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1 Radiative Efficiencies for Fluorinated Esters: Indirect 2 Global Warming Potentials of Hydrofluoroethers

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12 **Abstract**

13 Density Functional Theory (DFT) has been used with an empirically-derived correction for the
14 wavenumbers of vibrational band positions to predict the infrared spectra of several fluorinated esters
15 (FESs). Radiative efficiencies (REs) were then determined using the Pinnock et al. method and these
16 were used with atmospheric lifetimes from the literature to determine the direct global warming
17 potentials of FESs. FESs, in particular fluoroalkylacetates, alkylfluoroacetates and
18 fluoroalkylformates, are potential greenhouse gases and their likely long atmospheric lifetimes and
19 relatively large REs, compared to their parent HFEs, make them active contributors to global
20 warming. Here, we use the concept of indirect global warming potential (indirect GWP) to assess the
21 contribution to the warming of several commonly used HFEs emitted from the Earth's surface,
22 explicitly taking into account that these HFEs will be converted into the corresponding FESs in the
23 troposphere. The indirect GWP can be calculated using the radiative efficiencies and lifetimes of the
24 HFE and its degradation FES products. We found that the GWPs of the HFEs studied can be increased
25 by 100-1600 % when taking account of the cumulative effect due to the secondary FESs formed
26 during HFE atmospheric oxidation. This effect may be particularly important for non-segregated HFEs
27 and some segregated HFEs, which may contribute significantly more to global warming than can be
28 concluded from examination of their direct GWPs.

29

30

1. Introduction

Hydrofluoroethers (HFEs) are being used as chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), hydrofluorocarbon (HFC) and perfluorocarbon (PFC) replacements in a number of industrial applications, such as their use as cleaning solvents, heat transfer agents in refrigeration, carrier fluids or even as anaesthetic agents in the pharmaceutical industry.^{[1],[2],[3]} These HFEs possess zero ozone depletion potentials since they do not contain Cl atoms. HFEs were designed to react easily with OH radicals in the troposphere because of the inclusion of H atoms in the structure, which minimizes their contribution to global warming. Several studies have been carried out to determine the impact that HFEs have on climate, through the measurement of infrared spectra, atmospheric lifetimes (τ), radiative efficiencies (REs) and global warming potentials (GWPs) (see e.g. Sihra et al, 2001^[4] and Bravo et al., 2010^[5]). However, although HFEs may be destroyed relatively quickly in the atmosphere, this process does not remove the C-F bonds, which can still absorb IR radiation and stay in the troposphere for longer periods of time. It is important therefore to understand the mechanisms of HFE oxidation in the atmosphere and the impact on climate of their degradation products.

It is well known that fluorinated esters (FESs) are the primary products of the atmospheric oxidation of HFEs (see e.g. Wallington et al. 1997^[6], Christensen et al. 1998^[7], 1999^[8]; Ninomiya et al., 2000^[9] and Oyaro et al., 2004^[10]). Like most organic compounds, FESs containing C-H bonds are removed from the troposphere by reactions with atmospheric oxidants, with reaction with OH radicals being their primary removal process.^{[11],[12],[13],[14]} Dissolution in seawater and clouds has been considered a potentially significant sink since some FESs are known to be readily hydrolyzed.^[15] However, there are insufficient Henry's Law and solubility data available for FESs to fully assess this loss process. Some recent studies have revealed that dissolution in clouds might not be an important atmospheric sink for FESs whereas dissolution in oceans could be a more efficient pathway.^[16] This means that wet deposition in clouds is perhaps not such an important sink as previously believed and FESs will remain in the troposphere until they are removed by OH or are dissolved in the ocean. Taking into account the fact that other chemical degradation processes such as reactions with Cl, NO₃ or O₃, along with photolysis, are considered to be unimportant atmospheric degradation pathways for FESs,^{[14], [15]} their tropospheric lifetimes are expected to be determined mainly by OH radicals.

The atmospheric oxidation of HFEs will lead to different sets of FESs depending on the parent HFE molecule. For *segregated* HFEs, in which the perfluorinated part of the molecule is separated from the fully hydrogenated part by the ether oxygen (R_HOR_F), segregated fluorinated esters are the primary oxidation products. For instance, the *perfluoroalkylformates* C₄F₉OC(O)H and n-C₃F₇OC(O)H are the major degradation products of HFE-7100 (C₄F₉OCH₃) and HFE-7000 (C₃F₇OCH₃), respectively.^{[6], [9]}

66 On the other hand, the *perfluoroalkylacetate* $C_4F_9OC(O)CH_3$ is the major product for HFE-7200
67 ($C_4F_9OCH_2CH_3$).^[7] Non-segregated HFEs have hydrogen and/or fluorine atom on both sides of the
68 ether link, and their oxidation products depend on which H atom can be more easily abstracted. For
69 example, Chen et al.^[13] reported $CF_3CHFOC(O)H$ and the *alkylfluoroformate* $FC(O)OCH_3$ as the
70 primary oxidation products of $CF_3CHFOCH_3$. Other groups have reported *alkyl* and
71 *fluoroalkylfluoroacetates* in the HFE atmospheric oxidation, e.g. $CH_3OC(O)CF_3$ from $CH_3OCH(CF_3)_2$
72 oxidation^[17] or $CF_3C(O)OCHF_2$ from $CF_3CHClOCHF_2$ oxidation.^[18] Lastly, some product distribution
73 studies have shown that the FES oxidation leads to the formation of fluorinated acetic acid and the
74 corresponding anhydrides along with CF_2O and its hydrolysis products CO_2 and HF.^{[19], [18], [20]}
75 It is important to assess the environmental compatibility of new chemical compounds and to have an
76 understanding of their impact on global warming. In order to achieve this, it is not enough simply to
77 focus on the radiative properties of the parent compound. It is also important to consider oxidation
78 mechanisms and the radiative properties of stable intermediate products in order to assess their impact
79 on global warming. At present, there are no determinations of REs or GWPs for FESs from direct
80 measurements. In the present study we examine these properties on the basis of previous theoretical
81 and experimental work from our laboratories on the REs and GWPs of HFEs^{[5], [21]} and PFCs^[22]. In
82 our publication on PFCs, we reported a theoretical method for determining infrared spectra and REs
83 (and hence GWPs where an atmospheric lifetime was known or could reasonably be inferred). The
84 calculated RE is extremely sensitive to the exact position of the C-F stretch at around 1250 cm^{-1} and
85 the raw calculated frequencies cannot be used directly in radiative transfer models. Thus, we used a
86 combination of theoretical and experimental results to obtain a very precise correction to the band
87 position generated directly from the density functional theory (DFT) or *ab initio* calculations.
88 Furthermore, in subsequent work^[21], we extended and tested the method for HFEs and
89 hydrofluoropolyethers (HFPEs). The results showed that the method gave predictions in very good
90 agreement with experimental values. One of the aims of the present study is to apply this method to
91 calculate IR spectra and REs for FESs and to predict these quantities for a range of related compounds.
92 This is the first study to report data of cross sections, REs and GWPs for FESs. The FESs studied
93 belong to the series *fluoroalkylformates*, *fluoroalkylacetates*, *fluoroalkylfluoroformates*, and
94 *fluoroalkylfluoroacetates*.

95

96 2. Methodology

97 Radiative forcing per unit concentration change or radiative forcing efficiency, is a fundamental
98 parameter which measures the change in the Earth's radiation balance for a 1 ppbv increase in
99 concentration of the greenhouse gas. For any gas, this efficiency depends on the spectral variation of

100 the absorption cross-section, as the energy available to be absorbed in the atmosphere depends on this
101 *via* both the Planck function and the absorption spectra of other species in the atmosphere [see e.g.
102 Pinnock et al., 1995 ^[23]. Pinnock et al. ^[23] created a simple model for radiative forcing that allows the
103 straightforward determination of the radiative efficiency, *RE*, of a gas from its experimentally
104 measured infrared spectrum without the use of a complex radiative transfer model. In this approach,
105 the *RE* is given by:

$$106 \quad RE = \sum_{i=1}^{250} 10 \overline{\sigma}_i(\overline{\nu}_i) F_i(\overline{\nu}_i) \quad (I)$$

107 where $\overline{\sigma}_i(\overline{\nu}_i)$ is the absorption cross section in $\text{cm}^2 \text{ molecule}^{-1}$ averaged over a 10 cm^{-1} interval around
108 the wavenumber $\overline{\nu}_i$, and $F_i(\overline{\nu}_i)$ is the instantaneous, cloudy sky, radiative forcing per unit cross
109 section in $\text{W m}^{-2} (\text{cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1})^{-1}$ for a 0 to 1 ppbv increase in absorber. The values for $F_i(\overline{\nu}_i)$
110 as a function of wavenumber were determined by Pinnock et al. ^[23] using their narrowband radiative
111 transfer model. This expression can be applied directly to experimentally determined infrared
112 absorption cross sections.

113 The methods used here for the calculation of infrared spectra, REs and GWPs have been described
114 elsewhere ^{[22],[21]} but are briefly set out here. The Gaussian03 software package ^[24] was used to
115 perform the computational calculations. Molecular structures were first optimized at B3LYP/6-31G**
116 level of theory, followed by calculation of vibrational frequencies. No symmetry constraints were
117 imposed and, for all molecules, the absence of negative frequencies confirmed that we had obtained a
118 minimum on the potential energy surface. When more than one minimum was found, the structure
119 with the lowest Gibbs free energy was used for the calculation of radiative efficiencies. Accurate REs
120 can only be obtained for fluorinated compounds if the position of the main C-F stretching vibrational
121 mode is determined very precisely. Following our previous work ^{[22],[21]} we use the expression $\overline{\nu}_{\text{scal}} =$
122 $0.977 \overline{\nu}_{\text{calc}} + 11.664 \text{ cm}^{-1}$ to obtain scaled wavenumbers that are used for the RE calculations. Other
123 groups ^{[25],[26]} have used similar approaches, although usually using a generic correction factor.

124 Furthermore, since the theoretical calculations provide integrated cross sections, A_i , (in $\text{cm}^2 \text{ molecule}^{-1}$
125 cm^{-1}) for each vibrational mode at a precise wavenumber, these data can be converted into average
126 cross sections over 10 cm^{-1} intervals simply by dividing by 10 cm^{-1} . The obtained data are then used
127 to calculate radiative efficiencies and global warming potentials. The overall integrated cross section,
128 S_{calc} is simply the sum of the A_i over the appropriate wavenumber range.

129 Having calculated REs, GWPs over a variety of time horizons can be determined relative to carbon
130 dioxide if the lifetime for the FESs is known or can be estimated (see e.g. IPCC (2007) ^[27])

131 3. Results and Discussion.

132 In this section we present integrated cross sections, REs and GWPs obtained for several fluorinated
133 esters. The FESs expected from the tropospheric oxidation of HFEs may be classified as:
134 *fluoroalkylformates*, HC(O)O-R_F , *fluoroalkylacetates* $\text{CH}_3\text{-C(O)O-R}_F$, *fluoroalkylfluoroformates*
135 FC(O)O-R_F , and *fluoroalkylfluoroacetates* $\text{CF}_3\text{-C(O)-O-R}_F$ where R_F is an alkyl chain with at least one
136 F atom.

137 3.1 Infrared Absorption Cross Sections and Radiative Efficiencies

138 Only a few studies have reported experimental infrared spectra for FESs. These show that FESs are
139 potentially greenhouse gases since they absorb infrared radiation strongly between 1000 and 1400 cm^{-1}
140 ^{[28],[9],[20],[18]}. None of these studies reported integrated cross section data. Our integrated absorption
141 cross sections, S_{calc} , calculated between 0 and 2500 cm^{-1} using B3LYP/6-31G**, are presented in
142 Table 1. (The predicted infrared spectra are presented in the supplementary material).

143 To the best of our knowledge, measurements of REs for FESs have not been reported in the literature.
144 We have used our theoretically determined spectra to calculate REs using the Pinnock et al. ^[23] method
145 as described above in section 2. Predicted REs are summarized in Table 2, where they are compared
146 with previously reported values for the parent HFE. We can see in this table that the majority of FESs
147 possess larger REs than their parent HFEs, even when they have the same number of C-F bonds in the
148 molecular structure. For instance, this is observed in the following selected FES vs HFE couples (REs
149 in $\text{W m}^{-2} \text{ppbv}^{-1}$ given in parentheses): $\text{HC(O)OCF}_2\text{CF}_2\text{CF}_3$ vs. $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_3$ (0.55 vs. 0.37);
150 $\text{CH}_3\text{C(O)OCF}_2\text{CF}_2\text{CF}_3$ vs. $\text{C}_2\text{H}_5\text{OC}_4\text{F}_9$ (0.66 vs. 0.42); $\text{CF}_3\text{C(O)OCH}_2\text{CF}_3$ vs. $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$
151 (0.41 vs. 0.33), where FESs have significantly larger REs than their corresponding fluorinated ethers.
152 This can be simply rationalized if we consider that the infrared cross section spectrum depends
153 strongly on the nature of the molecular structure. This is illustrated in Figure 1 for the infrared spectra
154 of $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_3$ (HFE-7000) and $\text{HC(O)OCF}_2\text{CF}_2\text{CF}_3$. The ester, compared to the ether, has an
155 additional strong band in the 1100 cm^{-1} region of the spectrum where the radiative forcing function is
156 large. This feature can be assigned to the C—O—C(O)R stretch that occurs in these molecules.

157 The relationship between the REs and molecular structure has been investigated in previous studies by
158 examining how the integrated cross section and REs vary with the number of C-F bonds in the
159 molecule. ^{[25],[29],[22]} Figures 2 and 3 show the dependences on the number of C-F bonds of integrated
160 cross section and REs of the studied compounds. The REs clearly increase with the number of C-F
161 bonds. Slightly different REs are found for the different structures of FESs, *fluoroalkylformates*,

162 HC(O)O-R_F, *fluoroalkylacetates* CH₃-C(O)O-R_F, *fluoroalkylfluoroformates* FC(O)O-R_F, and
163 *fluoroalkylfluoroacetates* CF₃-C(O)-O-R_F. . In Figure 3, we compare the RE obtained for FESs with
164 those obtained using the same approaching for PFCs and HFEs in our previous publications.^{[22],[21]}
165 Here we see that FESs have greater radiative efficiencies than HFEs and PFCs with the same number
166 of C-F bonds. This observation is supported by other authors who have explained it in terms of the
167 greater contribution of C-F bonds adjacent to O atoms to the overall RE.^{[29],[27]} This is illustrated in the
168 series C₃F₈ (0.27), *c*-C₄F₈ (0.30), FC(O)OCF₂CF₂CF₃ (0.51) and CF₃C(O)OCF₂CF₃ (0.59) or in the
169 series CF₄ (0.08), CH₃OCF₂CF₂H (0.28), FC(O)OCF₃ (0.31) and HC(O)OCHF₂CF₃ (0.38) for 8 and 4
170 C-F bonds, respectively, with the RE in W m⁻² ppbv⁻¹ given in parentheses.

171 Furthermore, when we compare *fluoroalkylformates* with *alkylfluoroformates*, species with similar
172 molecular structure, we can observe that *fluoroalkylformate* have very similar REs to the analogous
173 *alkylfluoroformates* even though these compounds have one more F atom in the structure. For
174 example, this effect is observed for HC(O)OCF₃, HC(O)OCF₂CF₃ and HC(O)OCF₂CF₂CF₃ which
175 have REs similar to FC(O)OCF₃, FC(O)OCF₂CF₃ and FC(O)OCF₂CF₂CF₃, respectively. A different
176 effect is observed for the integrated cross section values. In this case, the effect of molecular structure
177 is almost the opposite to the observations for radiative efficiencies values. This can be explained
178 simply since *alkylfluoroformates* have one extra C-F bonds in the molecular structure compared with
179 their corresponding *fluoroalkylformates*, and this leads to an increase in the integrated cross section of
180 the molecule. This extra F atom, which is bonded to the carbonyl C atom, is separated from the
181 fluoroalkyl chain, and the C-F stretching vibration is located at around 1900 cm⁻¹. The radiative
182 forcing function is small in this spectral region and therefore its contribution to the overall REs in the
183 molecule is negligible. An analogous situation arises for bands associated with the carbonyl groups in
184 all FESs; these bands are observed at about 1800 cm⁻¹ and so make only a small contribution to the
185 RE.

186 **3.2 Implications for Atmospheric Chemistry and some Global Warming highlights.**

187 *Atmospheric fate of fluorinated esters*

188 As mentioned above, it is well-known that hydrofluorinated esters (FESs) are the primary products of
189 the atmospheric oxidation of hydrofluoroethers. However, there is a lack of knowledge about their
190 atmospheric fate. Since esters and some FESs are known to be easily hydrolyzed, it is often assumed
191 that they are easily removed through wet deposition, as is the case for hydrogenated carbonyl
192 compounds. However, recent studies have shown that wet deposition might not be an important sink
193 for all FESs and the OH initiated oxidation determines the atmospheric lifetimes of some of
194 them.^{[30],[11],[12],[13],[14],[16]} In the work of Kutsuna et al.^[16], the Henry's law constants and hydrolysis rate

195 constants are reported for the *fluoroalkylacetate* $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ and for the *alkylfluoroacetate*
196 $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ along with their lifetimes through dissolution in clouds and oceans. They found that
197 dissolution in clouds is not a significant atmospheric sink for either $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ or
198 $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$, and only dissolution in ocean water could be significant. In the same study, they
199 examined the effect of fluorination in esters and observed that fluorination drastically decreased the
200 solubility of the fluorinated esters $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ (0.58) and $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$ (0.12) compared to
201 the similar non-fluorinated esters $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}_3$ (5.9) and $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ (7.8), with Henry's
202 law constants in M atm^{-1} at 298K in parentheses. Therefore, reaction with the OH radical seems to be
203 the main degradation pathway for *fluoroalkylacetates* and *alkylfluoroacetates*. It is important to note
204 that some of these species have relatively long lifetimes with respect to reaction with OH radicals,
205 with values between 1 – 4 months. This is shown in Table 3 where some OH lifetimes found in the
206 literature are summarized for the FESs studied in the present work. It is clear from this table that the
207 lifetimes of FESs in the atmosphere have not been comprehensively studied. For *alkylfluoroformates*,
208 the lifetime with respect to reaction with OH radicals has only been reported for $\text{FC}(\text{O})\text{OCH}_3$ (1.8 yrs).
209 However, some studies show that halocarbonyl and haloacetic halide ($\text{R-C}(\text{O})\text{F}$) compounds have high
210 values of the Henry's law constants and may be removed easily by wet-deposition,^[31] and this
211 indicates that *alkylfluoroformates* in general may behave in this way, in contrast to the behaviour
212 observed for *fluoroalkylacetates* and *alkylfluoroacetates*. Up to now, there are no gas-to-water
213 equilibrium data for *fluoroalkylformates* in the literature. It is expected that they will be removed from
214 the atmosphere by wet-deposition by analogy with the non-fluorinated formates (see e.g. Wallington et
215 al., (1998)^[32]; Oyaro et al., (2004)^[10]). Nevertheless, the highly fluorinated nature of the segregated
216 compounds may decrease their solubility in water and their removal in the atmosphere through
217 reaction with OH radicals may be significant for *fluoroalkylformates*.

218 Furthermore, other studies indicate that photolysis of esters is not relevant in the troposphere and the
219 volatility of the compounds will probably render the atmospheric removal through dry deposition
220 mechanisms unlikely.^{[10],[14]} Finally, the oxidation of FESs leads mainly to the formation of the
221 fluorinated acids and anhydrides along with CF_2O , CO_2 and HF which are the hydrolysis products.
222 Acids and anhydrides are very soluble compounds and will be rapidly incorporated into clouds
223 droplets.^{[14],[19],[33]}

224 What is clear from this background is that the atmospheric lifetime for a lot of FESs is determined
225 mainly by OH initiated oxidation and further investigation of the atmospheric fate of FESs is needed.
226 In summary, FESs, in particular *fluoroalkylacetates*, *alkylfluoroacetates* and *fluoroalkylformates*, are
227 potential greenhouse gases and their likely long atmospheric lifetimes and relatively larger REs,
228 compared to their parent HFEs, make them active contributors to global warming.

229 *Global Warming Potentials of FESs and Indirect Global Warming Potentials of HFEs*

230 The GWP is one possible climate metric to place emissions on a CO₂-equivalent scale and we present
 231 GWPs for consistency with the earlier literature. The GWP concept takes into account both the RE and
 232 the lifetime of a gas. It is therefore defined as the radiative forcing of an emission of 1 kg of some
 233 compound at time zero, integrated over some given time horizon, divided by the same value for a 1 kg
 234 emission of carbon dioxide. The method used here is described at length in IPCC, 2007. ^[27, section 2.10.1]
 235 The predicted REs reported in this work along with absolute GWP for carbon dioxide and the
 236 atmospheric lifetimes can then be used to obtain the GWPs over 20, 100 and 500 yr time horizons. In
 237 Table 3, we present the atmospheric lifetimes with respect to OH radicals reported in literature. For
 238 some of the compounds, lifetimes have not been reported, but we can make estimates based on the
 239 behaviour of analogous compounds. For GWP calculations we consider OH oxidation to be the main
 240 tropospheric degradation pathway for selected FESs. We expect this to be valid for
 241 *fluoroalkylacetates*, *alkylfluoroacetates* and *fluoroalkylformates*, as discussed earlier. We report RE
 242 values from the adopted method of Pinnock et al. ^[23] in section 3.1, assuming the compounds are well-
 243 mixed in the atmosphere; however, the relatively short-lived species discussed here are unlikely to be
 244 well-mixed, and in particular their mixing ratios will fall off rapidly in the stratosphere. The actual
 245 distribution would likely depend on the location of the emissions from the Earth surface which would
 246 require sophisticated chemical-transport model calculations to ascertain. ^[4] This methodology will be
 247 necessary when the gas is emitted directly from the surface and then lifetime-corrections are needed.

248 The assessment of the contribution to the warming of a given HFE emitted from the Earth's surface
 249 should consider that this HFE will be converted into the corresponding FES in the troposphere. The
 250 new products have a cumulative contribution to the total absorption of radiation due to the emissions
 251 of the primary pollutants. Here we calculate the net global warming potential of the parent HFE as the
 252 sum of the direct HFE global warming and the indirect contributions due to the corresponding
 253 products (FESs). Here, we obtain the contribution of secondary products from their radiative
 254 efficiencies and their atmospheric time profiles:



257 For such a pair of consecutive reactions — assuming pseudo-first-order conditions — the time profile
 258 of a given FES for a pulse of HFE is:

259
$$[\text{FES}](t) = [\text{HFE}]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (\text{II})$$

260 where k_1 and k_2 are the rate constants toward OH radicals multiplied by the average OH radical
 261 concentrations.

262

263 The term:

$$264 \quad \alpha \frac{\int_0^h RE(FES)[FES](t)dt}{\int_0^h RE(CO_2)[CO_2](t)dt} \quad (III)$$

265 where α is the yield of a given FES, gives the contribution of such species to the net GWP of the
 266 parent HFE. Since the FESs studied here come from the atmospheric oxidation of their parent HFEs,
 267 which are supposed to possess a uniform vertical distribution through the troposphere, we also assume
 268 that FESs are well-mixed species.

269 The substitution of (II) into (III) and the following integrations gives equation (IV) which evaluates
 270 the indirect GWP of a determined HFE over a time horizon th due to its corresponding oxidation
 271 product i :

$$272 \quad IGWP_{th}^{HFE} = \sum_i \frac{M_{CO_2} \alpha_i RE_i}{M_{HFE} AGWP_{th}^{CO_2}} \left(\frac{\tau_i}{\tau_{HFE} - \tau_i} \right) \left[RE_{HFE} (1 - e^{-th/\tau_{HFE}}) - \tau_i (1 - e^{-th/\tau_i}) \right]$$

273 (IV)

274 where $AGWP_{th}^{CO_2}$ is the absolute GWP for CO_2 at the time horizon th in $W m^{-2} yr ppmv^{-1}$, M_{CO_2} and
 275 M_{HFE} are the molecular weights of CO_2 and the parent HFE, respectively, RE_i is the radiative
 276 efficiency of the product i (in $W m^{-2} ppmv^{-1}$); and τ_{HFE} and τ_i are the lifetimes of the parent HFE and
 277 the species i , respectively, obtained as $\tau = \frac{1}{k[OH]}$.

278 The net GWP will be the sum of the direct and indirect GWP:

$$279 \quad net - GWP_{th}^{HFE} = \frac{M_{CO_2} \tau_{HFE} (1 - e^{-th/\tau_{HFE}})}{M_{HFE} AGWP_{th}^{CO_2}} \left[RE_{HFE} + \sum_i \frac{\alpha_i RE_i \tau_i}{\tau_{HFE} - \tau_i} \left(1 - \frac{\tau_i (1 - e^{-th/\tau_i})}{\tau_{HFE} (1 - e^{-th/\tau_{HFE}})} \right) \right]$$

281 (V)

282 Direct, indirect and net-GWPs for some common HFEs are summarized in Table 4. Figure 4 shows the
 283 behaviour of the direct and net-GWP for three compounds whose oxidations lead to different FESs:

284 HFE-7200 ($C_4F_9OC_2H_5$), HFE-7000 ($C_3F_7OCH_3$) and $(CF_3)_2CHOCH_3$. In this Figure, the $AGWP_{th}^{CO_2}$
 285 at each time horizon was calculated using the IPCC, 2007 ^[27] expression, where $RF_{CO_2} = 0.01413 \text{ W m}^{-2}$
 286 ppm^{-1} and the decay of a pulse of CO_2 with time t is given by $a_0 + \sum_{i=1}^3 a_i \cdot e^{-t/\tau_i}$, where $a_0 = 0.217$,
 287 $a_1 = 0.259$, $a_2 = 0.338$, $a_3 = 0.186$, $\tau_1 = 172.9$ years, $\tau_2 = 18.51$ years, and $\tau_3 = 1.186$ years. This plot is
 288 expanded (Figure 4b) to show the behaviour for short time horizons. The resulting profiles are
 289 different in all cases depending on the RE values and on the absolute and relative rate constants for
 290 reaction with OH. For HFE-7200 ($C_4F_9OC_2H_5$), the net-GWP and direct-GWP are similar, showing
 291 that the indirect contribution due to products is small but non negligible. $C_4F_9OC(O)CH_3$ is the main
 292 oxidation product of HFE-7200 ($\alpha = 0.8$) but it has a short lifetime (0.06 yrs) and thus a very low
 293 contribution to the net-GWP. On the other hand, $C_4F_9OC(O)H$ is also found as a product ($\tau = 3$ yrs
 294 and $RE = 0.59 \text{ W m}^{-2} \text{ ppbv}^{-1}$). Nevertheless, the yield of this compound is small, $\alpha = 0.2$, and so its
 295 contribution to the net GWP is also low.

296 The oxidation of HFE-7000 leads to $C_3F_7OC(O)H$ as the only product. The lifetime of $C_3F_7OC(O)H$
 297 (2.6 yrs) is on the same order as the lifetime of HFE-7000 (4.8 yrs) whereas its RE ($0.55 \text{ W m}^{-2} \text{ ppbv}^{-1}$)
 298 is 70% larger than the HFE-7000 ($0.32 \text{ W m}^{-2} \text{ ppbv}^{-1}$). Consequently, the net-GWP is significantly
 299 higher than the direct-GWP for time horizons up to one hundred years.

300 Finally, $(CF_3)_2CHOCH_3$ leads to $(CF_3)_2CHOC(O)H$ as the major oxidation product, which has a
 301 lifetime 12 times longer (3.2 vs. 0.27 yrs) and an RE twice as large (0.35 vs. $0.19 \text{ W m}^{-2} \text{ ppbv}^{-1}$) than
 302 the parent HFE. At times longer than 0.25 years, the concentration of $(CF_3)_2CHOC(O)H$ exceeds that
 303 of the parent compound, $(CF_3)_2CHOCH_3$. The combination of both effects makes the net-GWP for
 304 this HFE extremely large compared to the direct-GWP for hundreds of years.

305 Table 4 summarizes the net-GWPs of some common HFEs whose atmospheric chemistry has been
 306 reported in the literature. For segregated FESs only one oxidation pathway is possible and the yields of
 307 the corresponding fluoroalkylformate are close to the unity. However, as was commented above,
 308 $C_4F_9OC_2H_5$ (HFE-7200) has two different H atoms leading to the fluoroalkylacetate $C_4F_9OC(O)CH_3$
 309 and the corresponding fluoroalkylformate $C_4F_9OC(O)H$ as major and minor oxidation products. On the
 310 other hand, non segregated FESs will lead to different species in their atmospheric oxidation
 311 depending on the strength of the C-H bond of the abstracted H atom. ^[10] On reaction with OH, some
 312 HFEs can undergo decomposition *via* C-C bond scission and release of CF_3 radicals, which can then
 313 produce COF_2 . ^[32] This species can be rapidly removed by wet deposition, as described earlier, and we
 314 have not taken this compound into account in the net-GWP calculation.

315 In general, the net-GWPs values obtained are between 2-16 times larger than the direct-GWPs for the
316 studied HFEs at 20, 100 and 500 yrs. For segregated HFEs the contribution of the indirect-GWP is
317 very significant. For instance, net-GWP₁₀₀ values of 1320 and 1200 were found for C₂F₅OCH₃ and
318 CF₃OCH₃, respectively, in contrast with their corresponding direct-GWP₁₀₀, 573 and 453,
319 respectively. These values are comparable with those of some well-known greenhouse gases such as
320 hydrofluorocarbons (HFCs). For example, GWP₁₀₀ values of 1430 and 4470 were reported in the
321 literature for CH₂FCF₃ and CF₃CH₃, respectively.^[27] For the non-segregated HFEs, net-GWP₁₀₀ values
322 are greater than the direct-GWP₁₀₀ values by more than a factor of ten, as is illustrated for
323 (CF₃)₂CHOCH₃ (288 vs. 18) and CF₃CH₂OCH₃ (63 vs. 6). On the other hand, for CF₃CHClOCHF₂ the
324 net-GWP₁₀₀ is only 35% larger than the direct-GWP₁₀₀ (577 vs. 429) since the lifetime of the only
325 oxidation product is very short.

326 On the basis of these results, some segregated HFEs may contribute significantly more to global
327 warming than can be concluded from examination of their direct GWPs, and the applicability of some
328 HFEs as environmentally-compatible CFCs, HFCs and PFC alternatives should be re-examined. As
329 shown, in the design and development of CFC substitutes, the consideration of the contribution of
330 atmospheric reaction products is a crucial factor to properly assess the impact on the global warming.

331

332 **4. Conclusion**

333 We have used density functional theory and the methodology developed in Bravo et al. (2010)^[22], to
334 predict infrared spectra, and calculate REs and GWPs for a number of FESs for the first time. FESs are
335 the major oxidation products of HFEs. Some of them such as *fluoroalkylacetates*, *alkylfluoroacetates*
336 and *fluoroalkylformates* remain in the atmosphere for long periods until removed by oxidation by OH
337 radicals and are potential greenhouse gases. The concept of indirect Global Warming Potential was
338 used here to assess the climate impact of secondary stable species in the troposphere. Using this
339 approach we found that the GWPs of HFEs can be increased within 100-1600 % taking into account
340 the cumulative effect due to the secondary FESs formed during HFE atmospheric oxidation. This
341 effect may be particularly significant for non segregated HFEs. Studies of the atmospheric chemistry
342 of FESs such as gas-to-water equilibrium and solubility, atmospheric lifetimes, infrared spectra and
343 reaction yields are needed to accurately assess the environmental impact of FESs and HFEs.

344

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348

349 6. Supplementary Information

350 In the supplementary data associated with this article are the frequencies and absolute intensities of the
351 vibrational modes of the studied FESs obtained using the B3LYP/6-31G** level of theory

352 7. References

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Tables and Figures

Table 1. Theoretically-determined integrated cross sections (between 0 and 2500 cm^{-1}) in $10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$

	FESs	S/ $10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$		FESs	S/ $10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$
<i>Fluoroalkylformates</i>	$\text{CF}_3\text{OC(O)H}$	30.9	<i>Fluoroalkylfluoroacetates</i>	$\text{CF}_3\text{C(O)OCH}_3$	23.2
	$\text{C}_2\text{F}_5\text{OC(O)H}$	35.6		$\text{CF}_3\text{C(O)OCF}_3$	43.2
	$\text{C}_3\text{F}_7\text{OC(O)H}$	41.2		$\text{CF}_3\text{C(O)OCH}_2\text{CH}_3$	25.5
	$\text{C}_4\text{F}_9\text{OC(O)H}$	46.6		$\text{CF}_3\text{C(O)OCH}_2\text{CF}_3$	37.0
	$\text{CF}_3\text{CHFOC(O)H}$	29.2		$\text{CF}_3\text{C(O)OCF}_2\text{CF}_3$	47.5
	$(\text{CF}_3)_2\text{CHOC(O)H}$	36.5		$\text{CF}_3\text{C(O)OCF}_2\text{CH}_3$	38.0
	$\text{CF}_3\text{CH}_2\text{OC(O)H}$	25.0		$\text{CF}_3\text{C(O)OCH}=\text{CH}_2$	27.6
	$\text{CF}_3\text{CH}_2\text{CH}_2\text{OC(O)H}$	26.1		$\text{CF}_3\text{C(O)OCH}_2\text{CH}=\text{CH}_2$	28.0
<i>Fluoroalkylacetates</i>				$\text{CF}_3\text{C(O)OCH}(\text{CF}_3)_2$	48.5
	$\text{CH}_3\text{C(O)OCF}_3$	34.0		$\text{CF}_3\text{C(O)OPh}$	31.9
	$\text{CH}_3\text{C(O)OC}_2\text{F}_5$	38.6		$\text{CF}_3\text{C(O)OCHF}_2$	36.1
	$\text{CH}_3\text{C(O)OC}_3\text{F}_7$	44.4		$\text{HCF}_2\text{C(O)OCH}_3$	17.2
	$\text{CH}_3\text{C(O)OC}_4\text{F}_9$	49.8		$\text{H}_2\text{CFC(O)OCH}_3$	14.0
				$\text{HCF}_2\text{C(O)OCH}_3$	30.2
<i>Fluoroalkylfluoroformates</i>	FC(O)OCH_3	18.4			
	$\text{FC(O)OCH}_2\text{F}$	23.5			
	$\text{FC(O)OCF}_2\text{H}$	30.5			
	FC(O)OCF_3	37.1			
	$\text{FC(O)OC}_2\text{F}_5$	41.7			
	$\text{FC(O)OCH}_2\text{CF}_3$	30.0			
	$\text{FC(O)OCF}_2\text{CH}_3$	32.2			
	$\text{FC(O)C}_3\text{F}_7$	47.4			

Table 2. Radiative efficiencies (in $\text{W m}^{-2} \text{ppbv}^{-1}$) calculated using theoretically-determined absorption cross-sections (Table 1), with wavenumber correction applied for selected fluorinated esters. These are compared with literature values for the parent HFEs where available. The REs assume that the compound is well-mixed in the atmosphere

FESs	RE (This work)	Parent HFE / Reference	RE / Reference
$\text{CF}_3\text{OC(O)H}$	0.32	CF_3OCH_3 (HFE-143a) [30][8][12]	0.19 [21]
$\text{C}_2\text{F}_5\text{OC(O)H}$	0.48	$\text{CH}_3\text{OCF}_2\text{CF}_3$ [20][11]	0.36 [21]
$\text{C}_3\text{F}_7\text{OC(O)H}$	0.55	$\text{CH}_3\text{OCF}_2\text{CF}_2\text{CF}_3$ (HFE-7000) [20][11][9]	0.37 [5]
$\text{C}_4\text{F}_9\text{OC(O)H}$	0.59	$\text{CH}_3\text{OC}_4\text{F}_9$ (HFE-7100); [6] $\text{CH}_3\text{CH}_2\text{OC}_4\text{F}_9$ (HFE-7200) [7]	0.36 [5] 0.42
$\text{CF}_3\text{CHFOC(O)H}$	0.38	$\text{CF}_3\text{CHFOCH}_3$ [13]	0.29 [25]
$(\text{CF}_3)_2\text{CHOC(O)H}$	0.35	$(\text{CF}_3)_2\text{CHOCH}_3$ [17]	0.31 [10]
$\text{CF}_3\text{CH}_2\text{OC(O)H}$	0.26	$\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$ (HFE-356mff) [10][32] $\text{CH}_3\text{OCH}_2\text{CF}_3$ [34]	0.33 [10] 0.19 [34]
$\text{CF}_3\text{CH}_2\text{CH}_2\text{OC(O)H}$	0.26	NA NA	NA NA
$\text{CH}_3\text{C(O)OCF}_3$	0.38	$\text{CH}_3\text{CH}_2\text{OCF}_3$ [34]	0.21 [34]
$\text{CH}_3\text{C(O)OC}_2\text{F}_5$	0.55	NA NA	NA NA
$\text{CH}_3\text{C(O)OC}_3\text{F}_7$	0.54	NA NA	NA NA
$\text{CH}_3\text{C(O)OC}_4\text{F}_9$	0.66	$\text{C}_2\text{H}_5\text{OC}_4\text{F}_9$ (HFE-7200) [7]	0.42 [5]
$\text{CH}_3\text{OC(O)F}$	0.08	$\text{CF}_3\text{CHFOCH}_3$ [13]	0.29 [25]
$\text{H}_2\text{FCOC(O)F}$	0.18	$\text{CH}_2\text{FOCH}_2\text{F}$ [35]	N/A
$\text{HF}_2\text{COC(O)F}$	0.32	$\text{HF}_2\text{COCF}_2\text{H}$ (HFE-134) [36] $\text{CF}_3\text{CHFOCHF}_2$ [34]	0.40 [37] 0.45 [34]
$\text{CF}_3\text{OC(O)F}$	0.31	$\text{CF}_3\text{OCFHCFC}_3$ (HFE-227me) [38] $\text{CF}_3\text{OCF}_2\text{H}$ (HFE-125) [39] [36]	0.40 [34] 0.41 [4]
$\text{C}_2\text{F}_5\text{OC(O)F}$	0.46	NA NA	NA NA
$\text{CF}_3\text{CH}_2\text{OC(O)F}$	0.31	NA NA	NA NA
$\text{CH}_3\text{CF}_2\text{OC(O)F}$	0.34	NA NA	NA NA
$\text{C}_3\text{F}_7\text{OC(O)F}$	0.51	NA NA	NA NA
$\text{CF}_3\text{C(O)OCH}_3$	0.26	$(\text{CF}_3)_2\text{CHOCH}_3/\text{CH}_3\text{OCH}_2\text{CF}_3$ [17][10][34]	0.31 [10] 0.19 [34]
$\text{CF}_3\text{C(O)OCF}_3$	0.48	NA NA	NA NA
$\text{CF}_3\text{C(O)OCH}_2\text{CH}_3$	0.29	NA NA	NA NA
$\text{CF}_3\text{C(O)OCH}_2\text{CF}_3$	0.41	$\text{CF}_3\text{CH}_2\text{OCH}_2\text{CF}_3$ [10]	0.33 [10]
$\text{CF}_3\text{C(O)OCF}_2\text{CF}_3$	0.59	NA NA	NA NA
$\text{CF}_3\text{C(O)OCF}_2\text{CH}_3$	0.51	NA NA	NA NA
$\text{CF}_3\text{C(O)OCH}=\text{CH}_2$	0.37	NA NA	NA NA
$\text{CF}_3\text{C(O)OCH}_2\text{CH}=\text{CH}_2$	0.33	NA NA	NA NA
$\text{CF}_3\text{C(O)OCH}(\text{CF}_3)_2$	0.47	NA NA	NA NA
$\text{CF}_3\text{C(O)OPh}$	0.37	NA NA	NA NA
$\text{CF}_3\text{C(O)OCHF}_2$	0.47	$\text{CF}_3\text{CHClOCHF}_2$ [18] $\text{CF}_3\text{CH}_2\text{OCHF}_2$	0.45 [40] 0.37 [34]
$\text{HCF}_2\text{C(O)OCH}_3$	0.08	NA NA	NA NA
$\text{H}_2\text{CFC(O)OCH}_3$	0.18	NA NA	NA NA
$\text{HCF}_2\text{C(O)OCH}_3$	0.41	NA NA	NA NA

Table 3. Global warming potentials (GWP) at time horizons of 20, 100 and 500 years calculated using literature values of atmospheric lifetimes and theoretically-determined radiative efficiencies calculated here (Table 2) applying the lifetime-dependent correction of Sihra et al. (2001)^[4] to crudely account for the departure of the vertical profile from well-mixed..

Compound	lifetimes (yr) / Reference	GWP ₂₀	GWP ₁₀₀	GWP ₅₀₀
CF ₃ OC(O)H	3.60 [12]	1970	561	170
C ₂ F ₅ OC(O)H	3.60 [11]	2020	575	174
C ₃ F ₇ OC(O)H	2.60 [11]	1270	361	109
C ₄ F ₉ OC(O)H	3.00 [6]	1270	362	110
CF ₃ CHFOC(O)H	3.20 [13]	1590	451	137
(CF ₃) ₂ CHOC(O)H	3.20	1090	310	94
CF ₃ CH ₂ OC(O)H	0.44 [10]	140	40	12
CF ₃ CH ₂ CH ₂ OC(O)H	0.30	79	22	7
CH ₃ C(O)OCF ₃	0.06	14	4	1
CH ₃ C(O)OC ₂ F ₅	0.06	15	4	1
CH ₃ C(O)OC ₃ F ₇	0.06	11	3	1
CH ₃ C(O)OC ₄ F ₉	0.06 [7]	11	3	1
CH ₃ OC(O)F	1.80 [13]	323	92	28
H ₂ FCOC(O)F	NA			
HF ₂ COC(O)F	NA			
CF ₃ OC(O)F	NA			
C ₂ F ₅ OC(O)F	NA			
CF ₃ CH ₂ OC(O)F	NA			
CH ₃ CF ₂ OC(O)F	NA			
C ₃ F ₇ OC(O)F	NA			
CF ₃ C(O)OCH ₃	0.33 [14]	97	28	8
CF ₃ C(O)OCF ₃	NA			
CF ₃ C(O)OCH ₂ CH ₃	0.06 [14]	10	3	1
CF ₃ C(O)OCH ₂ CF ₃	0.15 [14]	37	11	3
CF ₃ C(O)OCF ₂ CF ₃	NA			
CF ₃ C(O)OCF ₂ CH ₃	0.33	137	39	12
CF ₃ C(O)OCH=CH ₂	NA			
CF ₃ C(O)OCH ₂ CH=CH ₂	NA			
CF ₃ C(O)OCH(CF ₃) ₂	NA			
CF ₃ C(O)OPh	NA			
CF ₃ C(O)OCHF ₂	0.30	122	35	11
HCF ₂ C(O)OCH ₃	0.11 [14]	19	5	2
H ₂ CFC(O)OCH ₃	NA			
HCF ₂ C(O)OCH ₃	NA			
HCF ₂ C(O)OCF ₂ H	NA			

Table 4. Direct, indirect and net global warming potentials of some commons HFEs at time horizons of 20, 100 and 500 years. The parameters used for the calculation are also summarized here. The REs used for the HFEs were those reported in Table 2 applying the lifetime-dependent correction of Sihra et al. (2001)^[4] to crudely account for incomplete vertical mixing. The REs used for the FESs were those reported in Table 2. For FESs we used the lifetimes of Table 3.

HFE	Lifetimes(yrs) / Ref	FES	α	Ref	Indirect-GWP			Direct-GWP			Net-GWP		
					20	100	500	20	100	500	20	100	500
CF ₃ OCH ₃ (HFE-143a)	4.3 / [27]	CF ₃ OC(O)H	1.00	[30], [12]	2620	745	226	1580	453	138	4200	1200	364
C ₃ F ₇ OCH ₃ (HFE-7000)	4.8 / [5]	C ₃ F ₇ OC(O)H	1.00	[9]	1580	463	140	1730	499	152	3310	962	292
C ₂ F ₅ OCH ₃ (HFE-245cb2)	4.3 / [41]	C ₂ F ₅ OC(O)H	1.00	[20]	2520	745	226	2000	573	174	4520	1320	400
C ₄ F ₉ OCH ₃ (HFE-7100)	4.2 / [5]	C ₄ F ₉ OC(O)H	1.00	[6]	1570	458	139	1180	337	102	2750	795	241
C ₄ F ₉ OC ₂ H ₅ (HFE-7200)	0.91 / [5]	C ₄ F ₉ OC(O)H	0.20	[7]	332	95	29	243	69	21	575	164	50
		C ₄ F ₉ OC(O)CH ₃	0.80										
(CF ₃) ₂ CHOCH ₃	0.27 / [10]	(CF ₃) ₂ CHOC(O)H	0.66	[17]	948	270	82	63	18	5	1010	288	87
		CF ₃ C(O)OCH ₃	0.22										
CF ₃ CH ₂ OCH ₃	0.12 / [34]	CF ₃ CH ₂ OC(O)H	0.84	[34]	199	57	17	21	6	2	220	63	19
		CH ₃ C(O)OCF ₃	0.16										
CF ₃ CH ₂ OCH ₂ CF ₃	0.22 / [10]	CF ₃ C(O)OCH ₂ CF ₃	0.15	[10]	133	38	11	55	16	5	188	54	16
		CF ₃ CH ₂ OC(O)H	0.85	[32]									
CF ₃ CHClOCHF ₂	3.2 / [40]	CF ₃ C(O)OCHF ₂	0.85	[18]	148	148	13	1510	429	130	1660	577	143

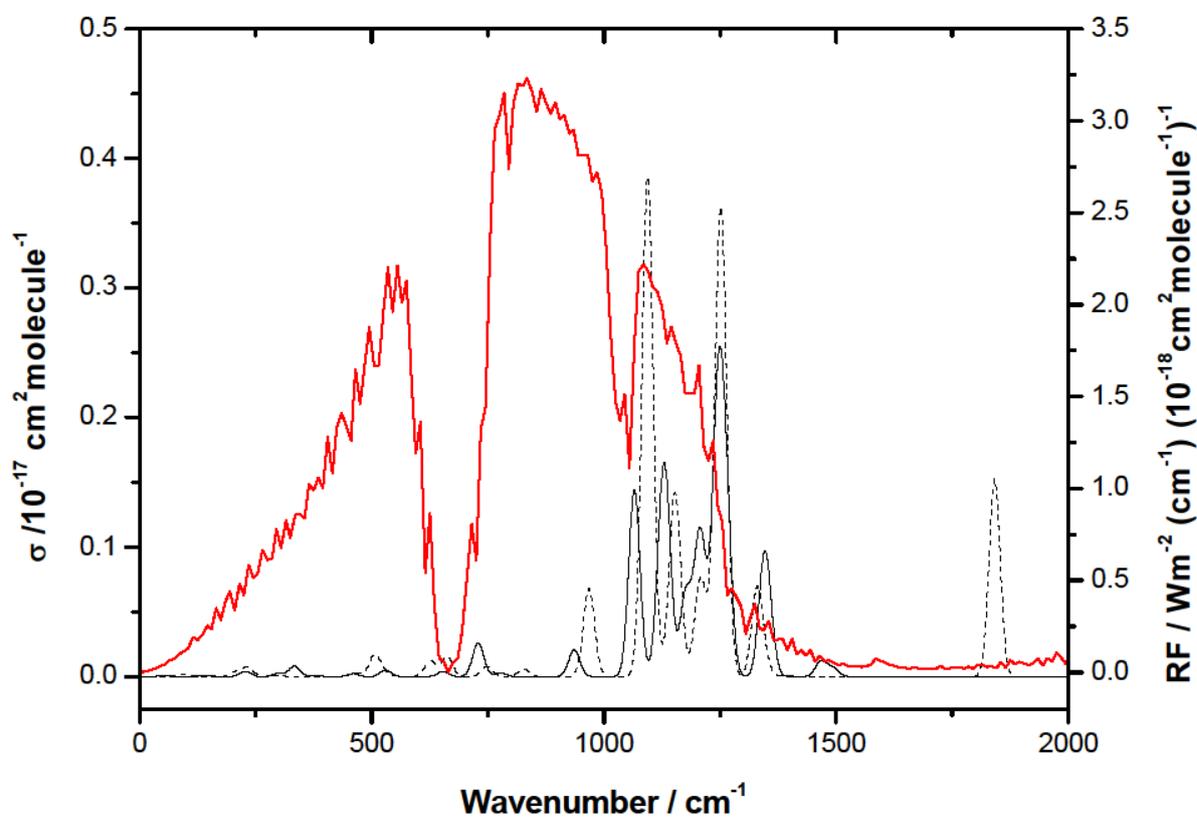


Figure 1. Calculated infrared spectra of $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_3$ (HFE-7000) and $\text{HC(O)OCF}_2\text{CF}_2\text{CF}_3$ are represented using solid and dashed curves, respectively. The calculated modes were convoluted with Gaussian functions of 14 cm^{-1} full width. The radiative forcing function used in the Pinnock et al. (1995) [23] model is represented in red curve.

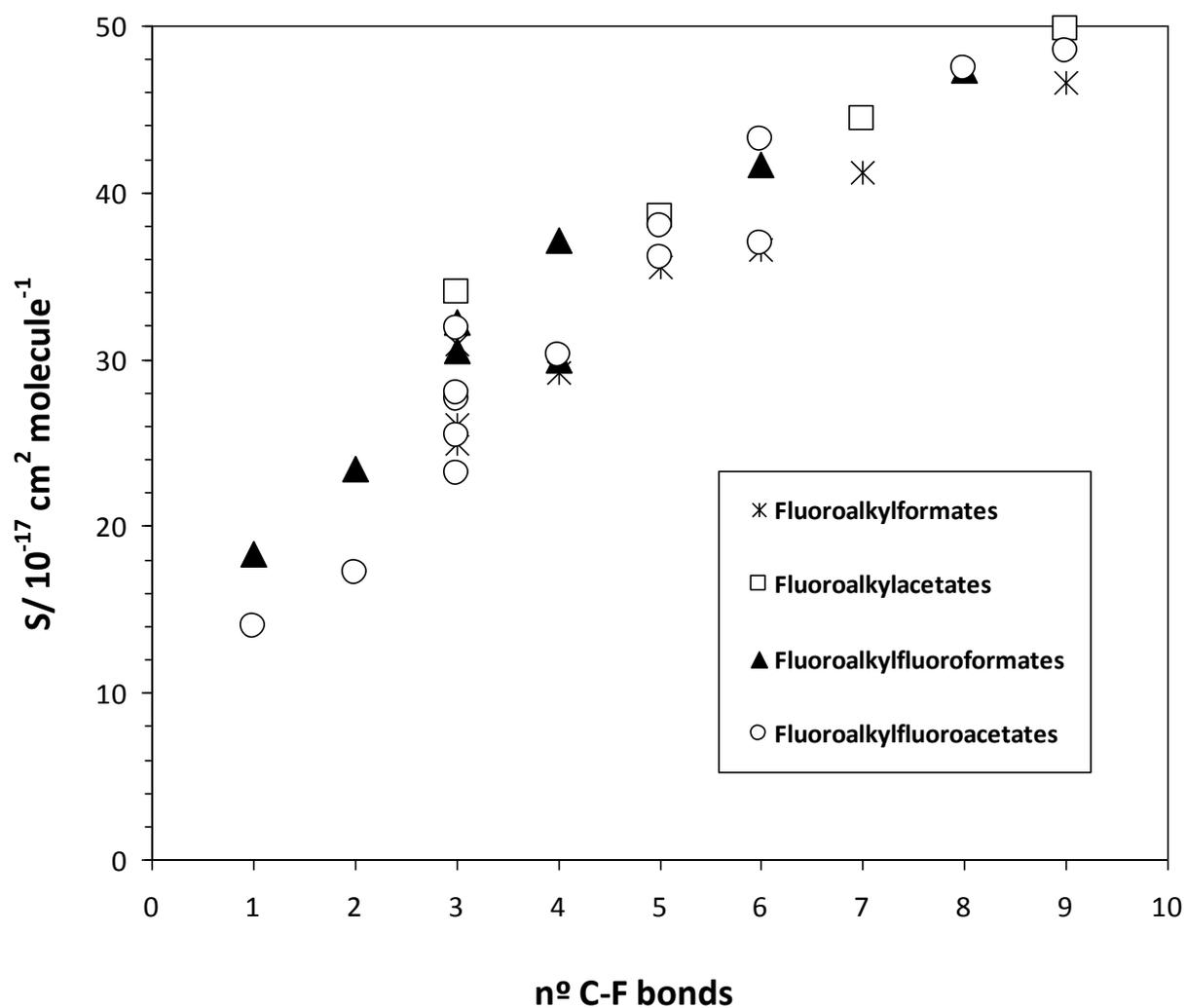


Figure 2. Plot of integrated cross section values, S , for computational B3LYP/6-31G** method versus the number of C-F bonds for the studied FESs. Data are taken from Table 1.

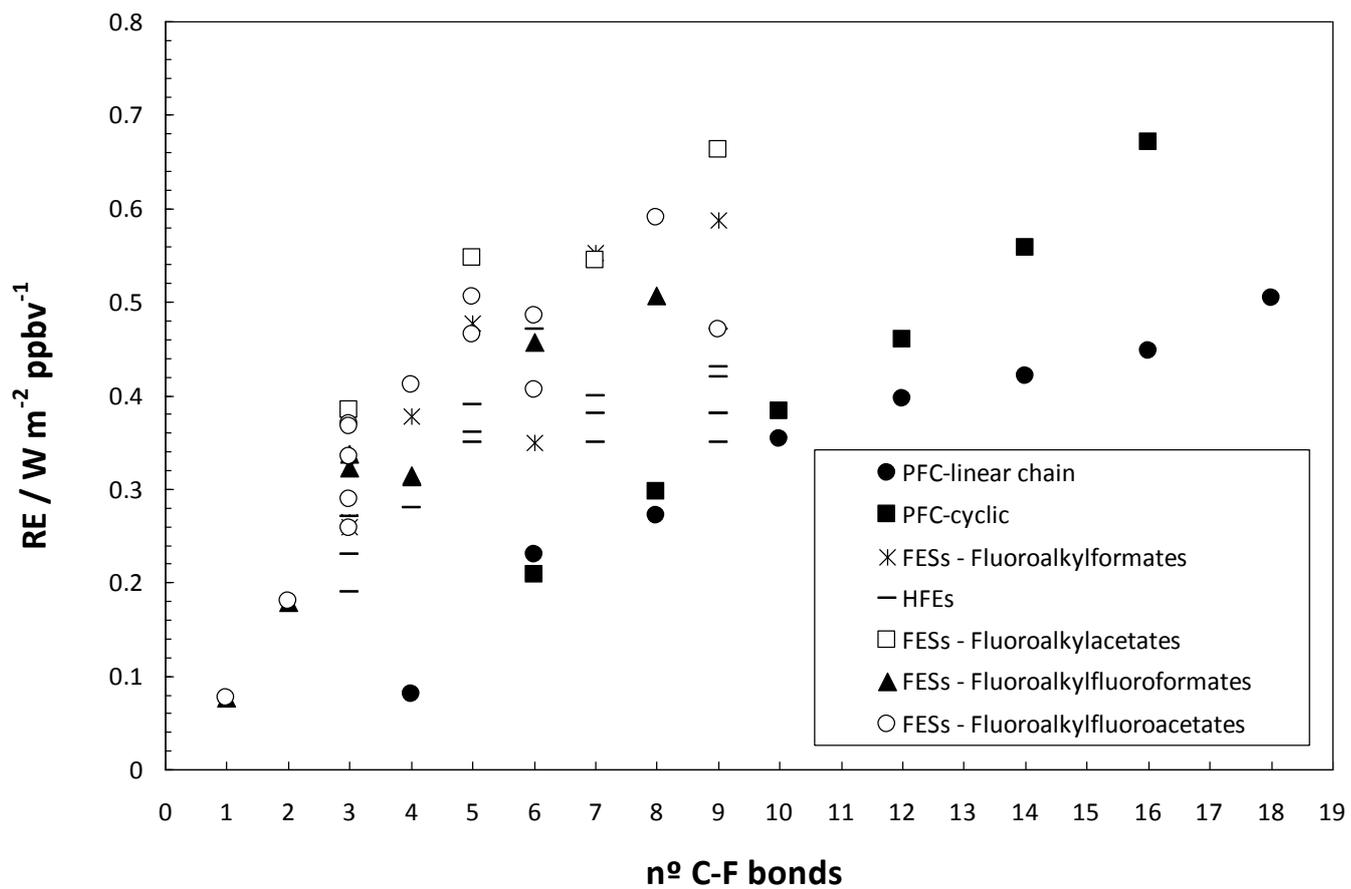


Figure 3. Plot of radiative efficiency values for the studied set of FESs versus the number of C-F bonds and comparison with PFCs (linear chain, cyclic and branched) and HFEs.

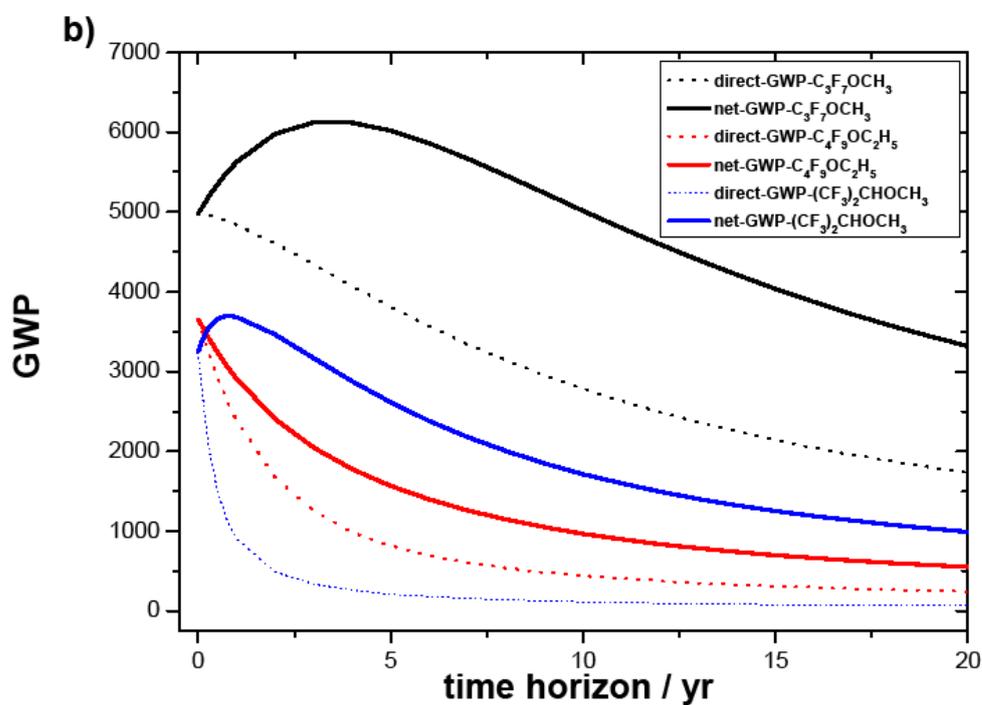
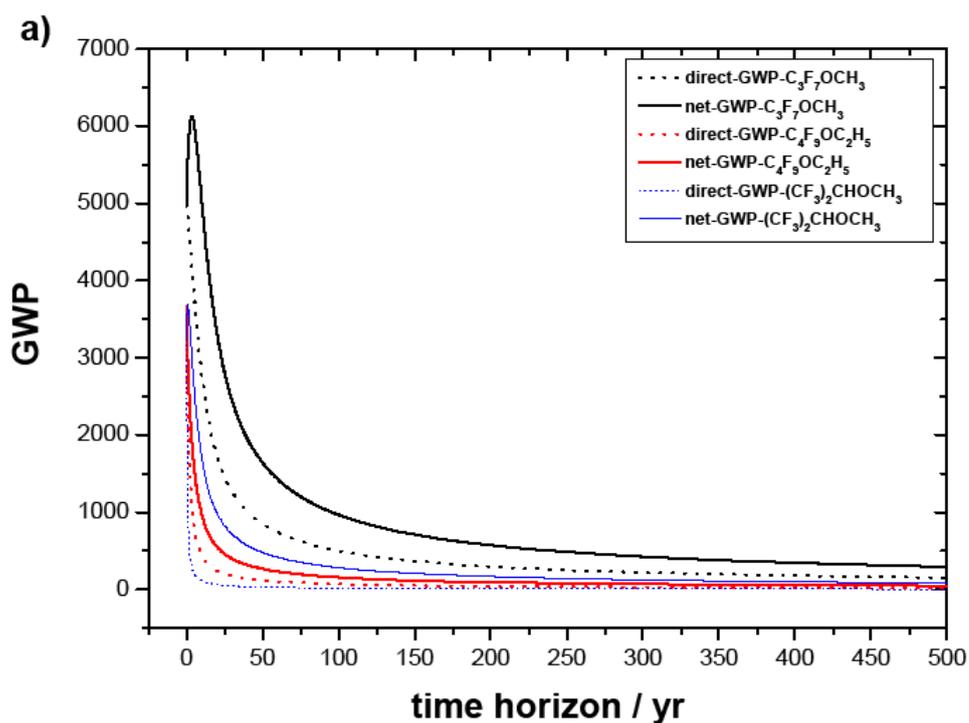


Figure 4. Plot of indirect, direct and net-GWP for HFE-7000 ($C_3F_7OCH_3$), HFE-7200 ($C_4F_9OC_2H_5$) and $(CF_3)_2CHOCH_3$ versus the time horizon at different ranges: a) 0-20 yrs; b) 0-500 yrs. Parameters used for this plot are summarized in Table 4.