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

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Abstract

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

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, NO_3 or O_3, 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 *perfluoroakylformates* $C_4F_9OC(O)H$ and n-$C_3F_7OC(O)H$ are the major degradation products of HFE-7100 ($C_4F_9OCH_3$) and HFE-7000 ($C_3F_7OCH_3$), respectively.[6], [9]

On the other hand, the *perfluoroalkylacetate* $C_4F_9OC(O)CH_3$ is the major product for HFE-7200 ($C_4F_9OCH_2CH_3$).[7] Non-segregated HFEs have hydrogen and/or fluorine atom on both sides of the ether link, and their oxidation products depend on which H atom can be more easily abstracted. For example, Chen et al.[13] reported $CF_3CHFOC(O)H$ and the *alkylfluoroformate* $FC(O)OCH_3$ as the primary oxidation products of $CF_3CHFOCH_3$. Other groups have reported *alkyl* and *fluoroalkylfluoroacetates* in the HFE atmospheric oxidation, *e.g.* $CH_3OC(O)CF_3$ from $CH_3OCH(CF_3)_2$ oxidation[17] or $CF_3C(O)OCHF_2$ from $CF_3CHClOCHF_2$ oxidation.[18] Lastly, some product distribution studies have shown that the FES oxidation leads to the formation of fluorinated acetic acid and the corresponding anhydrides along with CF_2O and its hydrolysis products CO_2 and HF.[19], [18], [20]

It is important to assess the environmental compatibility of new chemical compounds and to have an understanding of their impact on global warming. In order to achieve this, it is not enough simply to focus on the radiative properties of the parent compound. It is also important to consider oxidation mechanisms and the radiative properties of stable intermediate products in order to assess their impact on global warming. At present, there are no determinations of REs or GWPs for FESs from direct measurements. In the present study we examine these properties on the basis of previous theoretical and experimental work from our laboratories on the REs and GWPs of HFEs [5], [21] and PFCs[22]. In our publication on PFCs, we reported a theoretical method for determining infrared spectra and REs (and hence GWPs where an atmospheric lifetime was known or could reasonably be inferred). The calculated RE is extremely sensitive to the exact position of the C-F stretch at around 1250 cm^{-1} and the raw calculated frequencies cannot be used directly in radiative transfer models. Thus, we used a combination of theoretical and experimental results to obtain a very precise correction to the band position generated directly from the density functional theory (DFT) or *ab initio* calculations. Furthermore, in subsequent work [21], we extended and tested the method for HFEs and hydrofluoropolyethers (HFPEs). The results showed that the method gave predictions in very good agreement with experimental values. One of the aims of the present study is to apply this method to calculate IR spectra and REs for FESs and to predict these quantities for a range of related compounds.

This is the first study to report data of cross sections, REs and GWPs for FESs. The FESs studied belong to the series *fluoroakylformates*, *fluoroalkylacetates*, *fluoroalkylfluoroformates*, and *fluoroalkylfluoroacetates*.

2. Methodology

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

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

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

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

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

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

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

3. Results and Discussion.

In this section we present integrated cross sections, REs and GWPs obtained for several fluorinated esters. The FESs expected from the tropospheric oxidation of HFEs may be classified as: *fluoroakylformates*, HC(O)O-R_F, *fluoroalkylacetates* CH_3-C(O)O-R_F, *fluoroalkylfluoroformates* FC(O)O-R_F, and *fluoroalkylfluoroacetates* CF_3-C(O)-O-R_F where R_F is an alkyl chain with at least one F atom.

3.1 Infrared Absorption Cross Sections and Radiative Efficiencies

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

To the best of our knowledge, measurements of REs for FESs have not been reported in the literature. We have used our theoretically determined spectra to calculate REs using the Pinnock et al.[23] method as described above in section 2. Predicted REs are summarized in Table 2, where they are compared with previously reported values for the parent HFE. We can see in this table that the majority of FESs posses larger REs than their parent HFEs, even when they have the same number of C-F bonds in the molecular structure. For instance, this is observed in the following selected FES vs HFE couples (REs in W m^{-2} $ppbv^{-1}$ given in parentheses): $HC(O)OCF_2CF_2CF_3$ *vs.* $CH_3OCF_2CF_2CF_3$ (0.55 *vs.* 0.37); $CH_3C(O)OCF_2CF_2CF_2CF_3$ *vs.* $C_2H_5OC_4F_9$ (0.66 *vs.* 0.42); $CF_3C(O)OCH_2CF_3$ *vs.* $CF_3CH_2OCH_2CF_3$ (0.41 *vs.* 0.33), where FESs have significantly larger REs than their corresponding fluorinated ethers. This can be simply rationalized if we consider that the infrared cross section spectrum depends strongly on the nature of the molecular structure. This is illustrated in Figure 1 for the infrared spectra of $CH_3OCF_2CF_2CF_3$ (HFE-7000) and $HC(O)OCF_2CF_2CF_3$. The ester, compared to the ether, has an additional strong band in the 1100 cm^{-1} region of the spectrum where the radiative forcing function is large. This feature can be assigned to the C—O—C(O)R stretch that occurs in these molecules.

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

HC(O)O-R_F, *fluoroalkylacetates* CH_3-C(O)O-R_F, *fluoroalkylfluoroformates* FC(O)O-R_F, and *fluoroalkylfluoroacetates* CF_3-C(O)-O-R_F. . In Figure 3, we compare the RE obtained for FESs with those obtained using the same approaching for PFCs and HFEs in our previous publications.[22],[21]. Here we see that FESs have greater radiative efficiencies than HFEs and PFCs with the same number of C-F bonds. This observation is supported by other authors who have explained it in terms of the greater contribution of C-F bonds adjacent to O atoms to the overall RE.[29],[27] This is illustrated in the series C_3F_8 (0.27), c-C_4F_8 (0.30), FC(O)$OCF_2CF_2CF_3$ (0.51) and CF_3C(O)OCF_2CF_3 (0.59) or in the series CF_4 (0.08), $CH_3OCF_2CF_2H$ (0.28), FC(O)OCF_3 (0.31) and HC(O)OCHFCF_3 (0.38) for 8 and 4 C-F bonds, respectively, with the RE in W m^{-2} $ppbv^{-1}$ given in parentheses.

Furthermore, when we compare *fluoroakylformates* with *alkylfluoroformates*, species with similar molecular structure, we can observe that *fluoroalkylformate* have very similar REs to the analogous *alkylfluoroformates* even though these compounds have one more F atom in the structure. For example, this effect is observed for HC(O)OCF_3, HC(O)OCF_2CF_3 and HC(O)$OCF_2CF_2CF_3$ which have REs similar to FC(O)OCF_3, FC(O)OCF_2CF_3 and FC(O)$OCF_2CF_2CF_3$, respectively. A different effect is observed for the integrated cross section values. In this case, the effect of molecular structure is almost the opposite to the observations for radiative efficiencies values. This can be explained simply since *alkylfluoroformates* have one extra C-F bonds in the molecular structure compared with their corresponding *fluoroakylformates*, and this leads to an increase in the integrated cross section of the molecule. This extra F atom, which is bonded to the carbonyl C atom, is separated from the fluoroalkyl chain, and the C-F stretching vibration is located at around 1900 cm^{-1}. The radiative forcing function is small in this spectral region and therefore its contribution to the overall REs in the molecule is negligible. An analogous situation arises for bands associated with the carbonyl groups in all FESs; these bands are observed at about 1800 cm^{-1} and so make only a small contribution to the RE.

3.2 Implications for Atmospheric Chemistry and some Global Warming highlights.

Atmospheric fate of fluorinated esters

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

constants are reported for the *fluoroalkylacetate* $CH_3C(O)OCH_2CF_3$ and for the *alkylfluoroacetate* $CF_3C(O)OCH_3$ along with their lifetimes through dissolution in clouds and oceans. They found that dissolution in clouds is not a significant atmospheric sink for either $CH_3C(O)OCH_2CF_3$ or $CF_3C(O)OCH_3$, and only dissolution in ocean water could be significant. In the same study, they examined the effect of fluorination in esters and observed that fluorination drastically decreased the solubility of the fluorinated esters $CH_3C(O)OCH_2CF_3$ (0.58) and $CF_3C(O)OCH_3$ (0.12) compared to the similar non-fluorinated esters $CH_3C(O)OCH_2CH_3$ (5.9) and $CH_3C(O)OCH_3$ (7.8), with Henry's law constants in M atm^{-1} at 298K in parentheses. Therefore, reaction with the OH radical seems to be the main degradation pathway for *fluoroalkylacetates* and *alkylfluoroacetates*. It is important to note that some of these species have relatively long lifetimes with respect to reaction with OH radicals, with values between 1 – 4 months. This is shown in Table 3 where some OH lifetimes found in the literature are summarized for the FESs studied in the present work. It is clear from this table that the lifetimes of FESs in the atmosphere have not been comprehensively studied. For *alkylfluoroformates*, the lifetime with respect to reaction with OH radicals has only been reported for $FC(O)OCH_3$ (1.8 yrs). However, some studies show that halocarbonyl and haloacetic halide (R-C(O)F) compounds have high values of the Henry's law constants and may be removed easily by wet-deposition,[31] and this indicates that *alkylfluoroformates* in general may behave in this way, in contrast to the behaviour observed for *fluoroalkylacetates* and *alkylfluoroacetates*. Up to now, there are no gas-to-water equilibrium data for *fluoroalkylformates* in the literature. It is expected that they will be removed from the atmosphere by wet-deposition by analogy with the non-fluorinated formates (see e.g. Wallington et al., (1998) [32]; Oyaro et al., (2004) [10]). Nevertheless, the highly fluorinated nature of the segregated compounds may decrease their solubility in water and their removal in the atmosphere through reaction with OH radicals may be significant for *fluoroalkylformates*.

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

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

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

The GWP is one possible climate metric to place emissions on a CO_2-equivalent scale and we present GWPs for consistency with the earlier literature. The GWP concept takes into account both the RE and the lifetime of a gas. It is therefore defined as the radiative forcing of an emission of 1 kg of some compound at time zero, integrated over some given time horizon, divided by the same value for a 1 kg emission of carbon dioxide. The method used here is described at length in IPCC, 2007. [27, section 2.10.1] The predicted REs reported in this work along with absolute GWP for carbon dioxide and the atmospheric lifetimes can then be used to obtain the GWPs over 20, 100 and 500 yr time horizons. In Table 3, we present the atmospheric lifetimes with respect to OH radicals reported in literature. For some of the compounds, lifetimes have not been reported, but we can make estimates based on the behaviour of analogous compounds. For GWP calculations we consider OH oxidation to be the main tropospheric degradation pathway for selected FESs. We expect this to be valid for *fluoroalkylacetates*, *alkylfluoroacetates* and *fluoroalkylformates*, as discussed earlier. We report RE values from the adopted method of Pinnock et al.[23] in section 3.1, assuming the compounds are well-mixed in the atmosphere; however, the relatively short-lived species discussed here are unlikely to be well-mixed, and in particular their mixing ratios will fall off rapidly in the stratosphere. The actual distribution would likely depend on the location of the emissions from the Earth surface which would require sophisticated chemical-transport model calculations to ascertain.[4] This methodology will be necessary when the gas is emitted directly from the surface and then lifetime-corrections are needed.

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

$$\text{HFE} + \text{OH} \rightarrow \text{FES} \qquad (k_1)$$

$$\text{FES} + \text{OH} \rightarrow \text{Products} \qquad (k_2)$$

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

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

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

The term:

$$\alpha \frac{\int_0^{th} RE(FES)[FES](t)dt}{\int_0^{th} RE(CO_2)[CO_2](t)dt} \qquad \text{(III)}$$

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

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

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

(IV)

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 M_{HFE} are the molecular weights of CO_2 and the parent HFE, respectively, RE_i is the radiative 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 the species *i*, respectively, obtained as $\tau = \frac{1}{k[OH]}$.

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

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

(V)

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

HFE-7200 ($C_4F_9OC_2H_5$), HFE-7000 ($C_3F_7OCH_3$) and $(CF_3)_2CHOCH_3$. In this Figure, the $AGWP_{th}^{CO_2}$ at each time horizon was calculated using the IPCC, 2007 [27] expression, where RF_{CO_2} = 0.01413 W m^{-2} 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, a_1 = 0.259, a_2 = 0.338, a_3 = 0.186, τ_1 = 172.9 years, τ_2 = 18.51 years, and τ_3 = 1.186 years. This plot is expanded (Figure 4b) to show the behaviour for short time horizons. The resulting profiles are different in all cases depending on the RE values and on the absolute and relative rate constants for reaction with OH. For HFE-7200 ($C_4F_9OC_2H_5$), the net-GWP and direct-GWP are similar, showing that the indirect contribution due to products is small but non negligible. $C_4F_9OC(O)CH_3$ is the main oxidation product of HFE-7200 (α = 0.8) but it has a short lifetime (0.06 yrs) and thus a very low contribution to the net-GWP. On the other hand, $C_4F_9OC(O)H$ is also found as a product (τ = 3 yrs and RE = 0.59 W m^{-2} ppbv^{-1}). Nevertheless, the yield of this compound is small, α = 0.2, and so its contribution to the net GWP is also low.

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

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

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

In general, the net-GWPs values obtained are between 2-16 times larger than the direct-GWPs for the studied HFEs at 20, 100 and 500 yrs. For segregated HFEs the contribution of the indirect-GWP is very significant. For instance, net-GWP_{100} values of 1320 and 1200 where found for $C_2F_5OCH_3$.and CF_3OCH_3 , respectively, in contrast with their corresponding direct-GWP_{100}, 573 and 453, respectively. These values are comparable with those of some well-known greenhouse gases such as hydrofluorocarbons (HFCs). For example, GWP_{100} values of 1430 and 4470 where reported in the literature for CH_2FCF_3 and CF_3CH_3, respectively.[27] For the non-segregated HFEs, net-GWP_{100} values are greater than the direct-GWP_{100} values by more than a factor of ten, as is illustrated for $(CF_3)_2CHOCH_3$ (288 *vs.* 18) and $CF_3CH_2OCH_3$ (63 *vs.* 6). On the other hand, for $CF_3CHClOCHF_2$ the net-GWP_{100} is only 35% larger than the direct-GWP_{100} (577 *vs.* 429) since the lifetime of the only oxidation product is very short.

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

4. Conclusion

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

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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

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Tables and Figures

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

	FESs	**S/ 10^{-17} cm^2 $molecule^{-1}$**		**FESs**	**S/ 10^{-17} cm^2 $molecule^{-1}$**
Fluoroakylformates	$CF_3OC(O)H$	30.9	***Fluoroalkylfluoroacetates***	$CF_3C(O)OCH_3$	23.2
	$C_2F_5OC(O)H$	35.6		$CF_3C(O)OCF_3$	43.2
	$C_3F_7OC(O)H$	41.2		$CF_3C(O)OCH_2CH_3$	25.5
	$C_4F_9OC(O)H$	46.6		$CF_3C(O)OCH_2CF_3$	37.0
	$CF_3CHFOC(O)H$	29.2		$CF_3C(O)OCF_2CF_3$	47.5
	$(CF_3)_2CHOC(O)H$	36.5		$CF_3C(O)OCF_2CH_3$	38.0
	$CF_3CH_2OC(O)H$	25.0		$CF_3C(O)OCH=CH_2$	27.6
	$CF_3CH_2CH_2OC(O)H$	26.1		$CF_3C(O)OCH_2CH=CH_2$	28.0
Fluoroalkylacetates				$CF_3C(O)OCH(CF_3)_2$	48.5
	$CH_3C(O)OCF_3$	34.0		$CF_3C(O)OPh$	31.9
	$CH_3C(O)OC_2F_5$	38.6		$CF_3C(O)OCHF_2$	36.1
	$CH_3C(O)OC_3F_7$	44.4		$HCF_2C(O)OCH_3$	17.2
	$CH_3C(O)OC_4F_9$	49.8		$H_2CFC(O)OCH_3$	14.0
				$HCF_2C(O)OCH_3$	30.2
Fluoroalkylfluoroformates	$FC(O)OCH_3$	18.4			
	$FC(O)OCH_2F$	23.5			
	$FC(O)OCF_2H$	30.5			
	$FC(O)OCF_3$	37.1			
	$FC(O)OC_2F_5$	41.7			
	$FC(O)OCH2CF_3$	30.0			
	$FC(O)OCF2CH_3$	32.2			
	$FC(O)C_3F_7$	47.4			

Table 2. Radiative efficiencies (in W m^{-2} $ppbv^{-1}$) 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	
$CF_3OC(O)H$	0.32	CF_3OCH_3(HFE-143a)	[30][8][12]	0.19	[21]
$C_2F_5OC(O)H$	0.48	$CH_3OCF_2CF_3$	[20][11]	0.36	[21]
$C_3F_7OC(O)H$	0.55	$CH_3OCF_2CF_2CF_3$ (HFE-7000)	[20][11][9]	0.37	[5]
$C_4F_9OC(O)H$	0.59	$CH_3OC_4F_9$ (HFE-7100); $CH_3CH_2OC_4F_9$ (HFE-7200)	[6] [7]	0.36 0.42	[5]
$CF_3CHFOC(O)H$	0.38	$CF_3CHFOCH_3$	[13]	0.29	[25]
$(CF_3)_2CHOC(O)H$	0.35	$(CF_3)_2CHOCH_3$	[17]	0.31	[10]
$CF_3CH_2OC(O)H$	0.26	$CF_3CH_2OCH_2CF_3$ (HFE-356mff) $CH_3OCH_2CF_3$	[10][32] [34]	0.33 0.19	[10] [34]
$CF_3CH_2CH_2OC(O)H$	0.26	NA	NA	NA	NA
$CH_3C(O)OCF_3$	0.38	$CH_3CH_2OCF_3$	[34]	0.21	[34]
$CH_{3C}(O)OC_2F_5$	0.55	NA	NA	NA	NA
$CH_3C(O)OC_3F_7$	0.54	NA	NA	NA	NA
$CH_3C(O)OC_4F_9$	0.66	$C_2H_5OC_4F_9$ (HFE-7200)	[7]	0.42	[5]
$CH_3OC(O)F$	0.08	$CF_3CHFOCH_3$	[13]	0.29	[25]
$H_2FCOC(O)F$	0.18	CH_2FOCH_2F	[35]	N/A	
$HF_2COC(O)F$	0.32	HF_2COCF_2H (HFE-134) $CF_3CHFOCHF_2$	[36] [34]	0.40 0.45	[37] [34]
$CF_3OC(O)F$	0.31	$CF_3OCFHCF_3$ (HFE-227me) CF_3OCF_2H (HFE-125)	[38] [39] [36]	0.40 0.41	[34] [4]
$C_2F_5OC(O)F$	0.46	NA	NA	NA	NA
$CF_3CH_2OC(O)F$	0.31	NA	NA	NA	NA
$CH_3CF_2OC(O)F$	0.34	NA	NA	NA	NA
$C_3F_7OC(O)F$	0.51	NA	NA	NA	NA
$CF_3C(O)OCH_3$	0.26	$(CF_3)_2CHOCH_3$/$CH_3OCH_2CF_3$	[17][10][34]	0.31 0.19	[10] [34]
$CF_3C(O)OCF_3$	0.48	NA	NA	NA	NA
$CF_3C(O)OCH_2CH_3$	0.29	NA	NA	NA	NA
$CF_3C(O)OCH_2CF_3$	0.41	$CF_3CH_2OCH_2CF_3$	[10]	0.33	[10]
$CF_3C(O)OCF_2CF_3$	0.59	NA	NA	NA	NA
$CF_3C(O)OCF_2CH_3$	0.51	NA	NA	NA	NA
$CF_3C(O)OCH=CH_2$	0.37	NA	NA	NA	NA
$CF_3C(O)OCH_2CH=CH_2$	0.33	NA	NA	NA	NA
$CF_3C(O)OCH(CF_3)_2$	0.47	NA	NA	NA	NA
$CF_3C(O)OPh$	0.37	NA	NA	NA	NA
$CF_3C(O)OCHF_2$	0.47	$CF_3CHClOCHF_2$ $CF_3CH_2OCHF_2$	[18]	0.45 0.37	[40] [34]
$HCF_2C(O)OCH_3$	0.08	NA	NA	NA	NA
$H_2CFC(O)OCH_3$	0.18	NA	NA	NA	NA
$HCF_2C(O)OCH_3$	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}
$CF_3OC(O)H$	3.60	[12]	1970	561	170
$C_2F_5OC(O)H$	3.60	[11]	2020	575	174
$C_3F_7OC(O)H$	2.60	[11]	1270	361	109
$C_4F_9OC(O)H$	3.00	[6]	1270	362	110
$CF_3CHFOC(O)H$	3.20	[13]	1590	451	137
$(CF_3)_2CHOC(O)H$	3.20		1090	310	94
$CF_3CH_2OC(O)H$	0.44	[10]	140	40	12
$CF_3CH_2CH_2OC(O)H$	0.30		79	22	7
$CH_3C(O)OCF_3$	0.06		14	4	1
$CH_{3C}(O)OC_2F_5$	0.06		15	4	1
$CH_3C(O)OC_3F_7$	0.06		11	3	1
$CH_3C(O)OC_4F_9$	0.06	[7]	11	3	1
$CH_3OC(O)F$	1.80	[13]	323	92	28
$H_2FCOC(O)F$	NA				
$HF_2COC(O)F$	NA				
$CF_3OC(O)F$	NA				
$C_2F_5OC(O)F$	NA				
$CF_3CH_2OC(O)F$	NA				
$CH_3CF_2OC(O)F$	NA				
$C_3F_7OC(O)F$	NA				
$CF_3C(O)OCH_3$	0.33	[14]	97	28	8
$CF_3C(O)OCF_3$	NA				
$CF_3C(O)OCH_2CH_3$	0.06	[14]	10	3	1
$CF_3C(O)OCH_2CF_3$	0.15	[14]	37	11	3
$CF_3C(O)OCF_2CF_3$	NA				
$CF_3C(O)OCF_2CH_3$	0.33		137	39	12
$CF_3C(O)OCH=CH_2$	NA				
$CF_3C(O)OCH_2CH=CH_2$	NA				
$CF_3C(O)OCH(CF_3)_2$	NA				
$CF_3C(O)OPh$	NA				
$CF_3C(O)OCHF_2$	0.30		122	35	11
$HCF_2C(O)OCH_3$	0.11	[14]	19	5	2
$H_2CFC(O)OCH_3$	NA				
$HCF_2C(O)OCH_3$	NA				
$HCF_2C(O)OCF_2H$	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 where 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_3OCH_3 (HFE-143a)	4.3 / [27]	$CF_3OC(O)H$	1.00	[30], [12]	2620	745	226	1580	453	138	4200	1200	364
$C_3F_7OCH_3$ (HFE-7000)	4.8 / [5]	$C_3F_7OC(O)H$	1.00	[9]	1580	463	140	1730	499	152	3310	962	292
$C_2F_5OCH_3$ (HFE-245cb2)	4.3 / [41]	$C_2F_5OC(O)H$	1.00	[20]	2520	745	226	2000	573	174	4520	1320	400
$C_4F_9OCH_3$ (HFE-7100)	4.2 / [5]	$C_4F_9OC(O)H$	1.00	[6]	1570	458	139	1180	337	102	2750	795	241
$C_4F_9OC_2H_5$ (HFE-7200)	0.91 / [5]	$C_4F_9OC(O)H$ $C_4F_9OC(O)CH_3$	0.20 0.80	[7]	332	95	29	243	69	21	575	164	50
$(CF_3)_2CHOCH_3$	0.27 / [10]	$(CF_3)_2CHOC(O)H$ $CF_3C(O)OCH_3$	0.66 0.22	[17]	948	270	82	63	18	5	1010	288	87
$CF_3CH_2OCH_3$	0.12 / [34]	$CF_3CH_2OC(O)H$ $CH_3C(O)OCF_3$	0.84 0.16	[34]	199	57	17	21	6	2	220	63	19
$CF_3CH_2OCH_2CF_3$	0.22 / [10]	$CF_3C(O)OCH_2CF_3$ $CF_3CH_2OC(O)H$	0.15 0.85	[10] [32]	133	38	11	55	16	5	188	54	16
$CF_3CHClOCHF_2$	3.2 / [40]	$CF_3C(O)OCHF_2$	0.85	[18]	148	148	13	1510	429	130	1660	577	143

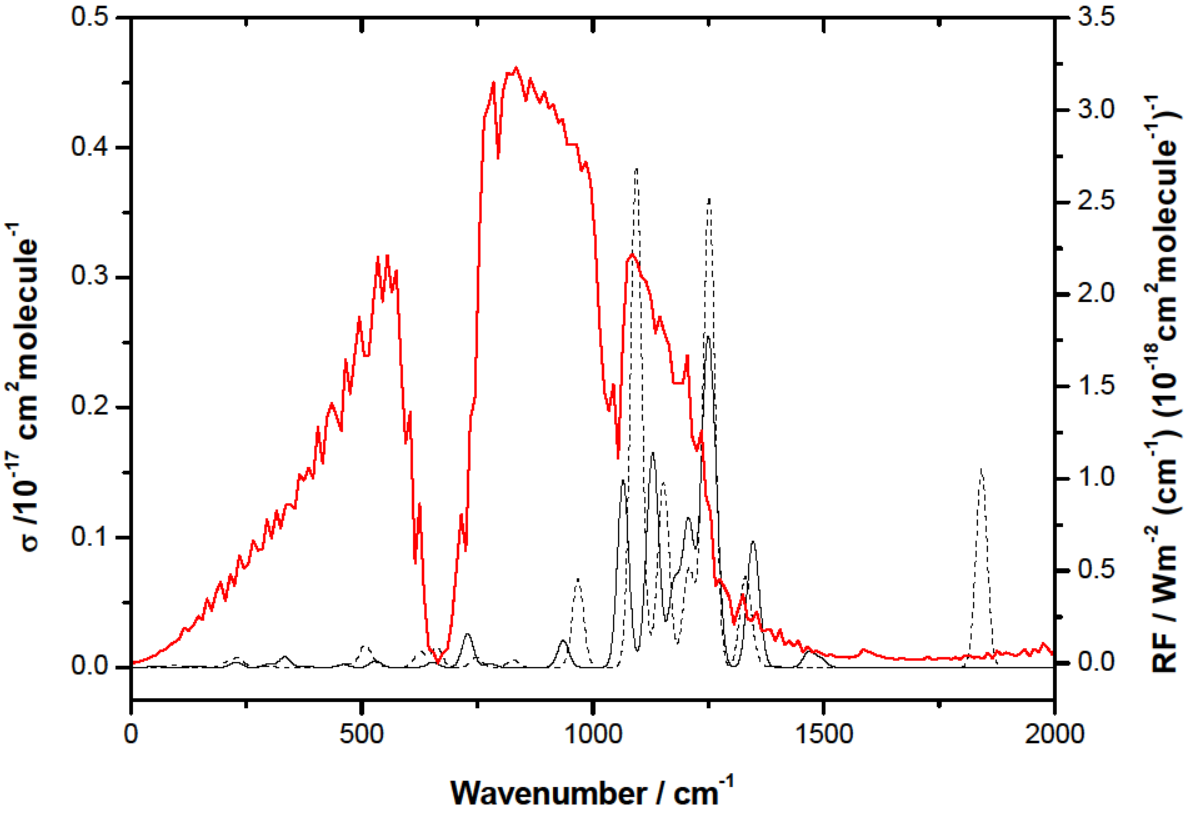

Figure 1. Calculated infrared spectra of $CF_3OCF_2CF_2CF_3$ (HFE-7000) and $HC(O)OCF_2CF_2CF_3$ are represented using solid and dashed curves, respectively. The calculated modes were convoluted with Gaussian functions of 14 cm^{-1} full width. The radiative forcing function used in the Pinnock et al. (1995) [23] model is represented in red curve.

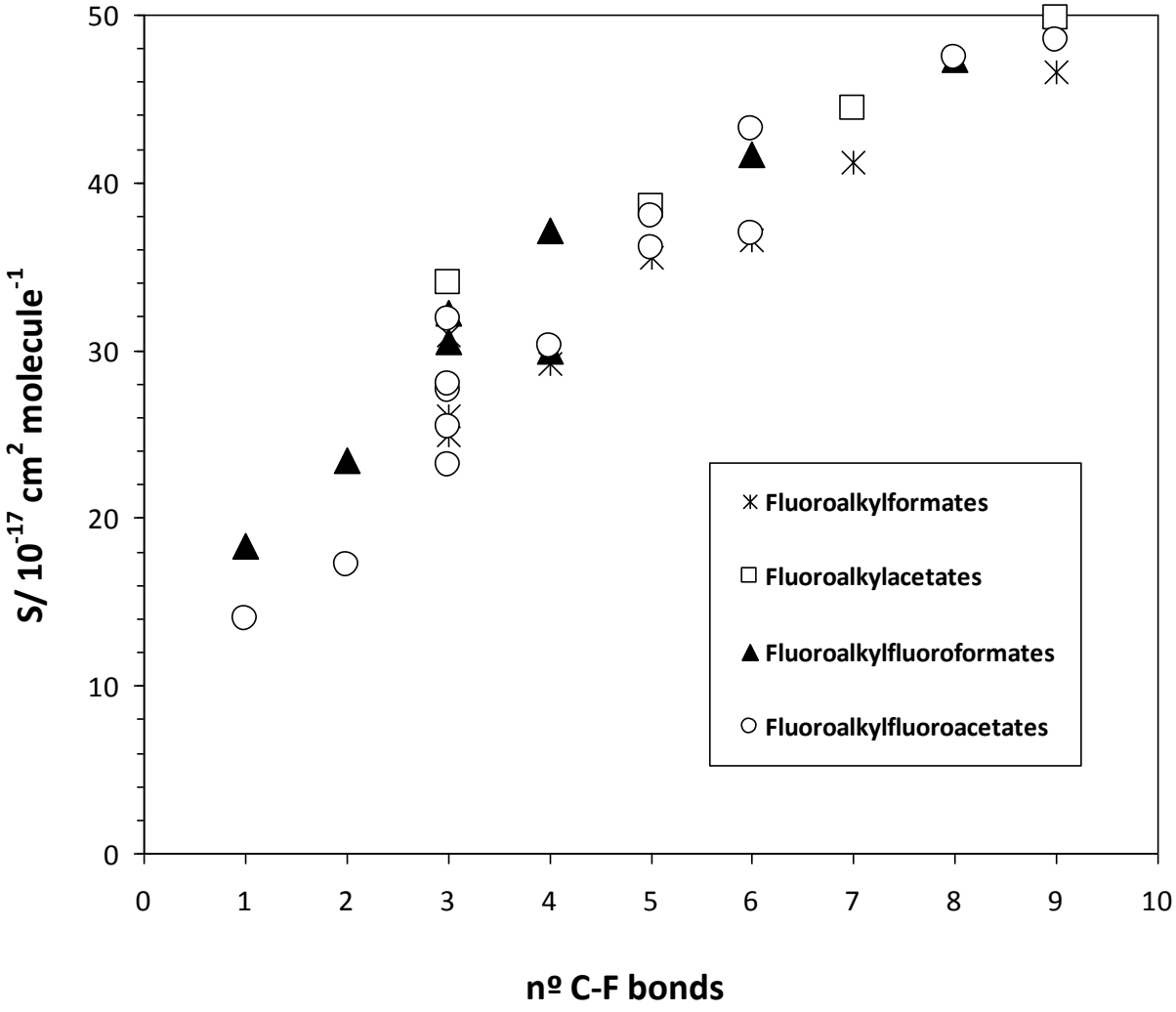

Figure 2. Plot of integrated cross section values, S, for computational B3LYP/6-31G** method versus the number of C-F bonds for the studied FESs. Data are taken from Table 1.

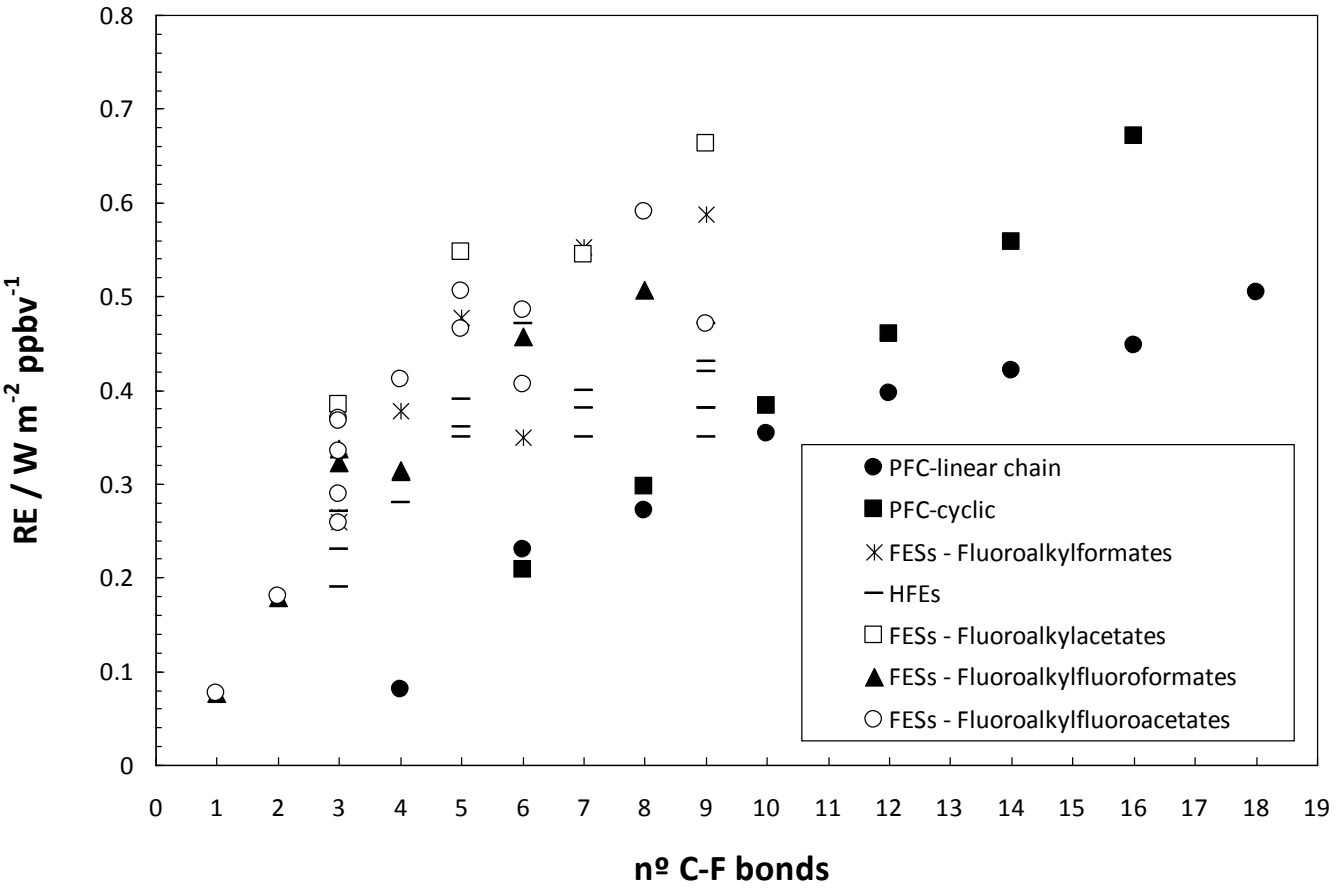

Figure 3. Plot of radiative efficiency values for the studied set of FESs versus the number of C-F bonds and comparison with PFCs (linear chain, cyclic and branched) and HFEs.

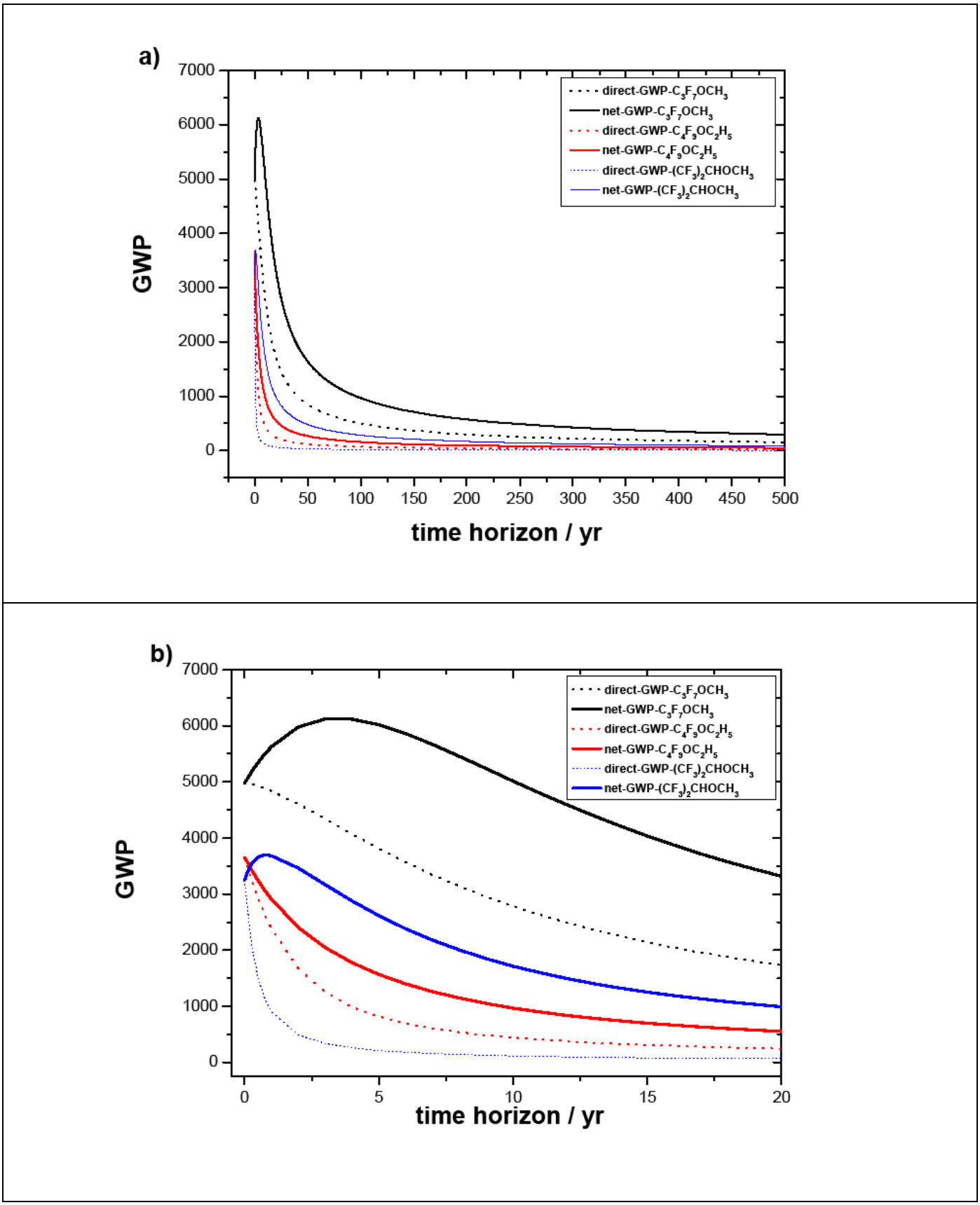

Figure 4. Plot of indirect, direct and net-GWP for HFE-7000 ($C_3F_7OCH_3$), HFE-7200 ($C_4F_9OC_2H_5$) and $(CF_3)_2CHOCH_3$ versus the time horizon at different ranges: a) 0-20 yrs; b) 0-500 yrs. Parameters used for this plot are summarized in Table 4.