-22	CHClF <sub>2</sub>	E	295	750 - 1380	10.0	[Orkin et al., 2003]	
			2	E	296	700 - 1400	10.1	[Sihra et al., 2001]	
				E	293	775 - 1375	10.1	[Ballard et al., 2000b]	G
				E	273	750 - 1400	10.2	[Highwood and Shine, 2000]	
				E				[Naik et al., 2000]	
				A		600 - 1500	11.6	[Papasavva et al., 1997]	
				E	296	765 - 1390	10.2	[Pinnock et al., 1995]	G
				E	296	735 - 1380	9.7	[Anastasi et al., 1994]	
				E	296	1070 - 1195	6.9	[ <i>Varanasi et al.</i> , 1994]	G
				E	287	765 - 1380	10.3	[ <i>Clerbaux et al.</i> , 1993]	Н
				E	293	755 - 1390	10.3	[Cappellani and Restelli, 1992]	
				E	293	775 - 1375	9.0	[ <i>McDaniel et al.</i> , 1991]	
				E		775 - 1397	9.5	[Fisher et al., 1990]	
				E		775 - 1170	9.4	[Varanasi and Chudamani, 1988b]	
1,1,2-Trichloro-2,2- lifluoroethane	354-21-2	HCFC-122	CHCl <sub>2</sub> CF <sub>2</sub> Cl	E	295	560 - 1360	10.4	[Orkin et al., 2003]	
,1,2-Trichloro-1,2- lifluoroethane	354-15-4	HCFC-122a	CHFClCFCl <sub>2</sub>	E	295	590 - 1380	9.9	[Orkin et al., 2003]	
2,2-Dichloro-1,1,1- rifluoroethane	306-83-2	HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	E	295	480 - 1430	13.1	[Orkin et al., 2003]	
				E E	296	700 - 1500	11.9	[Sihra et al., 2001] [Naik et al., 2000]	
				A		600 - 1500	14.1	[Papasavva et al., 1997]	
				E E	296	700 - 1400 480 - 1430	12.0 12.7	[Pinnock et al., 1995] [Olliff and Fischer, 1994]	G

				E	287	740 - 1450	12.9	[Clerbaux et al., 1993]	Н
				E	293	648 - 1440	12.7	[Cappellani and Restelli, 1992]	
				Е		649 - 1307	10.6	[Fisher et al., 1990]	
1,2-Dichloro-1,1,2- trifluoroethane	354-23-4	HCFC-123a	CHClFCF <sub>2</sub> Cl	E	295	450 - 1400	12.3	[Orkin et al., 2003]	
2-Chloro-1,1,1,2-	2837-89-	HCFC-124	CHClFCF <sub>3</sub>	E	296	700 - 1500	13.4	[Sihra et al., 2001]	
tetrafluoroethane	0	11C1 C-124	CHCh Cr3		290	700 - 1300	13.4	· -	
				E		500 4 <b>5</b> 00	4.5.5	[Naik et al., 2000]	
				A	20.6	600 - 1500	15.7	[ <i>Papasavva et al.</i> , 1997]	
				E	296	670 - 1435	13.8	[Pinnock et al., 1995]	G
				E E	287	675 - 1430	14.4	[Clerbaux et al., 1993]	Н
1.1 Diablems 1.2	1842-05-			E		440 - 1420	15.0	[Fisher et al., 1990]	
1,1-Dichloro-1,2-difluoroethane	3	HCFC-132c	CH <sub>2</sub> FCFCl <sub>2</sub>	E	295	425 - 1490	8.4	[Orkin et al., 2003]	
1,1-Dichloro-1- fluoroethane	1717-00- 6	HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	E	283	570 - 3100	8.1	[Le Bris et al., 2012]	
1100100111111	· ·			Е	295	540 - 1540	8.0	[Orkin et al., 2003]	
				E	296	700 - 1500	7.1	[Sihra et al., 2001]	
				E				[Naik et al., 2000]	
				A		600 - 1500	9.1	[Papasavva et al., 1997]	
				E	296	700 - 1500	8.3	[Imasu et al., 1995]	
				E	296	700 - 1470	7.2	[ <i>Pinnock et al.</i> , 1995]	G
				E		540 - 1480	7.6	[Olliff and Fischer, 1994]	
				E	287	710 - 1470	7.8	[Clerbaux et al., 1993]	Н
				E		555 - 1420	7.1	[Fisher et al., 1990]	
1-Chloro-1,1- difluoroethane	75-68-3	HCFC-142b	CH <sub>3</sub> CClF <sub>2</sub>	E	283	650 - 3500	10.8	[Le Bris and Strong, 2010]	
				Е	296	700 - 1500	9.6	[Sihra et al., 2001]	
				E				[Naik et al., 2000]	
				A		600 - 1500	11.8	[Papasavva et al., 1997]	
				E	296	650 - 1425	10.1	[ <i>Pinnock et al.</i> , 1995]	G
				E	287	650 - 1469	11.1	[Clerbaux et al., 1993]	Н
				E	293	647 - 1485	10.7	[Cappellani and Restelli, 1992]	
				E		649 - 1397	9.6	[Fisher et al., 1990]	
3,3-Dichloro-1,1,1,2,2-	422-56-0	HCFC-	CHCl <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	E	296	700 - 1400	18.0	[Sihra et al., 2001]	

pentafluoropropane		225ca							
				E				[Naik et al., 2000]	
				E	296	700 - 1400	14.6	[ <i>Pinnock et al.</i> , 1995]	
				E	287	695 - 1420	17.7	[Clerbaux et al., 1993]	H
1,3-Dichloro-1,1,2,2,3- pentafluoropropane	507-55-1	HCFC- 225cb	CHClFCF <sub>2</sub> CClF <sub>2</sub>	E	296	700 - 1400	15.2	[Sihra et al., 2001]	
				E				[Naik et al., 2000]	
				E	296	700 - 1500	16.6	[Imasu et al., 1995]	
				E	296	700 - 1400	15.1	[ <i>Pinnock et al.</i> , 1995]	
				E	287	715 - 1375	15.6	[Clerbaux et al., 1993]	H
(E)-1-Chloro-3,3,3- trifluoroprop-1-ene	102687- 65-0		trans-CF <sub>3</sub> CH=CHCl	Е	295	600 - 1800	17.4	[Andersen et al., 2008]	

<sup>4344</sup> Type of data: E, Experimental; A, Ab initio.

<sup>4345</sup>  $^{2}$  Integrated absorption cross-section in units of  $10^{-17}$  cm $^{2}$  molecule $^{-1}$  cm $^{-1}$  for the wavenumber interval specified.

<sup>4346 &</sup>lt;sup>3</sup> Database: H, HITRAN 2008; G, GEISA 2009.

**Table 5.** Lifetimes, radiative efficiencies (RE) and direct GWPs (relative to CO<sub>2</sub>) for hydrochlorofluorocarbons (HCFCs). Compounds in bold either have significant current atmospheric concentrations or a clear potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from *WMO* [2011] except those in italic (see text for details).

			Radiat	ive Efficiency (V	GWP 100-yr		
Acronym /	Formula	Lifetime	AR4	This study –	This study	AR4	This study
name		(yr)		const.	– lifetime		– lifetime
				profile	corr.		corr.
HCFC-21	CHCl <sub>2</sub> F	1.7	0.14	0.18	0.15	151	148
HCFC-22	CHClF <sub>2</sub>	11.9	0.20	0.22	0.21	1,810	1,760
HCFC-122	CHCl <sub>2</sub> CF <sub>2</sub> Cl	1.0		0.23	0.17		59
HCFC-122a	CHFClCFCl <sub>2</sub>	3.4		0.23	0.21		258
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	1.3	0.14	0.19	0.15	77	79
HCFC-123a	CHClFCF <sub>2</sub> Cl	4.0		0.25	0.23		370
HCFC-124	CHClFCF <sub>3</sub>	5.9	0.22	0.21	0.20	609	527
HCFC-132c	CH <sub>2</sub> FCFCl <sub>2</sub>	4.3		0.19	0.17		338
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	9.2	0.14	0.17	0.16	725	782
HCFC-142b	CH <sub>3</sub> CClF <sub>2</sub>	17.2	0.20	0.19	0.19	2,310	1,980
HCFC-225ca	CHCl <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	1.9	0.20	0.26	0.22	122	127
HCFC-225cb	CHClFCF <sub>2</sub> CClF <sub>2</sub>	5.9	0.32	0.32	0.29	595	525
(E)-1-Chloro-							
3,3,3-	trans-	26.0 days		0.22	0.04		1
trifluoroprop-	CF <sub>3</sub> CH=CHCl	26.0 days		0.22	0.04		1
1-ene							

**Table 6.** Integrated absorption cross-sections (*S*) for hydrofluorocarbons (HFCs) from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Acronym	Formula	Data <sup>1</sup>	T/K	Wn. range /cm <sup>-1</sup>	$S^2$	Reference	Database <sup>3</sup>
Trifluoromethane	75-46-7	HFC-23	CHF <sub>3</sub>	A	298			[Blowers and Hollingshead, 2009]	
				E	296	400 - 1500	11.8	[Gohar et al., 2004]	
				E	296	700 - 1500	11.7	[Sihra et al., 2001]	
				E	253	655 - 1415	10.1	[Highwood and Shine, 2000]	
				E				[Naik et al., 2000]	
				Α		600 - 1500	12.9	[Papasavva et al., 1997]	
				E	296	700 - 1400	12.7	[Pinnock et al., 1995]	
Difluoromethane	75-10-5	HFC-32	$CH_2F_2$	A	298			[Blowers and Hollingshead, 2009]	
				E	296	400 - 1550	5.8	[Gohar et al., 2004]	
				E	295	450 - 1480	5.9	[Orkin et al., 2003]	
				E	296	700 - 1500	5.7	[Sihra et al., 2001]	
				E	253	450 - 1475	5.6	[Highwood and Shine, 2000]	
				E				[Naik et al., 2000]	
				A		600 - 1500	6.1	[Papasavva et al., 1997]	
				E	297	995 - 1475	5.2	[Smith et al., 1996]	H
				E	296	700 - 1400	6.3	[Pinnock et al., 1995]	G
				E	297	995 - 1475	5.2	[M.S.F./R.A.L.]	G
Fluoromethane	593-53-3	HFC-41	CH <sub>3</sub> F	A	298			[Blowers and Hollingshead, 2009]	
				E	296	700 - 1400	1.5	[Sihra et al., 2001]	
				A		600 - 1500	1.7	[Papasavva et al., 1997]	
				E	296	700 - 1400	1.8	[Pinnock et al., 1995]	
1,1,1,2,2-Pentafluoroethane	354-33-6	HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	E	296	700 - 1480	15.5	[Young et al., 2009b]	
			2 3	E	295	460 - 1480	16.6	[Orkin et al., 2003]	
				E	296	700 - 1500	16.5	[Sihra et al., 2001]	
				E	293	550 - 1480	17.2	[Di Lonardo and Masciarelli, 2000]	G

				Е	253	550 - 1480	16.6	[Highwood and Shine, 2000]	
				E				[Naik et al., 2000]	
				Ā				[Good et al., 1998]	
				A		600 - 1500	16.8	[Papasavva et al., 1997]	
				E	296	700 - 1500	17.0	[Imasu et al., 1995]	
				E	296	700 - 1400	16.1	[Pinnock et al., 1995]	G
				E		460 - 1480	16.0	[Olliff and Fischer, 1994]	
				E	287	700 - 1465	16.1	[Clerbaux et al., 1993]	G
				Ē		500 - 1307	14.5	[Fisher et al., 1990]	_
1,1,2,2-Tetrafluoroethane	359-35-3	HFC-134	CHF <sub>2</sub> CHF <sub>2</sub>	E	296	450 - 1550	10.5	[Sihra et al., 2001]	
, , ,			- 2- 2	E				[Naik et al., 2000]	
				Ā				[Good et al., 1998]	
				E	296	450 - 2000	9.7	[Christidis et al., 1997]	
				A		600 - 1500	10.6	[Papasavva et al., 1997]	
				E	297	600 - 1700	11.4	[Smith et al., 1998]	Н
				E	296	450 - 1420	10.5	[Hurley-priv.com., 2003]	G
				E	297	600 - 1700	11.4	[M.S.F./R.A.L.]	G
1,1,1,2-Tetrafluoroethane	811-97-2	HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	E	296	250 - 2000	13.2	[Forster et al., 2005]	
, , ,			- 2 - 3	E	296	300 - 1550	13.1	[Gohar et al., 2004]	
				E	296	1035 - 1340	11.4	[Nemtchinov and Varanasi, 2004]	Н
				E	296	700 - 1500	12.4	[Hurley-priv.com., 2003]	G
				E	295	490 - 1550	13.6	[Orkin et al., 2003]	
				E	296	700 - 1550	12.4	[Sihra et al., 2001]	
				E	253	75 - 1540	13.6	[Highwood and Shine, 2000]	
				E				[Naik et al., 2000]	
				A		600 - 1500	13.6	[Papasavva et al., 1997]	
				E		600 - 1448	13.5	[Newnham et al., 1996]	
				E	296	700 - 1500	13.5	[Imasu et al., 1995]	
				E	296	700 - 1400	13.1	[Pinnock et al., 1995]	
				E		490 - 1510	13.4	[Olliff and Fischer, 1994]	
				E	287	815 - 1485	12.6	[Clerbaux et al., 1993]	Н
				Е	293	610 - 1490	13.2	[Cappellani and Restelli, 1992]	
				E		618 - 1420	12.2	[Fisher et al., 1990]	

					20.6	600 1600	10.5		
1.1.2 T.'C	120 66 0	HEC 142	CH ECHE	E	296	600 - 1600	12.5	[M.S.F./R.A.L.]	G
1,1,2-Trifluoroethane	430-66-0	HFC-143	CH <sub>2</sub> FCHF <sub>2</sub>	E	296	700 - 1550	7.1	[Sihra et al., 2001]	
				E		(00 1500	7.2	[Naik et al., 2000]	
				A	20.6	600 - 1500	7.2	[Papasavva et al., 1997]	
				E	296	700 - 1400	6.9	[Pinnock et al., 1995]	
				E	287	700 - 1500	6.9	[Clerbaux and Colin, 1994]	
				E	296	400 - 1500	7.6	[M.S.F./R.A.L.]	G
1,1,1-Trifluoroethane	420-46-2	HFC-143a	$CH_3CF_3$	E	296	700 - 1500	12.7	[Sihra et al., 2001]	
				Е	293	797 - 1460	12.8	[Di Lonardo and	G
				E	293	797 - 1400	12.0	Masciarelli, 2000]	U
				Е	253	800 - 1470	12.0	[Highwood and Shine,	
				E	233	600 - 1470	12.0	2000]	
				E				[Naik et al., 2000]	
				A				[Good et al., 1998]	
				E	297	700 - 1500	13.6	[Smith et al., 1998]	H, G
				A		600 - 1500	13.7	[Papasavva et al., 1997]	
				E	296	500 - 1500	12.3	[ <i>Pinnock et al.</i> , 1995]	G
				E	293	796 - 1474	12.8	[Olliff and Fischer, 1994]	
				E		555 - 1535	12.7	[Fisher et al., 1990]	
1,2-Difluoroethane	624-72-6	HFC-152	CH <sub>2</sub> FCH <sub>2</sub> F	A		600 - 1500	4.2	[Papasavva et al., 1997]	
				E		810 - 1510	3.7	[Wallington et al., 1994a]	
1,1-Difluoroethane	75-37-6	HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	E	296	700 - 1500	6.8	[Sihra et al., 2001]	
1,1 Dillusi sediane	75 57 6	111 0 1024	C113C111 2					[Highwood and Shine,	
				E	253	830 - 1500	6.7	2000]	
				E				[Naik et al., 2000]	
				E	293	840 - 1490	6.9	[Vander Auwera, 2000]	G
				A	2,5	600 - 1500	7.1	[ <i>Papasavva et al.</i> , 1997]	Ü
				E	296	700 - 1400	7.4	[Pinnock et al., 1995]	G
				E	287	840 - 1490	6.9	[Clerbaux et al., 1993]	Н
								[Cappellani and Restelli,	••
				Е	293	830 - 1485	6.9	1992]	
				E		775 - 1420	6.1	[Fisher et al., 1990]	
Fluoroethane	353-36-6	HFC-161	CH <sub>3</sub> CH <sub>2</sub> F	E	296	450 - 1600	2.4	[Sihra et al., 2001]	
				E				[Naik et al., 2000]	
				E	296	450 - 2000	2.2	[Christidis et al., 1997]	

				A		600 - 1500	2.4	[Papasavva et al., 1997]
1,1,1,2,2,3,3-Heptafluoropropane	2252-84-8	HFC-227ca	CF <sub>3</sub> CF <sub>2</sub> CHF <sub>2</sub>	E	296	450 - 1550	19.9	[Sihra et al., 2001]
				E	296	450 - 2000	20.9	[Christidis et al., 1997]
1,1,1,2,3,3,3-Heptafluoropropane	431-89-0	HFC-227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	E	296	400 - 1550	23.3	[Gohar et al., 2004]
				E	296	700 - 1500	22.3	[Sihra et al., 2001]
				E				[Naik et al., 2000]
				E	296	700 - 1400	23.0	[ <i>Pinnock et al.</i> , 1995]
1,1,1,2,2,3-Hexafluoropropane	677-56-5	HFC- 236cb	CH <sub>2</sub> FCF <sub>2</sub> CF <sub>3</sub>	E	296	450 - 1550	17.0	[Sihra et al., 2001]
				E	296	450 - 2000	16.5	[Christidis et al., 1997]
1,1,1,2,3,3-Hexafluoropropane	431-63-0	HFC-236ea	CHF <sub>2</sub> CHFCF <sub>3</sub>	E	296	680 - 1320	17.2	[Gierczak et al., 1996]
1,1,1,3,3,3-Hexafluoropropane	690-39-1	HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	E	296	700 - 1500	22.8	[Sihra et al., 2001]
• •				E				[Naik et al., 2000]
				E	296	600 - 1350	22.6	[Gierczak et al., 1996]
				E	296	700 - 1400	23.3	[Pinnock et al., 1995]
1,1,1,2,2-Pentafluoropropane	1814-88-6	HFC- 245cb	CF <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	E	295	472 - 1490	18.1	[Orkin et al., 2003]
				E	296	450 - 1550	16.5	[Sihra et al., 2001]
				E	296	450 - 2000	15.8	[Christidis et al., 1997]
1,1,2,3,3-Pentafluoropropane	24270-66- 4	HFC-245ea	CHF <sub>2</sub> CHFCHF <sub>2</sub>	E	298	500 - 4000		[Rajakumar et al., 2006]
		HFC-						
1,1,1,2,3-Pentafluoropropane	431-31-2	245eb	CH <sub>2</sub> FCHFCF <sub>3</sub>	E	298	500 - 4000		[Rajakumar et al., 2006]
1,1,1,3,3-Pentafluoropropane	460-73-1	HFC-245fa	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	E	295	455 - 1485	19.8	[Orkin et al., 2003]
-,-,-,-,			223	E	296	640 - 1500	19.6	[Sihra et al., 2001]
				E				[Jain et al., 2000]
				Ē				[Naik et al., 2000]
				E		450 - 2325	20.6	[Ko et al., 1999]
1,1,1-Trifluoropropane	421-07-8	HFC-263fb	CH <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	Ē	298	500 - 4000		[Rajakumar et al., 2006]
2,2-Difluoropropane	420-45-1	HFC-272ca	CH <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	E	296	700 - 1500	5.7	[Sihra et al., 2001]
,			5- 2- 5	E	296	700 - 1400	5.6	[Pinnock et al., 1995]
1,1,1,2,2,3,3,4,4-Nonafluorobutane	375-17-7	HFC-329p	CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	E	296	700 - 1435	22.2	[Young et al., 2009b]
1,1,1,3,3-Pentafluorobutane	406-58-6	HFC- 365mfc	CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	E	296	665 - 1500	18.8	[Inoue et al., 2008]
				E				[Naik et al., 2000]
				E	298	600 - 1500		[Barry et al., 1997]
1,1-Difluoroethene	75-38-7	HFC-	$CH_2=CF_2$	E	296	745 - 1820	10.1	[Baasandorj et al., 2010]
		-	2 - 2					. J ,

Fluoroethene	75-02-5	1132a HFC-1141	CH <sub>2</sub> =CHF	Е	296	770 - 1740	4.8	[Baasandorj et al., 2010]
			_	E		770 - 1740	4.5	[Stoppa et al., 2009]
(Z)-1,2,3,3,3-Pentafluoroprop-1-ene	5528-43-8	(Z)-HFC- 1225ye	CF <sub>3</sub> CF=CHF(Z)	E	296	706 - 1812	19.3	[Papadimitriou et al., 2008a]
		•		E	296	710 - 2000	18.3	[Hurley et al., 2007]
(E)-1,2,3,3,3-Pentafluoroprop-1- ene	5595-10-8	(E)-HFC- 1225ye	CF <sub>3</sub> CF=CHF(E)	E	296	810 - 2000	18.4	[Hurley et al., 2007]
(Z)-1,3,3,3-Tetrafluoroprop-1-ene	29118-25- 0	(Z)-HFC- 1234ze	CF <sub>3</sub> CH=CHF(Z)	Е	296	720 - 2000	16.8	[Nilsson et al., 2009]
2,3,3,3-Tetrafluoroprop-1-ene	754-12-1	HFC- 1234yf	CF <sub>3</sub> CF=CH <sub>2</sub>	E	295	500 - 1900	17.2	[Orkin et al., 2010]
		•		E	296	540 - 1810	16.9	[Papadimitriou et al., 2008a]
				E	296	863 - 1745	16.1	[Nielsen et al., 2007]
(E)-1,3,3,3-Tetrafluoroprop-1-ene	1645-83-6	(E)-HFC- 1234ze	trans-CF <sub>3</sub> CH=CHF	E	295	500 - 1900	19.9	[Orkin et al., 2010]
				E	296	680 - 2000	19.4	[Søndergaard et al., 2007]
(Z)-1,1,1,4,4,4-Hexafluorobut-2- ene	692-49-9	(Z)-HFC- 1336	CF <sub>3</sub> CH=CHCF <sub>3</sub> (Z)	E	296	1100 - 1500	27.8	[Baasandorj et al., 2011]
3,3,3-Trifluoroprop-1-ene	677-21-4	HFC- 1243zf	CF <sub>3</sub> CH=CH <sub>2</sub>	E	298	650 - 2000	12.5	[Andersen et al., 2012a]
3,3,4,4,4-Pentafluorobut-1-ene	374-27-6	HFC- 1345zfc	$C_2F_5CH=CH_2$	E	298	650 - 2000	13.6	[Andersen et al., 2012a]
3,3,4,4,5,5,6,6,6-Nonafluorohex-1- ene	19430-93- 4		C <sub>4</sub> F <sub>9</sub> CH=CH <sub>2</sub>	E	298	650 - 2000	24.1	[Andersen et al., 2012a]
3,3,4,4,5,5,6,6,7,7,8,8,8- Tridecafluorooct-1-ene	25291-17- 2		$C_6F_{13}CH=CH_2$	E	298	650 - 2000	29.6	[Andersen et al., 2012a]
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10- Heptadecafluorodec-1-ene	21652-58- 4		$C_8F_{17}CH=CH_2$	E	298	650 - 2000	33.7	[Andersen et al., 2012a]

<sup>4357</sup> Type of data: E, Experimental; A, Ab initio.

<sup>4358</sup>  $^{2}$  Integrated absorption cross-section in units of  $10^{-17}$  cm $^{2}$  molecule $^{-1}$  cm $^{-1}$  for the wavenumber interval specified.

<sup>4359 &</sup>lt;sup>3</sup> Database: H, HITRAN 2008; G, GEISA 2009.

**Table 7.** Lifetimes, radiative efficiencies and direct GWPs (relative to CO<sub>2</sub>) for hydrofluorocarbons (HFCs). Compounds in bold either have significant current atmospheric concentrations or a clear potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from *WMO* [2011] except those in italic (see text for details). RE and GWP values in italic are based on previous publications (see text for details).

				tive Efficie m <sup>-2</sup> ppb <sup>-1</sup>		GWP 100-yr	
Acronym / name	Formula	Lifetime	AR4	This	This	AR4	This
		(yr)		study –	study –		study –
				const.	lifetime		lifetime
				profile	corr.		corr.
HFC-23	$CHF_3$	222.0	0.19	0.18	0.18	14,800	12,400
HFC-32	$CH_2F_2$	5.2	0.11	0.12	0.11	675	677
HFC-41	CH <sub>3</sub> F	2.8	0.02	0.03	0.02	92	116
HFC-125	$CHF_2CF_3$	28.2	0.23	0.23	0.23	3,500	3,170
HFC-134	$CHF_2CHF_2$	9.7	0.18	0.20	0.19	1,100	1,120
HFC-134a	$CH_2FCF_3$	13.4	0.16	0.17	0.16	1,430	1,300
HFC-143	$CH_2FCHF_2$	3.5	0.13	0.14	0.13	353	328
HFC-143a	CH <sub>3</sub> CF <sub>3</sub>	47.1	0.13	0.16	0.16	4,470	4,800
HFC-152	CH <sub>2</sub> FCH <sub>2</sub> F	0.4	0.09	0.08	0.04	53	16
HFC-152a	$CH_3CHF_2$	1.5	0.09	0.12	0.10	124	138
HFC-161	CH <sub>3</sub> CH <sub>2</sub> F	66.0 days	0.03	0.04	0.02	12	4
HFC-227ca	CF <sub>3</sub> CF <sub>2</sub> CHF <sub>2</sub>	28.2		0.27	0.27		2,640
HFC-227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	38.9	0.26	0.26	0.26	3,220	3,350
HFC-236cb	CH <sub>2</sub> FCF <sub>2</sub> CF <sub>3</sub>	13.1	0.23	0.24	0.23	1,340	1,210
HFC-236ea	CHF <sub>2</sub> CHFCF <sub>3</sub>	11.0	0.30			1,370	1,330
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	242.0	0.28	0.24	0.24	9,810	8,060
HFC-245ca	CH <sub>2</sub> FCF <sub>2</sub> CHF <sub>2</sub>	6.5	0.23		0.24	693	716
HFC-245cb	CF <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	47.1		0.25	0.24		4,620
HFC-245ea	CHF <sub>2</sub> CHFCHF <sub>2</sub>	3.2		0.18	0.16		235
HFC-245eb	CH <sub>2</sub> FCHFCF <sub>3</sub>	3.1		0.23	0.20		290
HFC-245fa	CHF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	7.7	0.28	0.26	0.24	1,030	858
HFC-263fb	CH <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	1.2		0.13	0.10		76
HFC-272ca	CH <sub>3</sub> CF <sub>2</sub> CH <sub>3</sub>	2.6		0.08	0.07		144
HFC-329p	CHF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	28.4		0.31	0.31		2,360
HFC-365mfc	CH <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	8.7	0.21	0.23	0.22	794	804
HFC-43-10mee	CF <sub>3</sub> CHFCHFCF <sub>2</sub> CF <sub>3</sub>	16.1	0.40		0.42	1,640	1,650
HFC-1132a	$CH_2=CF_2$	4.0 days		0.10	0.00		0
HFC-1141	CH <sub>2</sub> =CHF	2.1 days		0.09	0.00		0
(Z)-HFC-1225ye	$CF_3CF=CHF(Z)$	8.5 days		0.26	0.02		0
(E)-HFC-1225ye	$CF_3CF=CHF(E)$	4.9 days		0.25	0.01		0
(Z)-HFC-1234ze	$CF_3CH=CHF(Z)$	10.0 days		0.20	0.02		0
HFC-1234yf	CF <sub>3</sub> CF=CH <sub>2</sub>	10.5 days		0.23	0.02		0
(E)-HFC-1234ze	trans-CF <sub>3</sub> CH=CHF	16.4 days		0.28	0.04		1
(Z)-HFC-1336	$CF_3CH=CHCF_3(Z)$	22.0 days		0.42	0.07		2
HFC-1243zf	CF <sub>3</sub> CH=CH <sub>2</sub>	7.0 days		0.17	0.01		0
HFC-1345zfc	$C_2F_5CH=CH_2$	7.6 days		0.19	0.01		0
3,3,4,4,5,5,6,6,6-	$C_4F_9CH=CH_2$	7.6 days		0.35	0.03		Λ
Nonafluorohex-1-ene	$C_4\Gamma_9C\Pi-C\Pi_2$	7.6 days		0.55	0.03		0
3,3,4,4,5,5,6,6,7,7,8,8,							
8-Tridecafluorooct-1-	$C_6F_{13}CH=CH_2$	7.6 days		0.39	0.03		0
ene							
3,3,4,4,5,5,6,6,7,7,8,8,	$C_8F_{17}CH=CH_2$	7.6 days		0.44	0.03		0

4368 **Table 8.** Integrated absorption cross-sections (*S*) for chlorocarbons and hydrochlorocarbons from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Trivial name	Formula	Data <sup>1</sup>	T/K	Wn. range /cm <sup>-1</sup>	$S^2$	Reference	Database <sup>3</sup>
1,1,1-Trichloroethane	71-55-6	Methyl chloroform	CH <sub>3</sub> CCl <sub>3</sub>	Е	295	480 - 1490	5.1	[Orkin et al., 2003]	_
				E	296	700 - 1500	5.0	[Imasu et al., 1995]	
				E		669 - 1397	4.5	[Fisher et al., 1990]	
Perchloromethane, tetrachloromethane	56-23-5	Carbon tetrachloride	CCl <sub>4</sub>	E	297	750 - 812	6.2	[Nemtchinov and Varanasi, 2003]	G
				E	297	750 - 812	6.2	[Varanasi-priv.com., 2000]	Н
				E	298	730 - 825	5.9	[ <i>Orlando et al.</i> , 1992]	
				E	298	773 - 802	3.7	[Brown et al., 1987]	
				E	298	786 - 806	3.6	[ <i>Massie et al.</i> , 1985]	
				E		616 - 934	4.5	[Fisher et al., 1990]	
Chloromethane	74-87-3	Methyl chloride	CH <sub>3</sub> Cl	E		661 - 1646	1.4	[ <i>Grossman et al.</i> , 1997]	
Dichloromethane	75-09-2	Methylene chloride	$CH_2Cl_2$	A		250 - 3300	3.3	[Bera et al., 2009]	
Trichloromethane	67-66-3	Chloroform	CHCl <sub>3</sub>	E	295	540 - 1600	5.6	[McPheat and Duxbury, 2000]	
1,2-Dichloroethane	107-06-2		CH <sub>2</sub> ClCH <sub>2</sub> Cl	Е	293	600 - 1700	2.1	[Vander Auwera, 2000]	

<sup>4370 &</sup>lt;sup>1</sup> Type of data: E, Experimental; A, Ab initio.

<sup>4371 &</sup>lt;sup>2</sup> Integrated absorption cross-section in units of 10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> for the wavenumber interval specified.

<sup>4372 &</sup>lt;sup>3</sup> Database: H, HITRAN 2008; G, GEISA 2009.

Table 9. Lifetimes, radiative efficiencies and direct GWPs (relative to CO<sub>2</sub>) for chlorocarbons and hydrochlorocarbons. Compounds in bold either have significant current atmospheric concentrations or a clear potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from *WMO* [2011].

			Radiati	ve Efficiency  1)	GW	TP 100-yr	
Acronym / name	Formula	Lifetime (yr)	AR4	This study – const.	This study – lifetime	AR4	This study – lifetime
				profile	corr.		corr.
Methyl chloroform	CH <sub>3</sub> CCl <sub>3</sub>	5.0	0.06	0.08	0.07	146	160
Carbon tetrachloride	$CCl_4$	26.0	0.13	0.18	0.17	1,400	1,730
Methyl chloride	CH <sub>3</sub> Cl	1.0	0.01			13	12
Methylene chloride	$CH_2Cl_2$	0.4	0.03			9	9
Chloroform	CHCl <sub>3</sub>	0.4	0.11	0.14	0.08	31	16
1,2-Dichloroethane	CH <sub>2</sub> ClCH <sub>2</sub> Cl	65.0 days		0.02	0.01		1

**Table 10.** Integrated absorption cross-sections (*S*) for bromocarbons, hydrobromocarbons and halons from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Acronym / trivial name	Formula	Data <sup>1</sup>	T/K	Wn. range /cm <sup>-</sup>	$S^2$	Reference	Database <sup>3</sup>
Bromomethane	74-83-9	Methyl bromide	CH <sub>3</sub> Br	Е	296	450 - 2000	0.7	[Sihra et al., 2001]	
		•		E	296	450 - 2000	0.8	[Christidis et al., 1997]	
				E		550 - 1600	1.2	[ <i>Grossman et al.</i> , 1997]	
				E				[ <i>Graner</i> , 1981]	
Dibromomethane	74-95-3	Methylene bromide	$CH_2Br_2$	E	296	450 - 2000	2.1	[Sihra et al., 2001]	
				E	296	450 - 2000	2.0	[Christidis et al., 1997]	
Bromodifluoromethane	1511-62-2	Halon-1201	$CHBrF_2$	E,A	298	530 - 1460	10.2	[Charmet et al., 2010]	
				E	295	530 - 1400	10.1	[Orkin et al., 2003]	
				E	296	450 - 2000	10.0	[Sihra et al., 2001]	
				E	296	450 - 2000	9.9	[Christidis et al., 1997]	
Dibromodifluoromethane	75-61-6	Halon-1202	$CBr_2F_2$	E	295	400 - 1600	11.8	[Orkin et al., 2003]	
Bromochlorod if luoromethane	353-59-3	Halon-1211	$CBrClF_2$	E	296	450 - 2000	12.4	[Sihra et al., 2001]	
				E	296	450 - 2000	11.5	[Christidis et al., 1997]	
Bromotrifluoromethane	75-63-8	Halon-1301	$CBrF_3$	E	298	461 - 2500	16.7	[Charmet et al., 2008]	
				E	298	720 - 1250	15.4	[ <i>Drage et al.</i> , 2006]	
				E	295	720 - 1250	16.4	[Orkin et al., 2003]	
				E	296	450 - 2000	17.0	[Sihra et al., 2001]	
				Е		1040 - 1250	16.0	[Varanasi and Chudamani, 1988b]	
				E		1040 - 1250	16.1	[Ramanathan et al., 1985]	
2.D. 1.1.1				E		720 - 1250	15.9	[Person and Polo, 1961]	
2-Bromo-1,1,1- trifluoroethane	421-06-7	Halon-2301	$CH_2BrCF_3$	E	295	590 - 1510	12.8	[Orkin et al., 2003]	
2-Bromo-2-chloro-1,1,1-trifluoroethane	151-67-7	Halon-2311 / Halothane	CHBrClCF <sub>3</sub>	E	298	650 - 1500	12.2	[Andersen et al., 2012b]	
				E	295	480 - 1370	13.0	[Orkin et al., 2003]	
2-Bromo-1,1,1,2- tetrafluoroethane	124-72-1	Halon-2401	CHFBrCF <sub>3</sub>	E	295	490 - 1480	14.6	[Orkin et al., 2003]	
1,2-Dibromo-1,1,2,2- tetrafluoroethane	124-73-2	Halon-2402	CBrF <sub>2</sub> CBrF <sub>2</sub>	E	296	450 - 2000	15.4	[Sihra et al., 2001]	

Type of data: E, Experimental; A, Ab initio.
 Integrated absorption cross-section in units of 10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> for the wavenumber interval specified.
 Database: H, HITRAN 2008; G, GEISA 2009.

Table 11. Lifetimes, radiative efficiencies and direct GWPs (relative to CO<sub>2</sub>) for bromocarbons, hydrobromocarbons and halons. Compounds in bold either have significant current atmospheric concentrations or a clear potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from WMO [2011].

			Radiati	ve Efficiency  1)	GWP 100-yr		
Acronym / name	Formula	Lifetime (yr)	AR4	This study – const. profile	This study - lifetime corr.	AR4	This study  – lifetime  corr.
Methyl bromide	CH <sub>3</sub> Br	0.8	0.01	0.01	0.00	5	2
Methylene bromide	$CH_2Br_2$	0.3	0.01	0.02	0.01	2	1
Halon-1201	$CHBrF_2$	5.2	0.14	0.17	0.15	404	376
Halon-1202	$CBr_2F_2$	2.9		0.31	0.27		231
Halon-1211	$CBrClF_2$	16.0	0.30	0.31	0.29	1,890	1,750
Halon-1301	$CBrF_3$	65.0	0.32	0.31	0.30	7,140	6,290
Halon-2301	CH <sub>2</sub> BrCF <sub>3</sub>	3.4		0.15	0.14		173
Halon-2311 /	CUDCICE	1.0		0.10	0.12		41
Halothane	CHBrClCF <sub>3</sub>	1.0		0.18	0.13		41
Halon-2401	CHFBrCF <sub>3</sub>	2.9		0.21	0.19		184
Halon-2402	CBrF <sub>2</sub> CBrF <sub>2</sub>	20.0	0.33	0.34	0.31	1,640	1,470

**Table 12.** Integrated absorption cross-sections (*S*) for fully fluorinated species from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Acronym	Formula	Data <sup>1</sup>	T/K	Wn. range /cm <sup>-1</sup>	$S^2$	Reference	Database <sup>3</sup>
Nitrogen trifluoride	7783-54- 2		NF <sub>3</sub>	Е	296	400 - 2000	7.0	[Robson et al., 2006]	
Sulphur hexafluoride	2551-62- 4		$SF_6$	E				[Vlachogiannis et al., 2005]	
				E E	296	900 - 1000	20.7	[Hurley-priv.com., 2003] [Jain et al., 2000]	G
				Ē	295	925 - 955	18.8	[Varanasi-priv.com., 2000]	Н
				E	216	925 - 955	18.9	[Varanasi et al., 1994]	H
				E		640 - 1225	20.2	[Ko et al., 1993]	
				E			18.0	[Chapados, 1988]	
				E			17.6	[ <i>McDowell et al.</i> , 1986]	
				E			17.6	[Dunn et al., 1982]	
				E			18.3	[Brodbeck et al., 1980]	
				E			22.6	[Kim et al., 1980]	
				E			17.9	[Schatz and Hornig, 1953]	
(Trifluoromethyl)sulfur pentafluoride	373-80-8		SF <sub>5</sub> CF <sub>3</sub>	E	298	599 - 2500	28.6	[Rinsland et al., 2003]	Н
				E	296	670 - 1325	25.2	[Hurley-priv.com., 2003]	G
				E	296	400 - 1330	26.5	[Nielsen et al., 2002]	
				E	296	700 - 2000	25.4	[Sihra et al., 2001]	
				E	296	670 - 1325	25.4	[Sturges et al., 2000]	
Sulfuryl fluoride	2699-79- 8		$SO_2F_2$	Е	296	805 - 1760	13.0	[Andersen et al., 2009]	
	O			Е		500 - 1542	13.6	[Dillon et al., 2008]	
				E,A	296	500 - 1542	14.0	[Papadimitriou et al., 2008b]	
Perfluoromethane, tetrafluoromethane	75-73-0	PFC-14	$\mathrm{CF}_4$	A	<b>-</b> 27 0	700 - 1400	19.3	[Bravo et al., 2010b]	
				E	296	1230 - 1300	19.0	[Hurley et al., 2005]	
				Ē	296	1230 - 1300	21.9	[Hurley-priv.com., 2003]	G
				E	296	500 - 1400	21.9	[Sihra et al., 2001]	•
				Ē	296	1250 - 1290	19.1	[Varanasi-priv.com., 2000]	Н

				A		600 - 1500	20.1	[Papasavva et al., 1997]	
				E	300	590 - 1320	18.5	[Roehl et al., 1995]	
				E	293	1255 - 1310	17.3	[McDaniel et al., 1991]	
				E		1255 - 1310	14.0	[Varanasi and Chudamani, 1988b]	
				E		1255 - 1310	16.9	[Golden et al., 1978]	
Perfluoroethane	76-16-4	PFC-116	$C_2F_6$	A			26.3	[Bera et al., 2010]	
				E	297	700 - 1400	23.0	[Bravo et al., 2010b]	
				A		700 - 1400	22.5	[Bravo et al., 2010b]	
				E	296	1061 - 1285	21.0	[Zou et al., 2004]	H
				E	296	450 - 1500	21.6	[Sihra et al., 2001]	
				E	293	675 - 1400	22.8	[Ballard et al., 2000a]	
				E	253	680 - 1380	22.8	[Highwood and Shine, 2000]	
				E	296	690 - 1360	21.5	[Highwood et al., 1999]	G
				A		600 - 1500	22.7	[Papasavva et al., 1997]	
				Е	300	480 - 1385	21.6	[Roehl et al., 1995]	
				Е				[Varanasi and Chudamani, 1988b]	
				E				[ <i>Mills et al.</i> , 1958]	
				E	293	690 - 1360	22.2	[M.S.F./R.A.L.]	G
Perfluorocyclopropane	931-91-9	PFC-c216	$c-C_3F_6$	A		0 - 2500	16.9	[Bravo et al., 2010b]	
Perfluoropropane	76-19-7	PFC-218	$C_3F_8$	Α			30.4	[Bera et al., 2010]	
1 1			3 0	Е	297	700 - 1400	26.8	[Bravo et al., 2010b]	
				Α		700 - 1400	27.6	[Bravo et al., 2010b]	
				E	296	500 - 1500	27.5	[Sihra et al., 2001]	
				E	300	500 - 1550	22.0	[Roehl et al., 1995]	
Perfluorocyclobutane	115-25-3	PFC-318	$c-C_4F_8$	Α		0 - 2500	22.1	[Bravo et al., 2010b]	
,			4 0	E	297	550 - 1500	21.7	[Vasekova et al., 2006]	
				E	297	550 - 1500	22.2	[Ballard et al., 2000a]	
				E	253	555 - 1460	21.6	[Highwood and Shine, 2000]	
				E	297	555 - 1430	21.8	[M.S.F./R.A.L.]	G
Perfluorobutane	355-25-9	PFC-31-10	$C_4F_{10}$	A			36.0	[Bera et al., 2010]	-
· · · · · · · · · · · · · · · ·	/		10	E	297	450 - 1500	31.7	[Bravo et al., 2010b]	
				A		0 - 2500	32.5	[Bravo et al., 2010b]	
				E	296	450 - 1500	31.7	[Sihra et al., 2001]	
				E	300	500 - 1550	27.2	[Roehl et al., 1995]	
Perfluorocyclopentene				<del>-</del>			_ · · -	L	

				Е	297	550 - 1800	20.9	[Vasekova et al., 2006]
Perfluoropentane	678-26-2	PFC-41-12	$n-C_5F_{12}$	E	297	210 - 2000	36.3	[Bravo et al., 2010b]
				A		0 - 2500	37.2	[Bravo et al., 2010b]
				E	300	500 - 1550	34.6	[Roehl et al., 1995]
Perfluorohexane	355-42-0	PFC-51-14	$n-C_6F_{14}$	E	297	210 - 2000	38.5	[Bravo et al., 2010b]
				A		0 - 2500	41.8	[Bravo et al., 2010b]
				E	300	500 - 1550	39.6	[Roehl et al., 1995]
Perfluoroheptane	335-57-9	PFC-61-16	$n-C_7F_{16}$	E	296	500 - 4000	44.7	[Ivy et al., 2012]
		PFC-71-18	$C_8F_{18}$	E	296	500 - 4000	52.3	[Ivy et al., 2012]
				E	297	700 - 1400	45.6	[Bravo et al., 2010b]
				A		700 - 1400	50.9	[Bravo et al., 2010b]
Perfluorodecalin (mixed)	306-94-5	PFC-91-18	$C_{10}F_{18}$	A		0 - 2500	43.2	[Bravo et al., 2010b]
				E	296	0 - 1500	39.1	[Shine et al., 2005b]
Doubly and deadin (air)	60433-		oia C. E	٨		0 - 2500	12.1	[Page of al. 2010b]
Perfluorodecalin (cis)	11-6		$\operatorname{cis-C_{10}F_{18}}$	A		0 - 2300	43.4	[Bravo et al., 2010b]
				E	296	655 - 1370	37.9	[Shine et al., 2005b]
Perfluorodecalin (trans)	60433-		trans-C <sub>10</sub> F <sub>18</sub>	A		0 - 2500	43.0	[Bravo et al., 2010b]
Territorodecami (trans)	12-7		uans-C <sub>10</sub> 1 18	А		0 - 2300	45.0	[Bravo et al., 20100]
				E	296	655 - 1360	35.6	[Shine et al., 2005b]
Perfluoroethene	116-14-3	PFC-1114	$CF_2 = CF_2$	E	296	1080 - 1400	12.0	[Drage et al., 2006]
				E	298	1080 - 1400	12.9	[Acerboni et al., 2001]
Perfluoropropene	116-15-4	PFC-1216	CF <sub>3</sub> CF=CF <sub>2</sub>	E	298	970 - 1850	23.5	[Acerboni et al., 2001]
Perfluorobuta-1,3-diene	685-63-2		CF <sub>2</sub> =CFCF=CF <sub>2</sub>	E			20.7	[Bravo et al., 2010b]
				A			21.9	[Bravo et al., 2010b]
				E	298	900 - 1850	21.8	[Acerboni et al., 2001]
Perfluorobut-1-ene	357-26-6		CF <sub>3</sub> CF <sub>2</sub> CF=CF <sub>2</sub>	E	296	635 - 1830	24.0	[Young et al., 2009a]
Perfluorobut-2-ene	360-89-4		CF <sub>3</sub> CF=CFCF <sub>3</sub>	E	298	500 - 1410	25.3	[Cometto et al., 2010]
				E	296	650 - 1500	28.8	[Young et al., 2009a]

<sup>4397</sup> Type of data: E, Experimental; A, Ab initio.

 $<sup>4398 \</sup>qquad {}^2 \text{ Integrated absorption cross-section in units of } 10^{\text{-}17} \text{ cm}^2 \text{ molecule}^{\text{-}1} \text{ cm}^{\text{-}1} \text{ for the wavenumber interval specified.}$ 

<sup>4399 &</sup>lt;sup>3</sup> Database: H, HITRAN 2008; G, GEISA 2009.

**Table 13.** Lifetimes, radiative efficiencies and direct GWPs (relative to CO<sub>2</sub>) for fully fluorinated species. Compounds in bold either have significant current atmospheric concentrations or a clear potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from *WMO* [2011] except those in italic (see text for details). RE and GWP values in italic are based on previous publications (see text for details).

			Radiati	ve Efficiency  1)	(W m <sup>-2</sup> ppb <sup>-</sup>	GW	P 100-yr
Acronym / name	Formula	Lifetime (yr)	AR4	This study – const. profile	This study – lifetime corr.	AR4	This study  – lifetime  corr.
Nitrogen trifluoride	NF <sub>3</sub>	500.0	0.21	0.21	0.20	17,200	16,100
Sulphur hexafluoride	SF <sub>6</sub>	3,200.0	0.52	0.57	0.57	22,800	23,500
(Trifluoromethyl)sulfur pentafluoride	SF <sub>5</sub> CF <sub>3</sub>	800.0	0.57	0.60	0.59	17,700	17,400
Sulfuryl fluoride	$SO_2F_2$	36.0		0.21	0.20		4,090
PFC-14	$CF_4$	50,000.0	0.10	0.09	0.09	7,390	6,630
PFC-116	$C_2F_6$	10,000.0	0.26	0.25	0.25	12,200	11,100
PFC-c216	$c-C_3F_6$	3,000.0	0.42	0.23	0.23	17,300	9,200
PFC-218	$C_3F_8$	2,600.0	0.26	0.28	0.28	8,830	8,900
PFC-318	$c-C_4F_8$	3,200.0	0.32	0.32	0.32	10,300	9,540
PFC-31-10	$C_4F_{10}$	2,600.0	0.33	0.37	0.36	8,860	9,200
Perfluorocyclopentene	$c-C_5F_8$	31.0 days		0.33	0.08		2
PFC-41-12	$n-C_5F_{12}$	4,100.0	0.41	0.41	0.41	9,160	8,550
PFC-51-14	$n-C_6F_{14}$	3,100.0	0.49	0.45	0.44	9,300	7,910
PFC-61-16	$n-C_7F_{16}$	3,000.0		0.51	0.50		7,820
PFC-71-18	$C_8F_{18}$	3,000.0		0.56	0.55		7,620
Perfluorodecalin (mixed)	$C_{10}F_{18}$	2,000.0	0.56	0.56	0.55	7,500	7,190
Perfluorodecalin (cis)	$cis-C_{10}F_{18}$	2,000.0		0.57	0.56		7,240
Perfluorodecalin (trans)	trans- $C_{10}F_{18}$	2,000.0		0.49	0.48		6,290
PFC-1114	$CF_2 = CF_2$	1.1 days		0.12	0.00		0
PFC-1216	CF <sub>3</sub> CF=CF <sub>2</sub>	4.9 days		0.25	0.01		0
Perfluorobuta-1,3-diene	CF <sub>2</sub> =CFCF=CF <sub>2</sub>	1.1 days		0.24	0.00		0
Perfluorobut-1-ene	CF <sub>3</sub> CF <sub>2</sub> CF=CF <sub>2</sub>	6.0 days		0.30	0.02		0
Perfluorobut-2-ene	CF <sub>3</sub> CF=CFCF <sub>3</sub>	31.0 days		0.29	0.07		2

Table 14. Integrated absorption cross-sections (*S*) for halogenated alcohols and ethers from the literature. Spectra used in RE calculations in the present study are indicated in bold.

Name	CAS#	Acronym	Formula	Data <sup>1</sup>	T/K	Wn. range /cm <sup>-1</sup>	$S^2$	Reference	Data base <sup>3</sup>
(Difluoromethoxy)trifluoromethane	3822-68-2	HFE-125	CHF <sub>2</sub> OCF <sub>3</sub>	A	277	0 - 1500		[Blowers et al., 2008a]	
•				A				[Blowers et al., 2007]	
				E	296	450 - 1650	31.7	[Sihra et al., 2001]	
				E	295	980 - 1510	31.2	[Orkin et al., 1999]	
				A				[Good et al., 1998]	
				E	298	475 - 1590	32.9	[Heathfield et al., 1998]	
				Е	296	450 - 2000	29.2	[Christidis et al., 1997]	
(Difluoromethoxy)difluoromethane	1691-17-4	HFE-134 (HG-00)	$CHF_2OCHF_2$	A		31 - 2500	26.5	[Bravo et al., 2011a]	
				Е	296	700 - 1500	25.7	[Andersen et al., 2010a]	
				A	277	0 - 1500		[Blowers et al., 2008a]	
				A				[ <i>Blowers et al.</i> , 2007]	
				E	298	25 - 3250	25.0	[Myhre et al., 1999]	
				E	295	741 - 1443	25.4	[Orkin et al., 1999]	
				A				[Good et al., 1998]	
				E	298	750 - 1480	25.6	[Heathfield et al., 1998]	
				E	296	700 - 1500	25.5	[Imasu et al., 1995]	
				E		770 - 1430	25.3	[Garland et al., 1993]	
Trifluoro(methoxy)methane	421-14-7	HFE-143a	CH <sub>3</sub> OCF <sub>3</sub>	A		78 - 1503	22.3	[Bravo et al., 2011a]	
·				A	277	0 - 1500		[Blowers et al., 2008a]	
				A				[Blowers et al., 2007]	
				E	296	550 - 1520	19.9	[Sihra et al., 2001]	
				E				[Christensen et al., 1999]	
				A				[Good et al., 1998]	
1,1,1,2-Tetrafluoro-2- (trifluoromethoxy)ethane	2356-62-9	HFE-227ea	CF <sub>3</sub> CHFOCF <sub>3</sub>	A				[Blowers et al., 2007]	
(				Е	298	485 - 1600	37.0	[Oyaro et al., 2005]	
				Ē	296	645 - 1460	33.3	[Takahashi et al., 2002]	
				E	298	700 - 1500	41.0	[Jain et al., 2001]	
				E	296	700 - 1500	36.9	[Imasu et al., 1995]	
				E,A	296	500 - 2000	38.4	[Suga et al., 1994]	
2-Chloro-1-(difluoromethoxy)-1,1,2- trifluoroethane	13838-16-9	HCFE-235ca2 (enflurane)	CHF <sub>2</sub> OCF <sub>2</sub> CHFCl	E	298	650 - 1500	26.8	[Andersen et al., 2012b]	
						800 - 1500	25.1	[Dalmasso et al., 2006]	
2-Chloro-2-(difluoromethoxy)-1,1,1- trifluoroethane	26675-46-7	HCFE-235da2 (isoflurane)	CHF <sub>2</sub> OCHClCF <sub>3</sub>	Е	298	650 - 1500	29.1	[Andersen et al., 2010c]	
				E		400 - 1500	28.5	[Ryan and Nielsen, 2010]	
				Е	296	450 - 1650	27.5	[Sihra et al., 2001]	
				Е	296	450 - 2000	26.3	[Christidis et al., 1997]	
1-(Difluoromethoxy)-1,1,2,2-tetrafluoroethane	32778-11-3	HFE-236ca	CHF2OCF2CHF2	A				[Blowers et al., 2007]	

2-(Difluoromethoxy)-1,1,1,2-tetrafluoroethane	57041-67-5	HFE-236ea2 (desflurane)	CHF <sub>2</sub> OCHFCF <sub>3</sub>	A		43 - 2500	31.9	[Bravo et al., 2011a]
				E	298	650 - 1500	31.3	[Andersen et al., 2010c]
				A				[Blowers et al., 2007]
				E	298	485 - 1530	30.3	[Oyaro et al., 2005]
				E	296	700 - 1500	29.9	[Imasu et al., 1995]
1,1,1-Trifluoro-2-(trifluoromethoxy)ethane	20193-67-3	HFE-236fa	CF <sub>3</sub> CH <sub>2</sub> OCF <sub>3</sub>	A				[Blowers et al., 2007]
•				E	296	700 - 1500	33.5	[Imasu et al., 1995]
1,1,1,2,2-Pentafluoro-2-methoxy-ethane	22410-44-2	HFE-245cb2	CF <sub>3</sub> CF <sub>2</sub> OCH <sub>3</sub>	A		45 - 1501	26.0	[Bravo et al., 2011a]
•				A				[Blowers et al., 2007]
				E	296	700 - 1500	24.6	[Imasu et al., 1995]
1,1-Difluoro-2-(trifluoromethoxy)ethane	84011-15-4	HFE-245fa1	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>3</sub>	A				[Blowers et al., 2007]
•				E	296	700 - 1500	27.9	[Imasu et al., 1995]
2-(Difluoromethoxy)-1,1,1-trifluoroethane	1885-48-9	HFE-245fa2	CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	Α				[Blowers et al., 2007]
•				E	298	470 - 1550	26.5	[Oyaro et al., 2005]
				E	296	450 - 1550	26.3	[Sihra et al., 2001]
				E	296	450 - 2000	25.1	[Christidis et al., 1997]
				E	296	700 - 1500	26.3	[Imasu et al., 1995]
2,2,3,3,3-Pentafluoropropan-1-ol	422-05-9		CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> OH	E	298	600 - 4000	20.5	[Antiñolo et al., 2012b]
• •				E	298	490 - 1500	18.0	[Sellevåg et al., 2007]
				E	296	700 - 1500	17.9	[Imasu et al., 1995]
1,1,2,2-Tetrafluoro-1-methoxyethane	425-88-7	HFE-254cb1	CH <sub>3</sub> OCF <sub>2</sub> CHF <sub>2</sub>	A		66 - 2500	20.1	[Bravo et al., 2011a]
•				A				[Blowers et al., 2007]
				E	298	500 - 1600	19.6	[Heathfield et al., 1998]
				E	296	700 - 1500	19.1	[Imasu et al., 1995]
1,1,1-Trifluoro-2-methoxyethane	460-43-5	HFE-263fb1	CF <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	E	296	600 - 1600	15.5	[Osterstrom et al., 2012]
•				A				[Bravo et al., 2011a]
				A				[Blowers et al., 2007]
				E	298	500 - 1525	15.3	[Ovaro et al., 2005]
				E	296	700 - 1500	15.2	[Imasu et al., 1995]
1,1,2,2-Tetrafluoro-1-	690-22-2	HFE-263m1	CF3OCH2CH3	A		42 - 1562	22.9	[Bravo et al., 2011a]
(trifluoromethoxy)ethane	090-22-2	HFE-203IIII	Cl <sup>3</sup> OCH <sub>2</sub> CH <sub>3</sub>	Α		42 - 1302	22.9	
				A				[Blowers et al., 2007]
				E	298	550 - 1550	22.0	[Oyaro et al., 2005]
3,3,3-Trifluoropropan-1-ol	2240-88-2		CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	E	298	500 - 4000	16.6	[Jimenez et al., 2010]
				E	298	515 - 1550	13.8	[Sellevåg et al., 2007]
				E	296	650 - 1530	14.6	[Waterland et al., 2005]
1,1,1,2,2-Pentafluoro-2-(1,1,2,2-	134769-21-4	HFE-329mcc2	CHF2CF2OCF2CF3	A				[Blowers et al., 2007]
tetrafluoroethoxy)ethane	131707 21 1	TH E 327 MCC2			206	700 - 1500	20.2	
2-(Difluoromethoxy)-1,1,1,3,3,3-				E	296	/00 - 1500	39.2	[Imasu et al., 1995]
hexafluoropropane	26103-08-2	HFE-338mmz1	$(CF_3)_2CHOCHF_2$	A				[Blowers et al., 2007]
• •				E	296	700 - 1500	35.4	[Imasu et al., 1995]
1,1,1,2,2-Pentafluoro-2-(2,2,2-trifluoroethoxy)ethane	156053-88-2	HFE-338mcf2	CF <sub>3</sub> CH <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	A				[Blowers et al., 2007]
aniaoroomon journe				E	296	700 - 1500	34.7	[Imasu et al., 1995]
1,1,1,3,3,3-Hexafluoro-2-	28523-86-6	Sevoflurane (HFE-	(CF <sub>3</sub> ) <sub>2</sub> CHOCH <sub>2</sub> F	Ā		39 - 2500	32.2	[Bravo et al., 2011a]

(fluoromethoxy)propane		347mmz1)						
(nuoromemoxy)propane		347HHHZ1)		Е	298	650 - 1500	30.2	[Andersen et al., 2010c]
				E	270	650 - 1500	30.6	[Ryan and Nielsen, 2010]
1,1,1,2,2,3,3-Heptafluoro-3-methoxypropane	375-03-1	HFE-347mcc3 (HFE-7000)	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	A		51 - 2500	31.1	[Bravo et al., 2011a]
1,1,1,2,2,3,3 Heptariaoro 3 methoxypropane	373 03 1	111 L 347 mee3 (111 L 7000)	C113OC1 2C1 2C1 3	E		700 - 1400	28.2	[Bravo et al., 2010a]
				A		700 - 1400	20.2	[Blowers et al., 2007]
				E		700 - 1500	27.4	[Ninomiya et al., 2000]
				E	296	700 - 1500	29.5	[Imasu et al., 1995]
1-(2,2-Difluoroethoxy)-1,1,2,2,2-				E	290	700 - 1300	29.3	
pentafluoroethane	171182-95-9	HFE-347mcf2	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	A				[Blowers et al., 2007]
•				E	296	700 - 1500	30.2	[Imasu et al., 1995]
1,1,2,2-Tetrafluoro-1-(2,2,2- trifluoroethoxy)ethane	406-78-0	HFE-347pcf2	CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	A				[Blowers et al., 2007]
umuoroenioxy)eniane				E	298	500 - 1600	32.2	[Heathfield et al., 1998]
1,1,1,2,3,3,3-Heptafluoro-2-methoxypropane	22052-84-2	HFE-347mmy1	(CF <sub>3</sub> ) <sub>2</sub> CFOCH <sub>3</sub>	A				[Blowers et al., 2007]
, , , , , , , , , , , , , , , , , , ,		<b>,</b>	(= 3/2 = = = 3	Е	296	700 - 1500	28.6	[Imasu et al., 1995]
1,1,1,2,3,3-Hexafluoro-3-methoxypropane	382-34-3	HFE-356mec3	CH3OCF2CHFCF3	A				[Blowers et al., 2007]
-,-,-,-,e,e				E	296	700 - 1500	25.8	[Imasu et al., 1995]
	333-36-8	HFE-356mff2	CF <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	A				[Blowers et al., 2007]
			322 3	E	298	500 - 1600	27.2	[Oyaro et al., 2004]
				E	296	500 - 1500	28.1	[Sihra et al., 2001]
				E	295	500 - 1600	27.7	[Orkin et al., 1999]
				E				[Wallington et al., 1998]
1-(2,2-Difluoroethoxy)-1,1,2,2-tetrafluoroethane	50807-77-7	HFE-356pcf2	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>2</sub> CHF <sub>2</sub>	A				[Blowers et al., 2007]
				E	296	700 - 1500	24.9	[Imasu et al., 1995]
3-(Difluoromethoxy)-1,1,2,2- tetrafluoropropane	35042-99-0	HFE-356pcf3	CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>	A				[Blowers et al., 2007]
1 1				E	296	700 - 1500	24.8	[Imasu et al., 1995]
1,1,2,2,3,3-Hexafluoro-1-methoxypropane	160620-20-2	HFE-356pcc3	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>	A				[Blowers et al., 2007]
31 1		1	J 2 2 2	E	296	700 - 1500	23.4	[Imasu et al., 1995]
1,1,1,3,3,3-Hexafluoro-2-methoxypropane	13171-18-1	HFE-356mmz1	(CF <sub>3</sub> ) <sub>2</sub> CHOCH <sub>3</sub>	A				[Blowers et al., 2007]
31 1			\ J/2	E	298	475 - 1550	25.8	[Oyaro et al., 2004]
				E	296	700 - 1500	25.7	[Imasu et al., 1995]
1,1,1,2,2-Pentafluoro-3-methoxypropane	378-16-5	HFE-365mcf3	CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	E	296	650 - 1500	20.7	[Thomsen et al., 2011]
-,-,-, <del>-</del> ,			3 223	A				[Blowers et al., 2007]
				E	298	490 - 1525	19.5	[Oyaro et al., 2004]
				E	296	700 - 1500	19.6	[Imasu et al., 1995]
1-Ethoxy-1,1,2,2,2-pentafluoroethane	22052-81-9	HFE-365mcf2	CF <sub>3</sub> CF <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	A	270	96 - 1520	27.8	[Bravo et al., 2011a]
1-Ethoxy-1,1,2,2-tetrafluoroethane	512-51-6	HFE-374pc2	CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	A		70 1320	27.0	[Blowers et al., 2007]
1 Editory 1,1,2,2 terrationocularie	312 31 0	т 2 3/чре2	2111 201 2001120113	E	298	500 - 1600	20.9	[Heathfield et al., 1998]
				E	296	700 - 1500	20.7	[Imasu et al., 1995]
4,4,4-Trifluorobutan-1-ol	461-18-7		CF <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	E	298	500 - 4000	10.6	[Jimenez et al., 2010]
1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)-2-	2378-02-1		(CF <sub>3</sub> ) <sub>3</sub> COH	Е	296	700 - 1500	37.4	[Imasu et al., 1995]
propanol 2,2,3,3,4,4,5,5-Octafluorocyclopentanol	16621-87-7		-(CF <sub>2</sub> ) <sub>4</sub> CH(OH)-	Е	296	700 - 1500	21.1	[Imasu et al., 1995]

-(Difluoromethoxy)-2- (difluoromethoxy)difluoromethoxy)-1,1,2,2- etrafluoroethane	188690-77-9	HFE-43-10pccc124 (H-Galden 1040x, HG-11)	CHF <sub>2</sub> OCF <sub>2</sub> OC <sub>2</sub> F <sub>4</sub> OCHF <sub>2</sub>	A		21 - 2500	80.9	[Bravo et al., 2011a]
				E	296	700 - 1440	67.9	[Wallington et al., 2009]
				E	296	450 - 1600	66.5	[Sihra et al., 2001]
				Е	295	963 - 1587	84.9	[Cavalli et al., 1998]
				Е	296	450 - 2000	65.5	[Christidis et al., 1997]
1,1,2,2,3,3,4,4-Nonafluoro-4-methoxybutane	163702-07-6	HFE-449s1 (HFE-7100)	$C_4F_9OCH_3$	A				[Bravo et al., 2011a]
1,1,2,2,3,3,1,110111111010 1 11101101179 1111111	103702 07 0	IN E 11981 (IN E 7100)	C41 90 C113	E	296	450 - 1550	36.0	[Sihra et al., 2001]
				Ē	270	700 - 1400	34.4	[Bravo et al., 2010a]
				E	295	700 1400	54.4	[Wallington et al., 1997]
	163702-07-6	n-HFE-7100	n-C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>	A	273	35 - 1501	36.0	[Bravo et al., 2011a]
	103702-07-0	n-111-E-7100	n-C41 90C113	A		33 - 1301	30.0	[Blowers et al., 2007]
				E	296	450 - 1520	22.7	[Sihra et al., 2001]
	163702-08-7	i-HFE-7100	: C E OCH		290	59 - 1501	33.7 39.3	
	103/02-06-/	t-fif'E-/100	<i>i</i> -C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>	A		39 - 1301	39.3	[Bravo et al., 2011a]
				A	200	450 1500	27.6	[Blowers et al., 2007]
Til 11000001111 (I 1 )	1 60700 05 4	HEE 560 M (HEE 5000)	C F OCH	E	296	450 - 1500	37.6	[Sihra et al., 2001]
-Ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane	163702-05-4	HFE-569sf2 (HFE-7200)	$C_4F_9OC_2H_5$	A				[Bravo et al., 2011a]
				E	296	500 - 1500	37.1	[Sihra et al., 2001]
				E		700 - 1400	38.5	[Bravo et al., 2010a]
				E				[Christensen et al., 1998]
	163702-05-4	n-HFE-7200	n-C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> H <sub>5</sub>	A		31 - 1519	38.1	[Bravo et al., 2011a]
				A				[Blowers et al., 2007]
	163702-06-5	i-HFE-7200	i-C <sub>4</sub> F <sub>9</sub> OC <sub>2</sub> H <sub>5</sub>	A		37 - 1519	41.4	[Bravo et al., 2011a]
				A				[Blowers et al., 2007]
				E	296	450 - 1400	32.7	[Sihra et al., 2001]
is(difluoromethoxy)difluoromethane	78522-47-1	HFE-236ca12 (HG-10)	CHF <sub>2</sub> OCF <sub>2</sub> OCHF <sub>2</sub>	A		36 - 2500	47.1	[Bravo et al., 2011a]
				E	298	25 - 3250	44.9	[Myhre et al., 1999]
				E	295	978 - 1584	51.9	[Cavalli et al., 1998]
,2-Bis(difluoromethoxy)-1,1,2,2- etrafluoroethane	188690-78-0	HFE-338pcc13 (HG-01)	CHF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCHF <sub>2</sub>	A		28 - 2500	53.6	[Bravo et al., 2011a]
dandorochiane				Е	298	25 - 3250	54.7	[Myhre et al., 1999]
				E	295	930 - 1501	60.4	[Cavalli et al., 1999]
1 1 2 2 2 11 2 -1	920-66-1		(CF <sub>3</sub> ) <sub>2</sub> CHOH	E E	293 296	700 - 1500	25.4	, ,
1,1,3,3,3-Hexafluoropropan-2-ol (Difluoromethoxy)-2-(2-(difluoromethoxy)-	920-00-1		(CF <sub>3</sub> ) <sub>2</sub> CHOH	E	290	/00 - 1500	25.4	[Imasu et al., 1995]
,1,2,2-tetrafluoroethoxy)-1,1,2,2-	205367-61-9	HG-02	HF <sub>2</sub> C-(OCF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> -OCF <sub>2</sub> H	A		20 - 2500	80.4	[Bravo et al., 2011a]
etrafluoroethane			2 - ( 2 2/2 - 0 - 2 - 2 - 1					, , , ,
,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12-							114.	
exadecafluoro-2,5,8,11-tetraoxadodecane	173350-37-3	HG-03	HF <sub>2</sub> C-(OCF <sub>2</sub> CF <sub>2</sub> ) <sub>3</sub> -OCF <sub>2</sub> H	A		17 - 2500	1	[Bravo et al., 2011a]
Oifluoromethoxy)((difluoromethoxy)difluoro							1	
ethoxy)difluoromethane	249932-25-0	HG-20	$HF_2C-(OCF_2)_2-OCF_2H$	A		35 - 2500	70.3	[Bravo et al., 2011a]
•			HF <sub>2</sub> C-					
1,3,3,5,5,7,7,8,8,10,10-Dodecafluoro-	249932-26-1	HG-21	OCF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> OCF <sub>2</sub> O-	A		24 - 2500	108.	[Bravo et al., 2011a]
4,6,9-tetraoxadecane	∠ <del>+</del> 7734-40-1	110-21	CF <sub>2</sub> H	Α		24 - 2300	0	[Diavo et at., 2011a]
1 2 2 5 5 7 7 0 0 Decelhors 2 4 6 9			Cr <sub>2</sub> rī				102	
,1,3,3,5,5,7,7,9,9-Decafluoro-2,4,6,8- etraoxanonane	188690-77-9	HG-30	HF <sub>2</sub> C-(OCF <sub>2</sub> ) <sub>3</sub> -OCF <sub>2</sub> H	A		30 - 2500	103.	[Bravo et al., 2011a]

1-Ethoxy-1,1,2,2,3,3,3-heptafluoropropane	22052-86-4		CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	A		67 - 1519	33.0	[Bravo et al., 2011a]
(2,2,2-Trifluoroethoxy)ethene	406-90-6	Fluoroxene	CF <sub>3</sub> CH <sub>2</sub> OCH=CH <sub>2</sub>	A		47 - 2500	23.5	[Bravo et al., 2011a]
1,1,2,2-Tetrafluoro-1-(fluoromethoxy)ethane	37031-31-5		CH <sub>2</sub> FOCF <sub>2</sub> CF <sub>2</sub> H	A		43 - 2500	25.0	[Bravo et al., 2011a]
2-Ethoxy-3,3,4,4,5-pentafluorotetrahydro-2,5-								
bis[1,2,2,2-tetrafluoro-1-	920979-28-8		$C_{12}H_5F_{19}O_2$	E	294	700 - 1400	55.9	[Javadi et al., 2007]
(trifluoromethyl)ethyl]-furan								
Fluoro(methoxy)methane	460-22-0		CH₃OCH₂F	A				[Blowers et al., 2008a]
Difluoro(methoxy)methane	359-15-9		$CH_3OCHF_2$	A				[Blowers et al., 2008a]
				A				[Blowers et al., 2007]
Fluoro(fluoromethoxy)methane	462-51-1		CH <sub>2</sub> FOCH <sub>2</sub> F	A				[Blowers et al., 2008a]
Difluoro(fluoromethoxy)methane	461-63-2		$CH_2FOCHF_2$	A				[Blowers et al., 2008a]
Trifluoro(fluoromethoxy)methane	2261-01-0		CH <sub>2</sub> FOCF <sub>3</sub>	A				[Blowers et al., 2008a]
1,1,2,2-Tetrafluoro-1,2-dimethoxyethane	73287-23-7	HG'-01	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> OCH <sub>3</sub>	A		16 - 2500	29.5	[Bravo et al., 2011a]
				E	296	200 - 1800	23.0	[Andersen et al., 2004]
1,1,2,2-Tetrafluoro-1-methoxy-2-(1,1,2,2-	485399-46-0	HG'-02	CH <sub>3</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>2</sub> CH <sub>3</sub>	A		29 - 2500	58.2	[Bravo et al., 2011a]
tetrafluoro-2-methoxyethoxy)ethane	483399-40-0	NG -02	CH <sub>3</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>2</sub> CH <sub>3</sub>	Α		29 - 2300	36.2	[Bravo et al., 2011a]
				E	296	200 - 1800	45.5	[Andersen et al., 2004]
3,3,4,4,6,6,7,7,9,9,10,10-Dodecafluoro-	485399-48-2	HG'-03	CH <sub>3</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>3</sub> CH <sub>3</sub>	A		20 - 2500	82.7	[Bravo et al., 2011a]
2,5,8,11-tetraoxadodecane	403399-40-2	NG-03	$CH_3O(CF_2CF_2O)_3CH_3$	Α		20 - 2300	02.7	[Bravo et al., 2011a]
				E	296	200 - 1800	63.4	[Andersen et al., 2004]
Difluorodimethoxymethane	54796-90-6	HG'-10	CH <sub>3</sub> OCF <sub>2</sub> OCH <sub>3</sub>	A		64 - 2500	26.1	[Bravo et al., 2011a]
•		HG'-20	CH <sub>3</sub> O(CF <sub>2</sub> O) <sub>2</sub> CH <sub>3</sub>	A		49 - 2500	51.8	[Bravo et al., 2011a]
		HG'-30	CH <sub>3</sub> O(CF <sub>2</sub> O) <sub>3</sub> CH <sub>3</sub>	A		41 - 2500	78.8	[Bravo et al., 2011a]
1,1,1,2,3,3-Hexafluoro-3-	428454-68-6	HFE-329me3	CF <sub>3</sub> CFHCF <sub>2</sub> OCF <sub>3</sub>	A				[Blowers et al., 2007]
(trifluoromethoxy)propane	120131 00 0	III E 32711103	C1 3C1 11C1 2CC1 3			-=		
1 (7):7				Е	296	670 - 1450	42.4	[Wallington et al., 2004]
1-(Difluoromethoxy)-1,1,2,3,3,3-	56860-85-6	HFE-338mec3	CF <sub>3</sub> CFHCF <sub>2</sub> OCF <sub>2</sub> H	A				[Blowers et al., 2007]
hexafluoropropane				г	200	620 1450	24.2	FO 4 1 20051
				E E	298 296	620 - 1450 680 - 1450	34.2 36.3	[Oyaro et al., 2005]
2 2 4 4 5 5 6 6 7 7 7 11 - 1 1 - 1	185689-57-0		CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> OH	E E		670 - 1510		[Wallington et al., 2004] [Waterland et al., 2005]
3,3,4,4,5,5,6,6,7,7,7-Undecafluoroheptan-1-ol 3,3,4,4,5,5,6,6,7,7,8,8,9,9-	183089-37-0		CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> OH	E	296	6/0 - 1510	26.8	[wateriana et al., 2005]
5,5,4,4,5,5,6,6,7,7,8,8,9,9,9- Pentadecafluorononan-1-ol	755-02-2		CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> CH <sub>2</sub> OH	E	296	600 - 1480	30.9	[Waterland et al., 2005]
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11- Nonadecafluoroundecan-1-ol	87017-97-8		CF <sub>3</sub> (CF <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> CH <sub>2</sub> OH	E	296	645 - 1450	24.7	[Waterland et al., 2005]
	425-87-6		CH OCE CHECI	Е	200	000 1500	17.0	[D=1
2-Chloro-1,1,2-trifluoro-1-methoxyethane	425-87-0	PFPMIE	CH <sub>3</sub> OCF <sub>2</sub> CHFCl	E	298	800 - 1500	17.0	[Dalmasso et al., 2006]
1-(Difluoro(trifluoromethoxy)methoxy)-	1200252 24 1		CF <sub>3</sub> OCF(CF <sub>3</sub> )CF <sub>2</sub> OCF <sub>2</sub> OC	Б	206	CEO 1500	50.2	[V
1,1,2,3,3,3-hexafluoro-2-	1309353-34-1	(perfluoropolymethylisopr	$F_3$	E	296	650 - 1500	59.2	[Young et al., 2006]
(trifluoromethoxy)propane	1107.02.5	opyl)	GE OGE GE	г		000 1065	20.0	[14 1: 4 1 2000]
1,1,2-Trifluoro-2-(trifluoromethoxy)ethene	1187-93-5	HFE-216	CF <sub>3</sub> OCF=CF <sub>2</sub>	E		890 - 1865	29.8	[Mashino et al., 2000]
Trifluoro(trifluoromethoxy)methane	1479-49-8		CF <sub>3</sub> OCF <sub>3</sub>	A		00 2500	20.0	[Blowers et al., 2008a]
Trifluoromethyl formate	85358-65-2		HCOOCF <sub>3</sub>	A		89 - 2500	30.9	[Bravo et al., 2011b]
Perfluoroethyl formate	313064-40-3		HCOOCE CE CE	A		59 - 1847	35.6	[Bravo et al., 2011b]
Perfluoropropyl formate	271257-42-2		HCOOCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	A		64 - 1847	41.2	[Bravo et al., 2011b]
Perfluorobutyl formate	197218-56-7		HCOOCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	A		37 - 1847	46.6	[Bravo et al., 2011b]
2,2,2-Trifluoroethyl formate	32042-38-9		HCOOCH <sub>2</sub> CF <sub>3</sub>	A		24 - 1808	25.0	[Bravo et al., 2011b]

37 - 1806	26.1	[Bravo et al., 2011b]
41 - 2500	29.2	[Bravo et al., 2011b]
37 - 2500	36.5	[Bravo et al., 2011b]
35 - 2500	49.8	[Bravo et al., 2011b]
60 - 2500	44.4	[Bravo et al., 2011b]
52 - 2500	38.6	[Bravo et al., 2011b]
71 - 2500	34.0	[Bravo et al., 2011b]
118 - 2500	18.3	[Bravo et al., 2011b]
29 - 2500	23.5	[Bravo et al., 2011b]
37 - 2500	30.5	[Bravo et al., 2011b]
77 - 1928	37.1	[Bravo et al., 2011b]
49 - 1928	41.7	[Bravo et al., 2011b]
0 - 2500	29.9	[Bravo et al., 2011b]
76 - 2500	32.2	[Bravo et al., 2011b]
0 - 1928	47.4	[Bravo et al., 2011b]
22 - 1883	43.2	[Bravo et al., 2011b]
19 - 1883	47.5	[Bravo et al., 2011b]
21 - 1873	38.0	[Bravo et al., 2011b]
24 - 1858	48.5	[Bravo et al., 2011b]
35 - 1734	27.6	[Bravo et al., 2011b]
49 - 1834	25.5	[Bravo et al., 2011b]
23 - 1844	37.0	[Bravo et al., 2011b]
22 - 1833	28.0	[Bravo et al., 2011b]
24 - 1839	23.2	[Bravo et al., 2011b]
23 - 1842	31.9	[Bravo et al., 2011b]
63 - 1805	14.0	[Bravo et al., 2011b]
31 - 1855	30.2	[Bravo et al., 2011b]
21 - 1836	17.2	[Bravo et al., 2011b]
27 - 1857	36.1	[Bravo et al., 2011b]
700 - 1400	21.4	, ,
700 1100	21.7	[Blowers et al., 2007]
298 465 - 1600	28.2	
2,0 100 1000	20.2	[Blowers et al., 2007]
298 675 - 1450	27.4	
2,0 0,5 1450	27.4	, ,
		[Blowers et al., 2007]
298 500 - 1450	43.7	[Oyaro et al., 2005]
298 600 - 4000	19.2	[Antiñolo et al., 2012b]
298 505 - 1500	13.6	[Sellevåg et al., 2007]
298 450 - 1500	29.2	[Sellevåg et al., 2007]
298 450 - 1500	21.4	[Sellevåg et al., 2007]
270 - 1300	21.4	[Blowers et al., 2007]
208 500 - 1520	13.0	[Ovaro et al., 2004]
		, ,
298 480 - 1880	40.5	[D'Anna et al., 2005]
	298 500 - 1520 298 480 - 1880	

3,3,3-Trifluoro-propanal	460-40-2	CF <sub>3</sub> CH <sub>2</sub> CHO	Е	298	600 - 1850	16.7	[Antiñolo et al., 2011]
			E	298	400 - 1900	14.2	[Sellevag et al., 2004a]
4,4,4-Trifluorobutanal	406-87-1	CF <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	E		1000 - 1850	17.0	[Antiñolo et al., 2012a]
2-Fluoroethanol	371-62-0	CH <sub>2</sub> FCH <sub>2</sub> OH	E	293	100 - 1600	6.2	[Sellevag et al., 2004b]
2,2-Difluoroethanol	359-13-7	CHF <sub>2</sub> CH <sub>2</sub> OH	E	293	100 - 1600	8.0	[Sellevag et al., 2004b]
2,2,2-Trifluoroethanol	75-89-8	CF <sub>3</sub> CH <sub>2</sub> OH	E	293	100 - 1600	15.9	[Sellevag et al., 2004b]
			E	296	700 - 1500	14.3	[Imasu et al., 1995]
1,1'-Oxybis[2-(difluoromethoxy)-1,1,2,2-tetrafluoroethane	205367-61-9	$HCF_2O(CF_2CF_2O)_2CF_2H$	E	295	650 - 1500	92.5	[Andersen et al., 2010b]
1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12- hexadecafluoro-2,5,8,11-Tetraoxadodecane	173350-37-3	$HCF_2O(CF_2CF_2O)_3CF_2H$	E	295	650 - 1500	85.2	[Andersen et al., 2010b]
1,1,3,3,4,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15 -eicosafluoro-2,5,8,11,14- Pentaoxapentadecane	173350-38-4	HCF <sub>2</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>4</sub> CF <sub>2</sub> H	Е	295	650 - 1500	70.2	[Andersen et al., 2010b]

4410 <sup>1</sup> Type of data: E, Experimental; A, Ab initio.

 $^{2}$  Integrated absorption cross-section in units of  $10^{-17}$  cm $^{2}$  molecule $^{-1}$  cm $^{-1}$  for the wavenumber interval specified.

<sup>3</sup> Database: H, HITRAN 2008; G, GEISA 2009.

**Table 15.** Lifetimes, radiative efficiencies and direct GWPs (relative to CO<sub>2</sub>) for halogenated alcohols and ethers. Compounds in bold either have significant current atmospheric concentrations or a clear potential for future emissions. Recommended RE and GWP 100-yr values are indicated in bold. Lifetimes are from *WMO* [2011] except those in italic (see text for details). RE and GWP values in italic are based on previous publications (see text for details).

			Radiati	ve Efficiency  1)	(W m <sup>-2</sup> ppb <sup>-</sup>	GW	P 100-yr
Acronym / name	Formula	Lifetime (yr)	AR4	This study – const. profile	This study - lifetime corr.	AR4	This study - lifetime corr.
HFE-125	CHF <sub>2</sub> OCF <sub>3</sub>	119.0	0.44	0.41	0.41	14,900	12,400
HFE-134 (HG-00)	CHF <sub>2</sub> OCHF <sub>2</sub>	24.4	0.45	0.46	0.44	6,320	5,560
HFE-143a	CH <sub>3</sub> OCF <sub>3</sub>	4.8	0.27	0.19	0.18	756	523
HFE-227ea	CF <sub>3</sub> CHFOCF <sub>3</sub>	51.6	0.40	0.45	0.44	1,540	6,450
HCFE-235ca2 (enflurane)	CHF <sub>2</sub> OCF <sub>2</sub> CHF Cl	4.3		0.45	0.41		583
HCFE-235da2	CHF <sub>2</sub> OCHClCF	3.5	0.38	0.47	0.42	350	491
(isoflurane)	3 CHF <sub>2</sub> OCF <sub>2</sub> CHF						
HFE-236ca	2	20.8		0.58	0.56		4,240
HFE-236ea2 (desflurane)	CHF <sub>2</sub> OCHFCF <sub>3</sub>	10.8	0.44	0.47	0.45	989	1,790
HFE-236fa	CF <sub>3</sub> CH <sub>2</sub> OCF <sub>3</sub>	7.5	0.34	0.38	0.36	487	979
HFE-245cb2	CF <sub>3</sub> CF <sub>2</sub> OCH <sub>3</sub>	4.9	0.32	0.36	0.33	708	654
HFE-245fa1	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>3</sub>	6.6	0.30	0.33	0.31	286	828
HFE-245fa2	CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	5.5	0.31	0.39	0.36	659	812
2,2,3,3,3- Pentafluoropropan-1-ol	CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> OH	0.3	0.24	0.27	0.14	42	19
HFE-254cb1	CH <sub>3</sub> OCF <sub>2</sub> CHF <sub>2</sub>	2.5	0.28	0.30	0.26	359	301
HFE-263fb1	CF <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	23.0 days	0.20	0.21	0.04	11	1
HFE-263m1	CF <sub>3</sub> OCH <sub>2</sub> CH <sub>3</sub>	0.4		0.22	0.13		29
3,3,3-Trifluoropropan-1-ol	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	12.0 days		0.20	0.02		0
HFE-329mcc2	CHF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub>	22.5	0.49	0.54	0.53	919	3,070
HFE-338mmz1	CF <sub>3</sub> (CF <sub>3</sub> ) <sub>2</sub> CHOCHF	21.2	0.41	0.45	0.44	380	2,620
HFE-338mcf2	CF <sub>3</sub> CH <sub>2</sub> OCF <sub>2</sub> C F <sub>3</sub>	7.5	0.43	0.47	0.44	552	929
Sevoflurane (HFE- 347mmz1)	(CF <sub>3</sub> ) <sub>2</sub> CHOCH <sub>2</sub> F	2.2		0.37	0.32		216
HFE-347mcc3 (HFE-7000)	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> C F <sub>3</sub>	5.0	0.34	0.37	0.35	575	530
HFE-347mcf2	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	6.6	0.41	0.45	0.42	374	854
HFE-347pcf2	CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	6.0	0.25	0.52	0.48	580	889
HFE-347mmy1	(CF <sub>3</sub> ) <sub>2</sub> CFOCH <sub>3</sub>	3.7	0.31	0.35	0.32	343	363
HFE-356mec3	CH <sub>3</sub> OCF <sub>2</sub> CHFC F <sub>3</sub>	3.8	0.30	0.33	0.30	101	387
HFE-356mff2	CF <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> C F <sub>3</sub>	105.0 days		0.36	0.17		17
HFE-356pcf2	CHF <sub>2</sub> CH <sub>2</sub> OCF <sub>2</sub> CHF <sub>2</sub>	5.7	0.37	0.40	0.37	265	719
HFE-356pcf3	CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>2</sub> CHF <sub>2</sub>	3.5	0.39	0.42	0.38	502	446
HFE-356pcc3	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> C	3.8	0.33	0.36	0.32	110	413

HFE-356mmz1	HF <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub> CHOCH <sub>3</sub>	97.1 days	0.30	0.33	0.15	27	14
HFE-365mcf3	CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> OC	19.3 days	0.27	0.29	0.05	11	1
HFE-365mcf2	H <sub>3</sub> CF <sub>3</sub> CF <sub>2</sub> OCH <sub>2</sub> C	0.6		0.41	0.26		58
HFE-374pc2	H <sub>3</sub> CHF <sub>2</sub> CF <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	5.0	0.25	0.32	0.30	557	627
4,4,4-Trifluorobutan-1-ol	CF <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> O H	4.0 days		0.12	0.01		0
1,1,1,3,3,3-Hexafluoro-2- (trifluoromethyl)-2- propanol	(CF <sub>3</sub> ) <sub>3</sub> COH			0.38			
2,2,3,3,4,4,5,5- Octafluorocyclopentanol	-(CF <sub>2</sub> ) <sub>4</sub> CH(OH)-	0.3	0.30	0.33	0.16	73	13
HFE-43-10pccc124 (H-Galden 1040x, HG-11)	CHF <sub>2</sub> OCF <sub>2</sub> OC <sub>2</sub> F <sub>4</sub> OCHF <sub>2</sub>	13.5	1.37	1.06	1.02	1,870	2,820
HFE-449s1 (HFE-7100)	C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>	4.7	0.31	0.40	0.36	297	421
n-HFE-7100	n-C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>	4.7		0.46	0.42		486
<i>i</i> -HFE-7100	i-C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>	4.7		0.38	0.35		407
HFE-569sf2 (HFE-7200)	$C_4F_9OC_2H_5$	0.8	0.30	0.44	0.30	59	57
n-HFE-7200	$n-C_4F_9OC_2H_5$	0.8		0.49	0.35		65
i-HFE-7200	$i-C_4F_9OC_2H_5$	0.8		0.36	0.25		44
HFE-236ca12 (HG-10)	CHF <sub>2</sub> OCF <sub>2</sub> OCH F <sub>2</sub>	25.0	0.66	0.67	0.65	2,800	5,350
HFE-338pcc13 (HG-01)	CHF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCHF <sub>2</sub>	12.9	0.87	0.89	0.86	1,500	2,910
1,1,1,3,3,3- Hexafluoropropan-2-ol	(CF <sub>3</sub> ) <sub>2</sub> CHOH	1.9	0.28	0.31	0.26	195	182
HG-02	HF <sub>2</sub> C– (OCF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> – OCF <sub>2</sub> H	12.9		1.29	1.24		2,730
HG-03	HF <sub>2</sub> C– (OCF <sub>2</sub> CF <sub>2</sub> ) <sub>3</sub> – OCF <sub>2</sub> H	12.9		1.83	1.76		2,850
HG-20	HF <sub>2</sub> C–(OCF <sub>2</sub> ) <sub>2</sub> – OCF <sub>2</sub> H HF <sub>2</sub> C–	25.0		0.94	0.92		5,300
HG-21	OCF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> OCF <sub>2</sub> O-CF <sub>2</sub> H	13.5		1.78	1.71		3,890
HG-30	HF <sub>2</sub> C–(OCF <sub>2</sub> ) <sub>3</sub> – OCF <sub>2</sub> H	25.0		1.69	1.65		7,330
1-Ethoxy-1,1,2,2,3,3,3- heptafluoropropane	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> OC H <sub>2</sub> CH <sub>3</sub>	0.8		0.41	0.28		61
Fluoroxene	CF <sub>3</sub> CH <sub>2</sub> OCH=C H <sub>2</sub>	3.6 days		0.28	0.01		0
1,1,2,2-Tetrafluoro-1- (fluoromethoxy)ethane 2-Ethoxy-3,3,4,4,5-	CH <sub>2</sub> FOCF <sub>2</sub> CF <sub>2</sub> H	6.2		0.37	0.34		871
pentafluorotetrahydro-2,5- bis[1,2,2,2-tetrafluoro-1- (trifluoromethyl)ethyl]-	$C_{12}H_5F_{19}O_2$	1.0		0.66	0.49		56
furan Fluoro(methoxy)methane	CH <sub>3</sub> OCH <sub>2</sub> F	73.0 days		0.165	0.07		13
Difluoro(methoxy)methan e	CH <sub>3</sub> OCHF <sub>2</sub>	1.1		0.23	0.17		144
Fluoro(fluoromethoxy)me thane	CH <sub>2</sub> FOCH <sub>2</sub> F	0.9		0.27	0.19		130
Difluoro(fluoromethoxy)	CH <sub>2</sub> FOCHF <sub>2</sub>	3.3		0.34	0.30		617

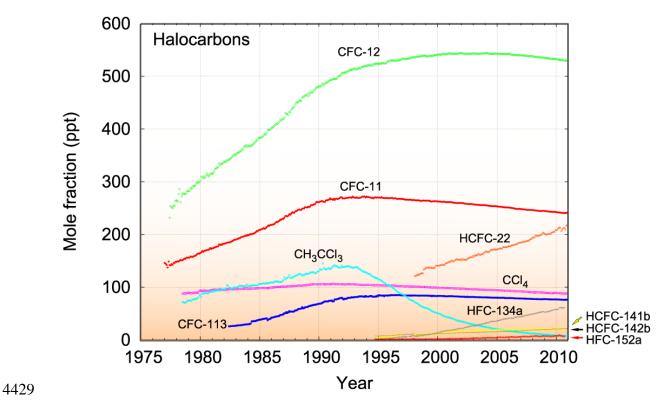
methane Trifluoro(fluoromethoxy) methane	CH <sub>2</sub> FOCF <sub>3</sub>	4.4		0.36	0.33	751
HG'-01	CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> O CH <sub>3</sub>	2.0		0.35	0.29	222
HG'-02	CH <sub>3</sub> O(CF <sub>2</sub> CF <sub>2</sub> O ) <sub>2</sub> CH <sub>3</sub>	2.0		0.67	0.56	236
HG'-03	CH <sub>3</sub> O(CF <sub>2</sub> CF <sub>2</sub> O ) <sub>3</sub> CH <sub>3</sub>	2.0		0.91	0.76	221
HG'-10	CH <sub>3</sub> OCF <sub>2</sub> OCH <sub>3</sub>			0.26		
HG'-20	CH <sub>3</sub> O(CF <sub>2</sub> O) <sub>2</sub> C H <sub>3</sub>			0.72		
HG'-30	CH <sub>3</sub> O(CF <sub>2</sub> O) <sub>3</sub> C H <sub>3</sub>			1.14		
HFE-329me3	CF <sub>3</sub> CFHCF <sub>2</sub> OC F <sub>3</sub>	40.0		0.48	0.48	4,550
HFE-338mec3	CF <sub>3</sub> CFHCF <sub>2</sub> OC F <sub>2</sub> H			0.51		
3,3,4,4,5,5,6,6,7,7,7- Undecafluoroheptan-1-ol	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> C H <sub>2</sub> OH	20.0 days		0.37	0.06	0
3,3,4,4,5,5,6,6,7,7,8,8,9,9, 9-Pentadecafluorononan- 1-ol	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> C H <sub>2</sub> OH	20.0 days		0.41	0.07	0
3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,11,11,11- Nonadecafluoroundecan- 1-ol	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> C H <sub>2</sub> OH	20.0 days		0.31	0.05	0
2-Chloro-1,1,2-trifluoro- 1-methoxyethane	CH <sub>3</sub> OCF <sub>2</sub> CHFC 1	1.4		0.27	0.21	122
PFPMIE (perfluoropolymethyliso	CF <sub>3</sub> OCF(CF <sub>3</sub> )C F <sub>2</sub> OCF <sub>2</sub> OCF <sub>3</sub>	800.0	0.65	0.66	<b>0.65</b> 10,300	9,710
<b>propyl)</b> HFE-216	CF <sub>3</sub> OCF=CF <sub>2</sub>	8.4 days		0.30	0.02	0
Trifluoro(trifluoromethox	CF <sub>3</sub> OCF <sub>3</sub>	o aa,s		0.53	0.02	v
y)methane		2.5			0.21	<b>500</b>
Trifluoromethyl formate Perfluoroethyl formate	HCOOCF <sub>3</sub> HCOOCF <sub>2</sub> CF <sub>3</sub>	3.5 3.5		0.35 0.49	0.31 0.44	588 580
Perfluoropropyl formate	HCOOCF <sub>2</sub> CF <sub>2</sub> C F <sub>3</sub>	2.6		0.58	0.50	376
Perfluorobutyl formate	HCOOCF <sub>2</sub> CF <sub>2</sub> C F <sub>2</sub> CF <sub>3</sub>	3.0		0.63	0.56	392
2,2,2-Trifluoroethyl formate	HCOOCH <sub>2</sub> CF <sub>3</sub>	0.4		0.27	0.16	33
3,3,3-Trifluoropropyl formate	HCOOCH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	0.3		0.27	0.13	17
1,2,2,2-Tetrafluoroethyl formate	HCOOCHFCF <sub>3</sub>	3.2		0.39	0.35	470
1,1,1,3,3,3- Hexafluoropropan-2-yl formate	HCOOCH(CF <sub>3</sub> )	3.2		0.37	0.33	333
Perfluorobutyl acetate	CH <sub>3</sub> COOCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	21.9 days		0.70	0.12	2
Perfluoropropyl acetate	CH <sub>3</sub> COOCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	21.9 days		0.60	0.11	2
Perfluoroethyl acetate	CH <sub>3</sub> COOCF <sub>2</sub> CF	21.9 days		0.56	0.10	2
Trifluoromethyl acetate Methyl carbonofluoridate Fluoromethyl	CH <sub>3</sub> COOCF <sub>3</sub> FCOOCH <sub>3</sub> FCOOCFH <sub>2</sub>	21.9 days 1.8		0.41 0.08 <b>0.19</b>	0.07 0.07	2 95

carbonofluoridate Difluoromethyl	FCOOCF <sub>2</sub> H		0.33		
carbonofluoridate Trifluoromethyl					
carbonofluoridate Perfluoroethyl	FCOOCF <sub>3</sub>		0.32		
carbonofluoridate	FCOOCF <sub>2</sub> CF <sub>3</sub>		0.48		
2,2,2-Trifluoroethyl carbonofluoridate	FCOOCH <sub>2</sub> CF <sub>3</sub>		0.33		
1,1-Difluoroethyl carbonofluoridate	FCOOCF <sub>2</sub> CH <sub>3</sub>	0.3	0.33	0.17	27
Perfluoropropyl	FCOOCF <sub>2</sub> CF <sub>2</sub> C		0.53		
carbonofluoridate Trifluoromethyl 2,2,2-	$F_3$		0.22		
trifluoroacetate	CF <sub>3</sub> COOCF <sub>3</sub>		0.49		
Perfluoroethyl 2,2,2-	CF <sub>3</sub> COOCF <sub>2</sub> CF		0.62		
trifluoroacetate 1,1-Difluoroethyl 2,2,2-	<sup>3</sup> CF <sub>3</sub> COOCF <sub>2</sub> CH	0.3	0.53	0.27	31
trifluoroacetate	3	0.3	0.55	0.27	31
1,1,1,3,3,3- Hexafluoropropan-2-yl 2,2,2-trifluoroacetate	CF <sub>3</sub> COOCH(CF <sub>3</sub> ) <sub>2</sub>		0.49		
Vinyl 2,2,2- trifluoroacetate	CF <sub>3</sub> COOCH=C H <sub>2</sub>		0.39		
Ethyl 2,2,2- trifluoroacetate	CF <sub>3</sub> COOCH <sub>2</sub> C H <sub>3</sub>	21.9 days	0.30	0.05	1
2,2,2-Trifluoroethyl 2,2,2-trifluoroacetate	CF <sub>3</sub> COOCH <sub>2</sub> CF	54.8 days	0.43	0.15	7
Allyl 2,2,2-trifluoroacetate	CF <sub>3</sub> COOCH <sub>2</sub> C HCH <sub>2</sub>		0.35		
Methyl 2,2,2- trifluoroacetate	CF <sub>3</sub> COOCH <sub>3</sub>	0.6	0.28	0.18	52
Phenyl 2,2,2-	CF <sub>3</sub> COOPh		0.39		
trifluoroacetate Methyl 2-fluoroacetate	H <sub>2</sub> CFCOOCH <sub>3</sub>		0.08		
Difluoromethyl 2,2-	HCF <sub>2</sub> COOCHF <sub>2</sub>		0.44		
difluoroacetate		40.1 dana		0.05	2
Methyl 2,2-difluoroacetate Difluoromethyl 2,2,2-	HCF <sub>2</sub> COOCH <sub>3</sub>	40.1 days	0.19	0.05	3
trifluoroacetate	CF <sub>3</sub> COOCHF <sub>2</sub>	0.3	0.49	0.24	27
2,2,3,3,4,4,4- Heptafluorobutan-1-ol	C <sub>3</sub> F <sub>7</sub> CH <sub>2</sub> OH	0.6	0.32	0.20	34
1,1,2-Trifluoro-2- (trifluoromethoxy)-ethane	CHF <sub>2</sub> CHFOCF <sub>3</sub>	9.8	0.36	0.35	1,240
1-Ethoxy-1,1,2,3,3,3-	CF <sub>3</sub> CHFCF <sub>2</sub> OC	0.4	0.35	0.19	23
hexafluoropropane 1,1,1,2,2,3,3-Heptafluoro-	$H_2CH_3$				
3-(1,2,2,2-	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> OC	67.0	0.59	0.58	6,490
tetrafluoroethoxy)- propane	HFCF <sub>3</sub>				,
2,2,3,3-Tetrafluoro-1-	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> O	91.3 days	0.25	0.11	13
propanol 2,2,3,4,4,4-Hexafluoro-1-	H CF <sub>3</sub> CHFCF <sub>2</sub> CH				
butanol	$_2$ OH	94.9 days	0.43	0.19	17
2,2,3,3,4,4,4-Heptafluoro- 1-butanol	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> OH	0.3	0.31	0.16	16
1,1,2,2-Tetrafluoro-3- methoxy-propane	CHF <sub>2</sub> CF <sub>2</sub> CH <sub>2</sub> O CH <sub>3</sub>	14.2 days	0.25	0.03	1
Perfluoro-2-methyl-3-	CF <sub>3</sub> CF <sub>2</sub> C(O)CF(	7.0 days	0.41	0.03	0

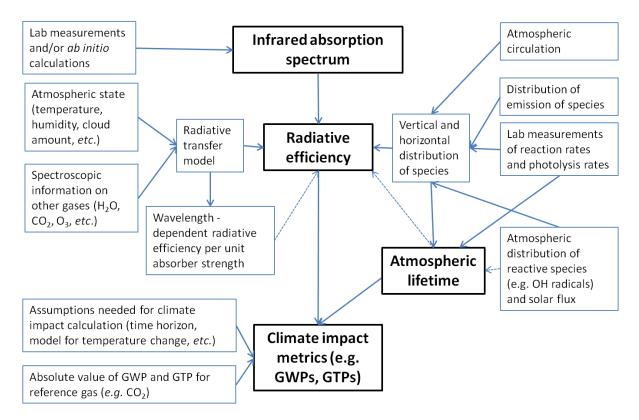
pentanone	$CF_3)_2$				
3,3,3-Trifluoro-propanal	CF <sub>3</sub> CH <sub>2</sub> CHO	2.0 days	0.16	0.00	0
4,4,4-Trifluorobutanal	CF <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO		0.16		
2-Fluoroethanol	CH <sub>2</sub> FCH <sub>2</sub> OH	20.4 days	0.10	0.02	1
2,2-Difluoroethanol	CHF <sub>2</sub> CH <sub>2</sub> OH	40.0 days	0.13	0.04	3
2,2,2-Trifluoroethanol	CF <sub>3</sub> CH <sub>2</sub> OH	0.3	0.20	0.10	20
1,1'-Oxybis[2- (difluoromethoxy)- 1,1,2,2-tetrafluoroethane	HCF <sub>2</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>2</sub> CF <sub>2</sub> H	26.0	1.18	1.15	4,920
1,1,3,3,4,4,6,6,7,7,9,9,10,1 0,12,12-hexadecafluoro- 2,5,8,11- Tetraoxadodecane	HCF <sub>2</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>3</sub> CF <sub>2</sub> H	26.0	1.46	1.43	4,490
1,1,3,3,4,4,6,6,7,7,9,9,10,1 0,12,12,13,13,15,15- eicosafluoro-2,5,8,11,14- Pentaoxapentadecane	HCF <sub>2</sub> O(CF <sub>2</sub> CF <sub>2</sub> O) <sub>4</sub> CF <sub>2</sub> H	26.0	1.50	1.46	3,630

Table 16. GWP and GTP for selected gases.

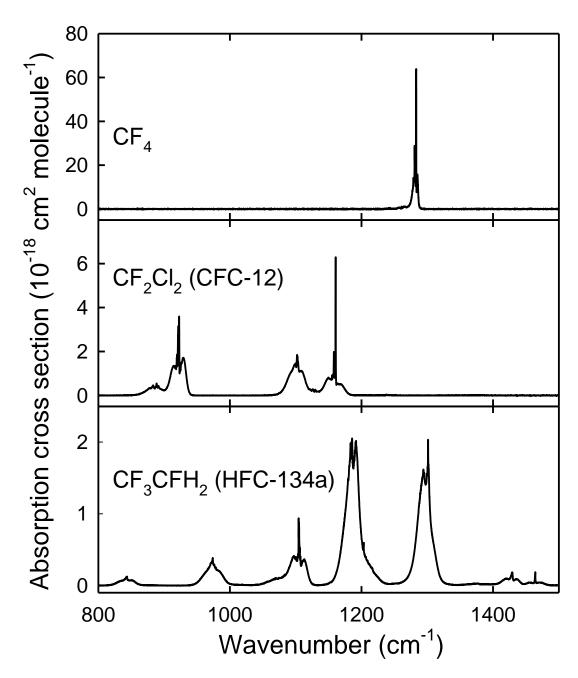
				GWP			GTP		
Acronym / name	Formula	Lifetime (yr)	RE (W m <sup>-</sup> 2 ppb <sup>-1</sup> )	20-yr	100-yr	500-yr	20-yr	50-yr	100-yr
CFC-11	CCl <sub>3</sub> F	45.0	0.26	6,900	4,660	1,490	6,890	4,890	2,340
CFC-12	$CCl_2F_2$	100.0	0.32	10,800	10,200	4,590	11,300	11,000	8,450
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	85.0	0.30	6,490	5,820	2,390	6,730	6,250	4,470
HCFC-22	CHClF <sub>2</sub>	11.9	0.21	5,280	1,760	503	4,200	832	262
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	9.2	0.16	2,550	782	223	1,850	271	111
HCFC-142b	CH <sub>3</sub> CClF <sub>2</sub>	17.2	0.19	5,020	1,980	567	4,390	1,370	356
HFC-23	$CHF_3$	222.0	0.18	10,800	12,400	8,720	11,500	13,000	12,700
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	13.4	0.16	3,710	1,300	371	3,050	703	201
HFC-152a	$CH_3CHF_2$	1.5	0.10	506	138	39	174	24	19
Methyl chloroform	CH <sub>3</sub> CCl <sub>3</sub>	5.0	0.07	578	160	46	317	34	22
Carbon tetrachloride	CCl <sub>4</sub>	26.0	0.17	3,480	1,730	504	3,280	1,570	479
Sulphur hexafluoride	SF <sub>6</sub>	3,200.0	0.57	17,500	23,500	31,500	18,900	23,800	28,200
PFC-14	$CF_4$	50,000.0	0.09	4,880	6,630	9,410	5,270	6,690	8,040



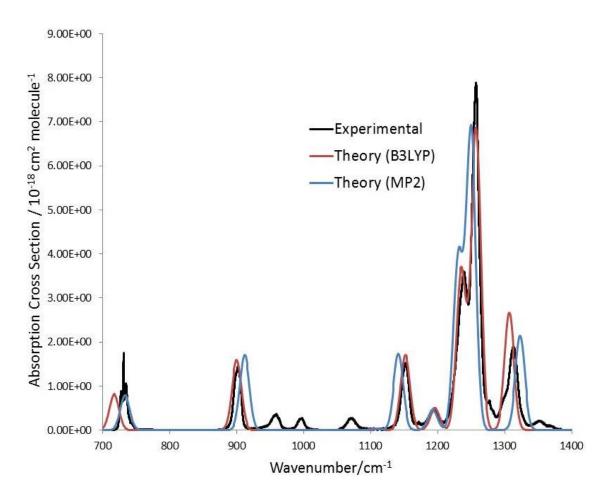
**Figure 1.** Atmospheric concentrations of 10 halocarbons from 1977-2010 averaged over the greenhouse gas monitoring network (between 7 and 10 stations) [from *WMO/GAW*, 2011].



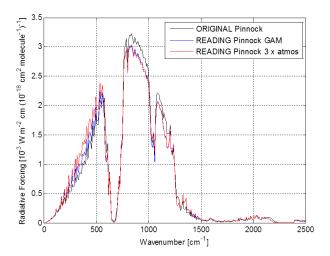
**Figure 2.** Schematic figure showing the main parameters required to compute climate impact metrics, and the additional inputs required in the calculation of those parameters. Dashed lines show where simpler techniques (based on the more complex models) are often employed (as is the case in this review).

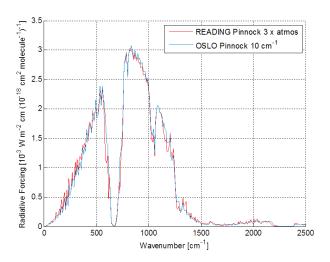


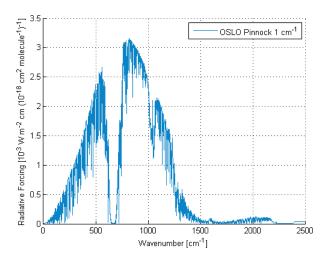
**Figure 3.** IR spectra of CF<sub>4</sub> (top panel), CF<sub>2</sub>Cl<sub>2</sub> (middle panel), and CF<sub>3</sub>CFH<sub>2</sub> (bottom panel) measured using 0.5 cm<sup>-1</sup> spectral resolution in 700 Torr of air diluent at 296 K [*Forster et al.*, 2005; *Hurley et al.*, 2005; *Sihra et al.*, 2001].



**Figure 4.** Comparison of experimental and theoretical (B3LYP/6-31G\*\*, MP2/6-31G\*\*) spectra for n-C<sub>4</sub>F<sub>10</sub>. The theoretical spectra were modeled using Gaussian functions of 14 cm<sup>-1</sup> full width. Data taken from *Bravo et al.* [2010b].



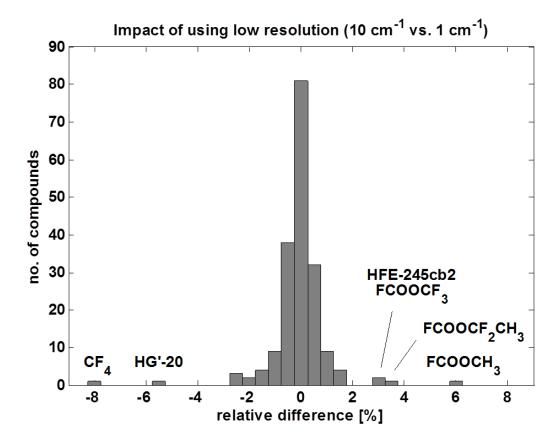




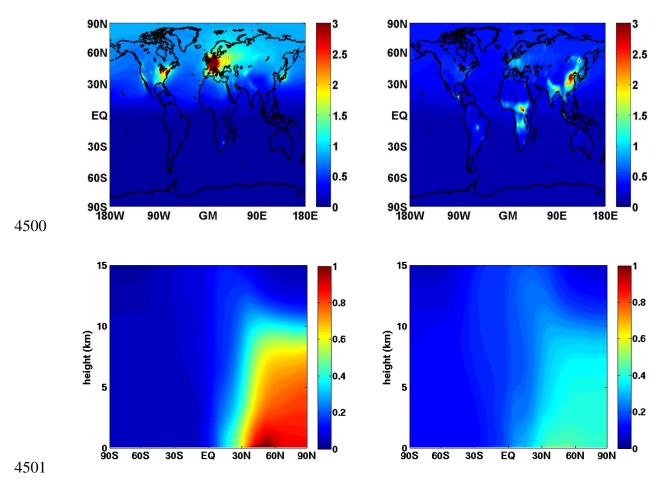
**Figure 5.** Radiative forcing efficiency (for a 0-1 ppb increase in mixing ratio) per unit cross section compared between the *Pinnock et al.* [1995] study and this study. The top panel shows the progression from the original Pinnock plot (using the Reading Narrow Band Model (NBM)) on incorporating an updated global-annual mean atmosphere (GAM) and then incorporating three atmospheres representing the tropics and extra-tropics, all at a

resolution of 10 cm<sup>-1</sup>. The middle panel shows a comparison of the Reading NBM and the Oslo Line-by-Line (LBL) model averaged to 10 cm<sup>-1</sup> resolution, using atmospheres representing the tropics and extra-tropics. The bottom panel shows the results from the Oslo LBL model at a resolution of 1 cm<sup>-1</sup>.

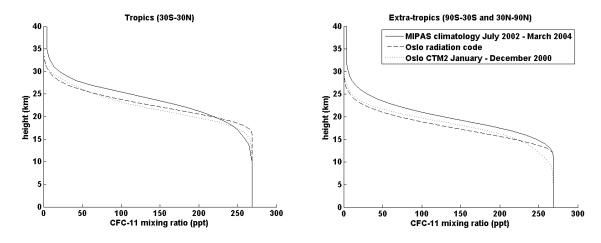




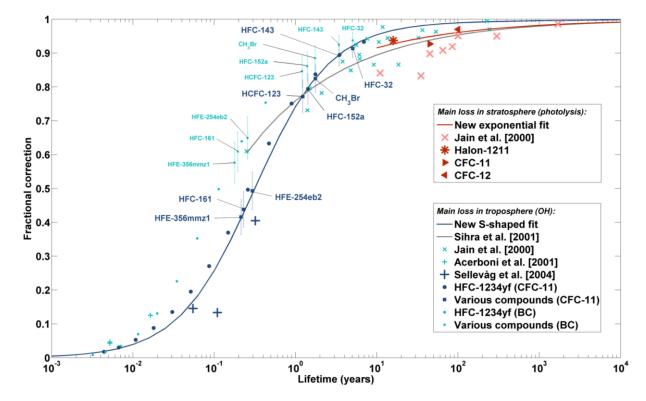
**Figure 6.** Relative difference in calculation of RE using 1 cm<sup>-1</sup> and 10 cm<sup>-1</sup> with the Pinnock plot shown in Figure 5 of the compounds investigated in this study. The original LBL calculations are performed with 0.2 cm<sup>-1</sup> and then converted to 1 cm<sup>-1</sup> and 10 cm<sup>-1</sup>.



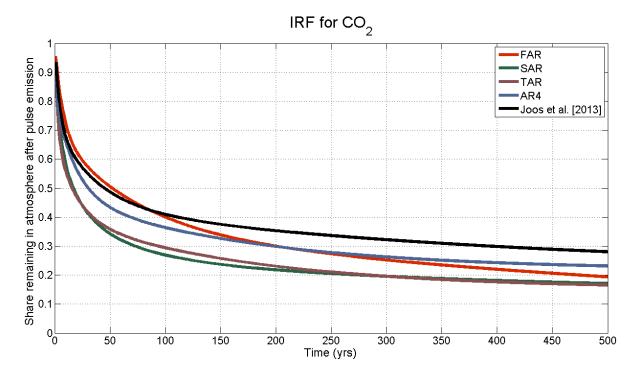
**Figure 7.** Annual average distribution of HFC-161 mixing ratio (ppb) at the surface (top panels) and averaged zonally (bottom) for the reference simulation with emission distribution as for CFC-11 (left) and the sensitivity simulation with emission distribution as for BC (right) calculated with the Oslo CTM2 model (see text for details).



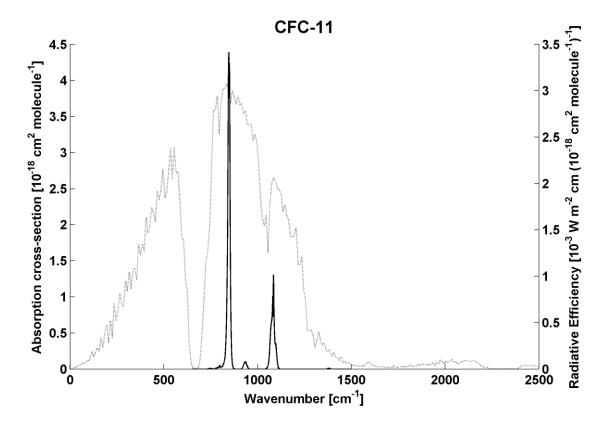
**Figure 8.** Vertical profiles of CFC-11 mixing ratio (ppt) in the tropics (left) and the extratropics (right) from MIPAS observations [*Hoffmann et al.*, 2008], the Oslo radiation code, and the Oslo CTM2 model. The profiles have been scaled to the year 1994 tropospheric mixing ratio of 269 ppt as in *Minschwaner et al.* [2012].



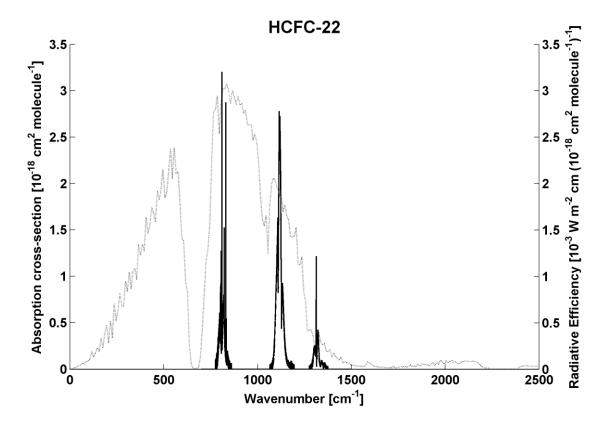
**Figure 9.** Factor needed to correct RE to account for non-uniform vertical and horizontal distribution versus atmospheric lifetime. The red symbols are for compounds whose main loss mechanism is stratospheric photolysis while the blue symbols are for compounds which are mainly lost in the troposphere by reaction with OH. Dark blue symbols have been used in the calculation of the *S*-shaped fit and dark red symbols have been used in the calculation of the exponential fit. Light blue and light red symbols are shown for comparison. The curve from *Sihra et al.* [2001] represents an empirical least squares fit to the fractional correction factors from *Jain et al.* [2000]. The parentheses designate whether the results are from the simulations with "CFC-11-like" or "BC-like" emission distribution. For the compounds where several different absorption bands have been used in the RF calculations, both the mean and the standard deviation of the fractional corrections are shown.



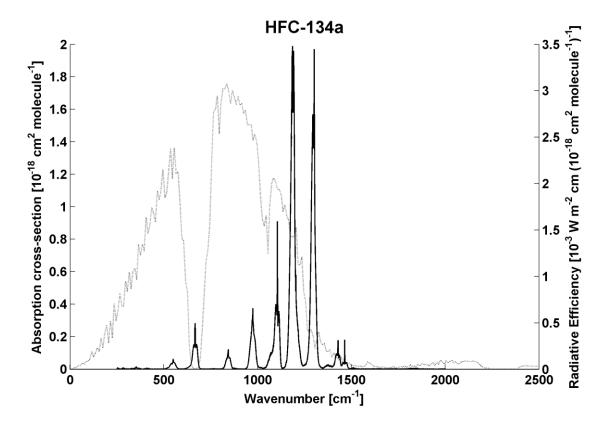
**Figure 10.** Impulse response functions from the four IPCC assessments and from the recent multi-model study of *Joos et al.* [2013]. Note that the IRF from FAR [*IPCC*, 1990] and SAR [*IPCC*, 1995] did not include climate-carbon cycle feedbacks, while these are included in IRFs from TAR [*IPCC*, 2001], AR4 [*IPCC*, 2007] and *Joos et al.* [2013].



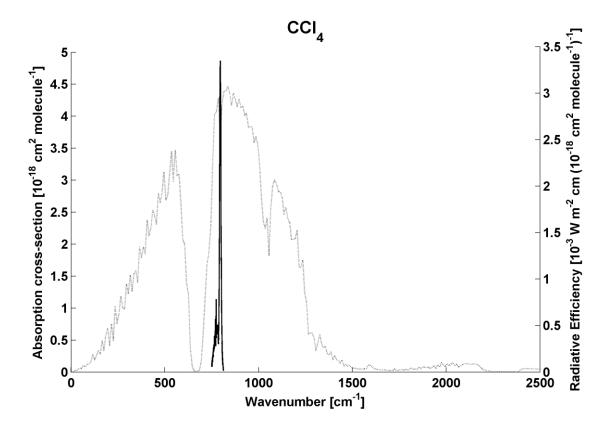
**Figure 11.** Absorption spectrum of CFC-11 at 296 K in 933 hPa (700 Torr) air diluent from *Sihra et al.* [2001] (solid line) and Oslo simulation of Pinnock curve (dotted line).



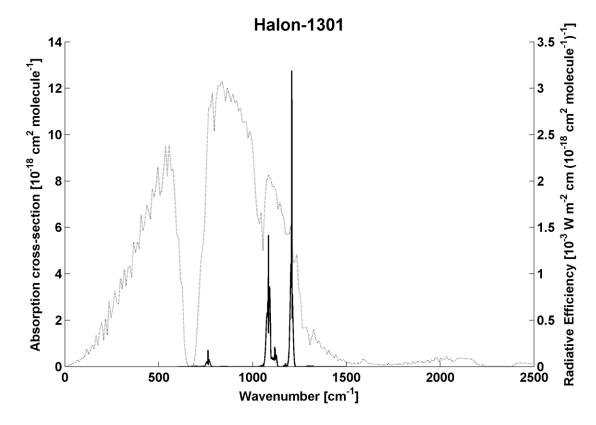
**Figure 12.** Absorption spectrum of HCFC-22 at 293 K in 800 hPa air diluent from *Ballard et al.* [2000b] (solid line) and Oslo simulation of Pinnock curve (dotted line).



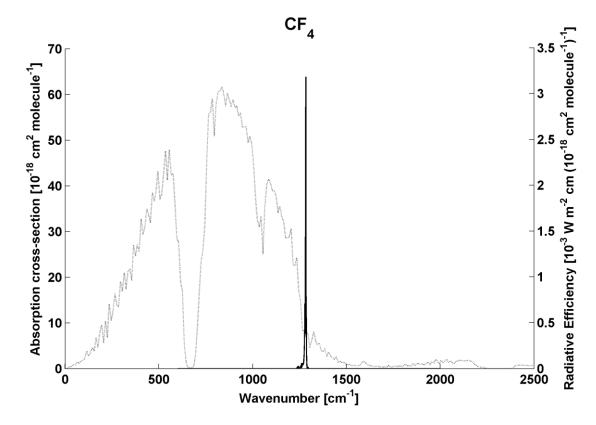
**Figure 13.** Absorption cross-section of HFC-134a from *Forster et al.* [2005] (solid line) and Oslo simulation of Pinnock curve (dotted line). The spectrum is a composite of measurements from five laboratory groups and has been measured under various temperatures and diluent gas pressures.



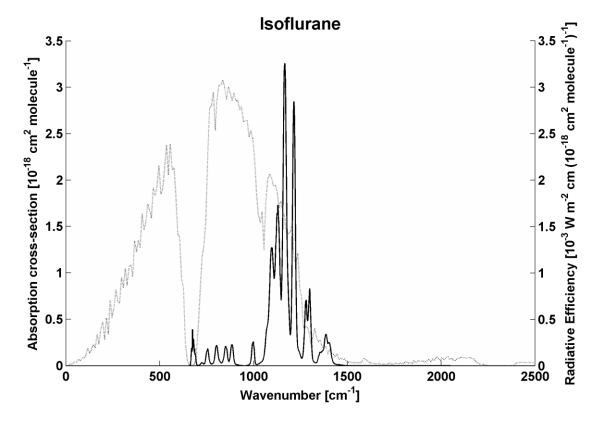
**Figure 14.** Absorption spectrum of CCl<sub>4</sub> at 296 K from *Nemtchinov and Varanasi* [2003] (solid line) and Oslo simulation of Pinnock curve (dotted line).



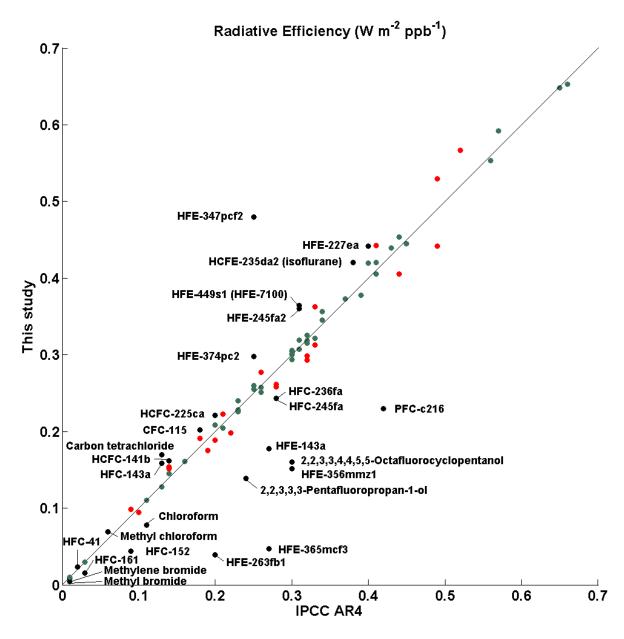
**Figure 15.** Absorption spectrum of Halon-1301 at 296 K in 933 hPa (700 Torr) air diluent from *Sihra et al.* [2001] (solid line) and Oslo simulation of Pinnock curve (dotted line).



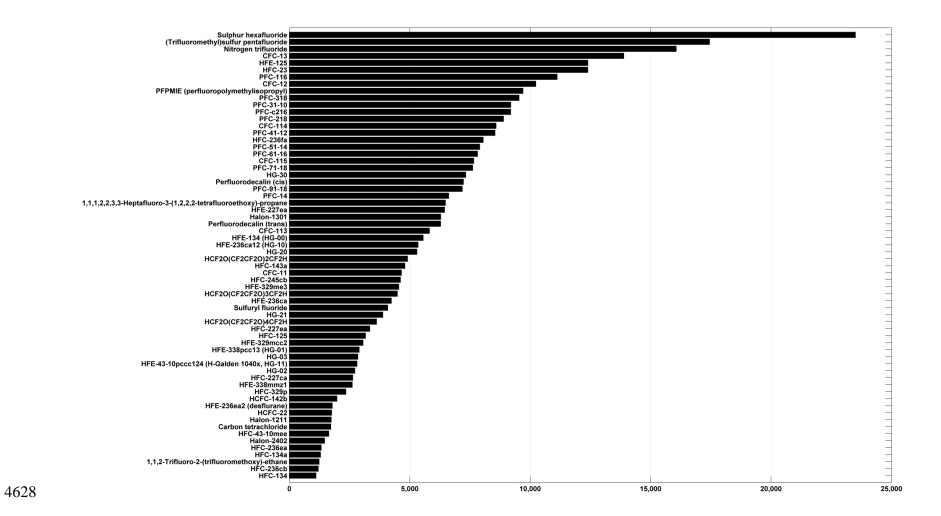
**Figure 16**. Absorption spectrum of CF<sub>4</sub> at 296 K in 933 hPa (700 Torr) air diluent from *Sihra et al.* [2001] (solid line) and Oslo simulation of Pinnock curve (dotted line).

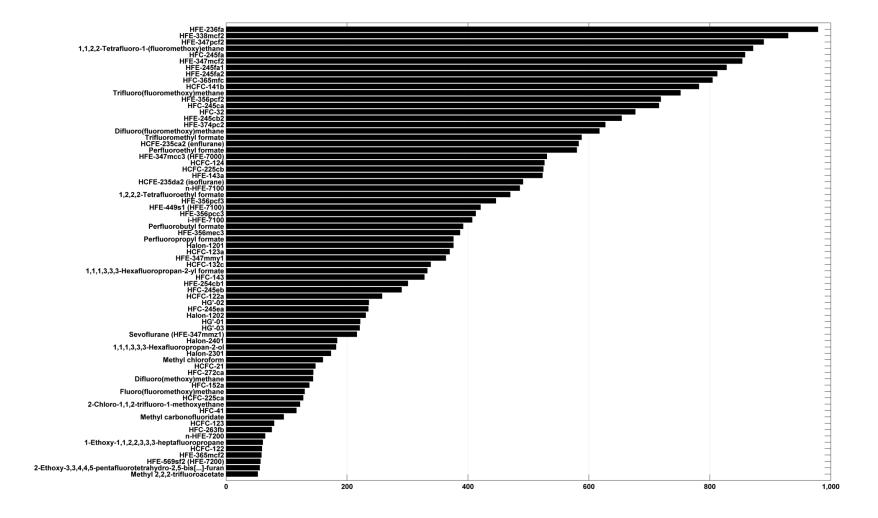


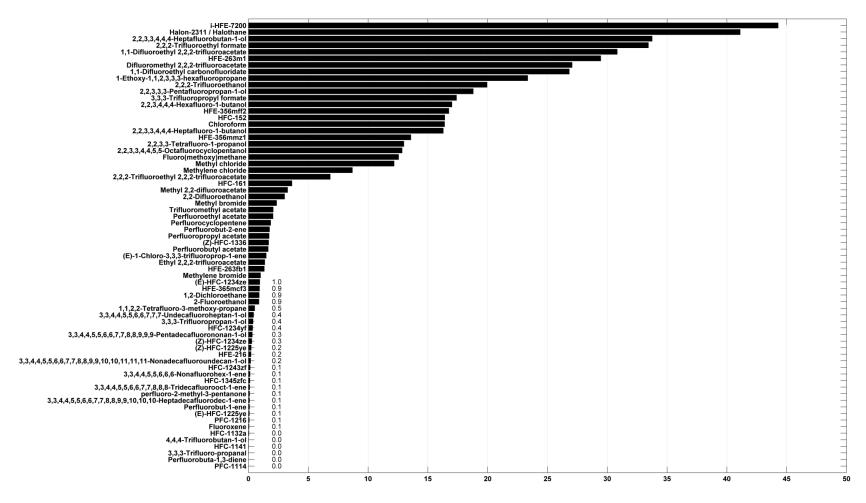
**Figure 17.** Absorption spectrum of isoflurane at 296 K in 933 mbar (700 Torr) air diluent from *Andersen et al.* [2010c] (solid line) and Oslo simulation of Pinnock curve (dotted line).



**Figure 18.** Comparison of radiative efficiencies calculated in this study (lifetime-corrected adjusted cloudy-sky) and from AR4 [*Forster et al.*, 2007]. Green dots represent compounds where the RE in this study is less than 5% different from AR4, while red and black dots represent compounds where the REs are significantly different (>5% and >10%, respectively). Black dots have been labeled and represent compounds where the RE calculated here is more than 10% different from AR4. Two compounds are off scale and therefore not shown in the plot: HFE-43-10pccc124 (H-Galden 1040x, HG-11) with a RE of 1.02 W m<sup>-2</sup> ppb<sup>-1</sup> calculated in the present study (compared to 1.37 W m<sup>-2</sup> ppb<sup>-1</sup> in AR4), and HFE-338pcc13 (HG-01) with a RE of 0.86 W m<sup>-2</sup> ppb<sup>-1</sup> calculated in the present study (compared to 0.87 W m<sup>-2</sup> ppb<sup>-1</sup> in AR4).







**Figure 19.** GWP 100-yr of all compounds calculated in this study.