

# Photolysis Study of Perfluoro-2-methyl-3-pentanone under Natural Sunlight Conditions

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The UV–vis and infrared absorption cross sections of perfluoro-2-methyl-3-pentanone ( $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ , 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone), has been obtained, and a photolysis study was carried out under natural sunlight conditions in the European simulation chamber, Valencia, Spain (EUPHORE). The photolysis loss rate,  $J_{\text{photol}}$ , equaled  $(6.4 \pm 0.3) \times 10^{-6} \text{ s}^{-1}$  in the period of 10–14 GMT, July 14, 2003 in Valencia (0.5 W, 39.5 N) and corresponded to an effective quantum yield of photolysis of  $0.043 \pm 0.011$  over the wavelength range of 290–400 nm; the error limits correspond to  $2\sigma$  from the statistical analyses. The atmospheric lifetime of  $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$  is estimated to be around 1 week, and the global warming potential of the compound is negligible.

## Introduction

The identification of suitable industrial alternatives to Halons is challenging due to the complex combination of performance, safety, and environmental properties required. Perfluoro-2-methyl-3-pentanone ( $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ , 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone, heptafluoroisopropyl pentafluoroethyl ketone, perfluoro(ethyl isopropyl ketone), perfluoro-(4-methylpentan-3-one), NOVEC 1230 3M), hereafter abbreviated PFMP, is a new fire protection fluid intended for applications such as critical electronics housed in occupied spaces. PFMP has also been suggested as a solvent for certain lubricants, a surface-cleaning agent, a blowing agent, and a surface shield component in Mg or Mg-alloy casting.

As part of ongoing work in our laboratory concerning the atmospheric chemistry of fluorinated industrial replacement compounds we have recorded the UV–vis and infrared spectra of PFMP and report here our findings on the photolysis of PFMP under natural sunlight conditions in the large outdoor simulation chamber, EUPHORE, in Valencia, Spain. The UV–vis spectrum and results from a photolysis study employing fluorescent “sunlamps” and “blacklamps” have previously been reported by Taniguchi et al. (1) who also investigated the possible reactions of PFMP with OH radicals, Cl atoms, and  $\text{O}_3$ . They concluded that PFMP will

be removed from the atmosphere by photolysis on a time scale of 1–2 weeks.

## Experimental Section

**UV–Vis Spectrum.** Absorption cross sections in the UV–vis region were measured at  $298 \pm 2 \text{ K}$  using an Agilent 8453E photodiode array spectrophotometer having a spectral resolution of 2 nm. The spectra were recorded in the wavelength range from 190 to 1100 nm at sampling intervals of 1 nm. The integration time was set to 0.5 s. The pressure of the pure PFMP vapor was in the range of 9–30 hPa and was measured using an MKS baratron-type 122A pressure transducer with a stated accuracy of  $\pm 0.15\%$ . A gas cell of  $8.0 \pm 0.1 \text{ cm}$  path length with quartz windows was used.

**Infrared Spectrum.** Infrared spectra of the pure gases at  $298 \pm 2 \text{ K}$  were recorded in the region of  $4000\text{--}400 \text{ cm}^{-1}$  using a Bruker IFS 113v FTIR spectrometer employing a nominal resolution of  $1.0 \text{ cm}^{-1}$  and Blackman–Harris 3-term apodization of the interferograms. A Ge/KBr beam splitter was used to cover the spectral region. To ensure optical linearity, a DTGS detector was used. Eight single-channel spectra, each recorded with 32 scans, were averaged to yield one background or sample spectrum. A gas cell of  $2.34 \pm 0.02 \text{ cm}$  equipped with windows of KBr was employed. The partial pressures of the gases in the cells were from 1 to 16 hPa and were measured using the MKS baratron pressure transducer as described before. The absorption cross sections were obtained from the absorbance spectra assuming that the gas was ideal and applying a baseline correction. The baseline correction was performed by subtracting a polynomial function, obtained by fitting the regions of the spectrum where no absorptions were expected.

The absorption cross section of a compound  $X$  at a specific wavenumber  $\tilde{\nu}$  is given by  $\sigma(\tilde{\nu}) = \{A_e\}/\{n_X\}l$ , where  $A_e(\tilde{\nu}) = -\ln\tau(\tilde{\nu})$  is the naperian absorbance,  $\tau$  is the transmittance,  $n_X$  is the number density of  $X$ , and  $l$  is the path length where the absorption takes place. The integrated absorption cross section,  $S$ , is given as the integral of  $\sigma(\tilde{\nu})$  over the absorption band or, as here, over regions of overlapping bands:

$$S = \int_{\text{band}} \sigma(\tilde{\nu}) d\tilde{\nu} \quad (1)$$

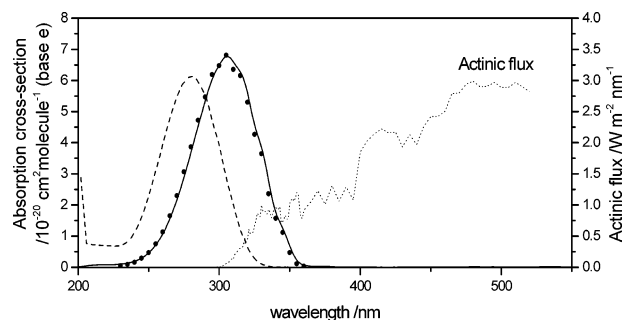
**Experiments Performed at EUPHORE.** A detailed description of the EUPHORE facility and the existing analytical instruments has been previously reported in the literature (2–6). The present photolysis experiments were carried out in a hemispherical outdoors simulation chamber of volume about  $195 \text{ m}^3$  made of FEP foil with a thickness of 0.127 mm. The FEP foil has a transmission of more than 75% of the solar radiation in the wavelength range between 290 and 550 nm. The chamber was equipped with a Nicolet Magna 550 FTIR spectrometer coupled with a white-type multireflection mirror system for in situ analysis. The optical path length was 553.5 m. FTIR spectra were recorded every 10 min by adding 570 interferograms with a resolution of  $1.0 \text{ cm}^{-1}$ .

The photolysis of PFMP was studied in purified, dry air (dewpoint less than  $-20^\circ \text{C}$ ) at  $T = 301\text{--}309 \text{ K}$  (see Becker (2) for a description of the drying and purification system). The large volume of the chamber minimizes the effects of wall reactions, thus resembling the free troposphere as closely as possible. Unlike the typical laboratory smog chamber, purified air is constantly added to compensate for loss through connections and loss due to continuous sampling by ozone and  $\text{NO}_x$  monitors, and this has to be corrected for as dilution of the sample in the data analysis. The mixing

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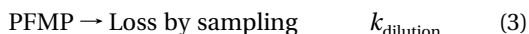
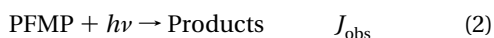
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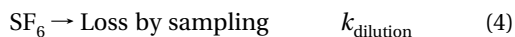


**FIGURE 1.** UV absorption cross sections of PFMP, 1,1,1,2,2,4,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone (full curve), and 2-pentanone (dashed curve). (●) Data from Taniguchi et al. (7). Dotted curve: actinic flux in the chamber at 15:20 (solar time).

ratio of PFMP in the chamber was initially ca. 1 ppm, and it may be reduced by photolysis (2) and dilution (3) as homogeneous gas-phase reactions do not play any role in the atmospheric loss (1).



Approximately 20 ppb of SF<sub>6</sub> was added to the reaction chamber to determine the overall dilution rate coefficient,  $k_{\text{dilution}}$ :



$$\ln\{[\text{SF}_6]_0/[\text{SF}_6]_t\} = k_{\text{dilution}}t \quad (5)$$

where [SF<sub>6</sub>]<sub>0</sub> and [SF<sub>6</sub>]<sub>t</sub> are the initial SF<sub>6</sub> concentration and that after a time *t*, respectively.

Thus, the apparent photolysis rate coefficient of PFMP,  $J_{\text{obs}}$ , can be obtained from the expression:

$$\ln\{[\text{PFMP}]_0\}/\{[\text{PFMP}]_t\} = (k_{\text{dilution}} + J_{\text{obs}})t \quad (6)$$

The effective quantum yield for the photolysis of the compound under study can be calculated according to the following expression:

$$\Phi_{\text{eff}} = J_{\text{obs}}/J_{\text{max}} \quad (7)$$

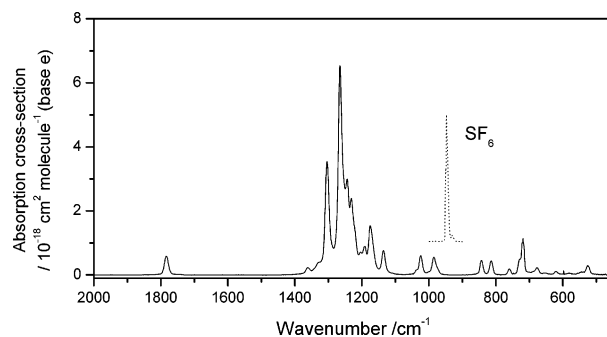
where the maximum photolysis rate coefficient,  $J_{\text{max}}$ , is given by:

$$J_{\text{max}} = \int \sigma(\lambda)F(\lambda) d\lambda \quad (8)$$

Here  $\sigma(\lambda)$  is the absorption cross section (base e) of the compound in units of cm<sup>2</sup> molecule<sup>-1</sup> and  $F(\lambda)$  is the solar actinic flux (photons cm<sup>-2</sup> s<sup>-1</sup>). The actinic flux was measured by a Bentham DM300 spectroradiometer as recently described by Wenger et al. (6), and the integration was carried out over the wavelength range of 290–400 nm.

## Results and Discussion

**UV–Vis Absorption Cross Section.** The UV–vis absorption cross section of PFMP at 298 ± 2 K was determined by a least-squares fit of the data from three independent measurements in pure gas at different pressures. The obtained UV–vis absorption cross section (base e) is shown in Figure 1 (the absorption cross section is available in JCAMP format as Supporting Information). The absorption band corresponds to the weak  $\pi^* \leftarrow n$  transition of the carbonyl group. When systematic errors in pressure measurements, temperature, optical path length, and instrumental drift are added



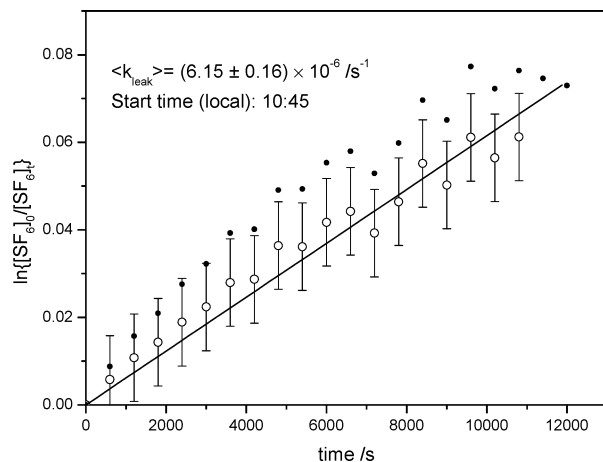
**FIGURE 2.** Infrared absorption cross section of PFMP (1,1,1,2,2,4,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone) overlaid by the  $\nu_3(\text{F}_{1u})$  band of SF<sub>6</sub>.

to the 2 $\sigma$  error from the least-squares fit (0.6%), it is estimated that the absolute error limit of the integrated cross section is approximately 2%. For comparison, Figure 1 includes the recently published data by Taniguchi et al. (7) and the UV spectrum of 2-pentanone (7), CH<sub>3</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, which is the only other ketone studied under similar conditions in the EUPHORE reactor (8). It is apparent that (i) the agreement between the two UV–vis data sets for PFMP is better than 5% in the region around the absorption maximum, (ii) the fluorinated ketone, PFMP, absorbs between 240 and 350 nm with a maximum around 305 nm and with an integrated absorption cross section apparently slightly larger than that of 2-pentanone (7), and (iii) the intensity maximum is red-shifted ca. 26 nm obviously caused by the electronegative substituents in the  $\alpha, \alpha'$ -positions in analogy with the situation in fluorinated propanones (9).

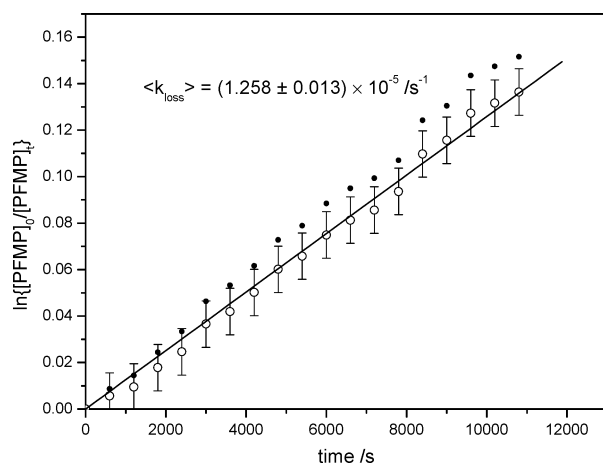
**Infrared Absorption Cross Section.** The integrated cross section of the absorption bands were determined by plotting the integrated absorbance against the product of the number density and the path length. None of the regression lines had a y-intercept significantly different from zero. A least-squares method that forced the regression line through zero was therefore used to determine the absorption intensities. Quantified systematic errors are pressure measurements (0.15%), path length (0.90%), and temperature (0.67%). The IR absorption cross section (base e) of PFMP is shown in Figure 2 (the IR absorption cross section is available in JCAMP format as Supporting Information). The integrated absorption cross section over the 1880–480 wavenumber region is  $(40.5 \pm 0.8) \times 10^{-17}$  cm molecule<sup>-1</sup>; the estimated uncertainty in the total absorption cross section of PFMP includes the additional 2 $\sigma$  error from the least-squares fit (0.7%) to the above-mentioned systematic errors.

We use the absorption cross section of HCFC-22, which has been critically evaluated by Ballard et al. (10), as a benchmark. Our measurements of HCFC-22 are constantly within 5% of the absorption intensities reported by Ballard and co-workers. In recent studies of a series fluorinated compounds (11–13), we demonstrated excellent agreement with previous results for the infrared cross sections. We therefore believe that our measurements of PFMP are not affected by any large systematic errors.

**Effective Quantum Yield of Photolysis.** A photolysis experiment with PFMP was carried out at the EUPHORE simulation chamber in Valencia, Spain (0.5 W, 39.5 N) during the month of July 2003. The removal of SF<sub>6</sub> and PFMP from the chamber was monitored by FTIR. The concentration of SF<sub>6</sub> was determined from the integrated intensity of the  $\nu_3(\text{F}_{1u})$  band around 947.5 cm<sup>-1</sup>, which does not overlap the PFMP absorption bands (see Figure 2). The relative concentrations of PFMP were determined by a spectral subtraction procedure involving the initial PFMP spectrum and a reference spectrum of water and limited to the carbonyl-

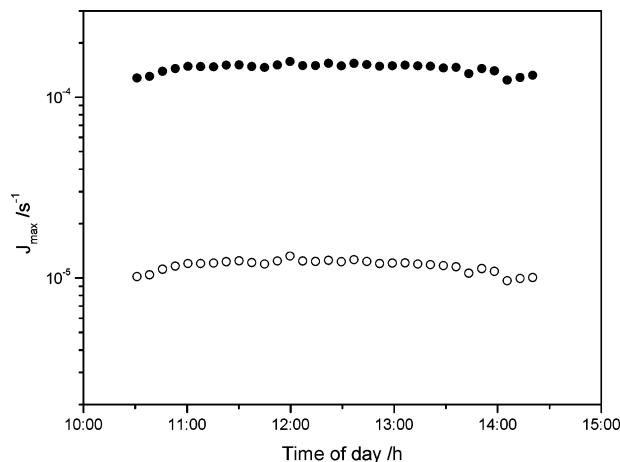


**FIGURE 3.** Plot of  $\ln\{[\text{SF}_6]_0/[\text{SF}_6]_t\}$  vs time, showing the mass loss from the reactor (Teflon) to the surrounding: (●) uncorrected data; (○) data corrected for changes in ( $P$ ,  $T$ ) during the experiment.



**FIGURE 4.** Plot of  $\ln\{[\text{PFMP}]_0/[\text{PFMP}]_t\}$  vs time, showing the total loss from the reactor (Teflon) during photolysis: (●) uncorrected data; (○) data corrected for changes in ( $P$ ,  $T$ ) during the experiment.

stretching band ( $1820\text{--}1760\text{ cm}^{-1}$ ); the carbonyl-stretching bands of the photolysis products  $\text{CF}_2\text{O}$  and  $\text{CF}_3\text{CFO}$  both fall at higher wavenumbers and do not overlap this band (1). The pressure and the temperature inside the chamber were not constant during the experiment. The observed reductions in  $\text{SF}_6$  and PFMP concentrations were therefore corrected according to the changes in pressure and temperature using the ideal gas law—the corrections being less than 1.5%. From a least-squares analysis of the decay in  $\text{SF}_6$  concentration (Figure 3), the dilution rate coefficient during the photolysis experiment was found to be  $(6.15 \pm 0.16) \times 10^{-6} \text{ s}^{-1}$  ( $2\sigma$ ). Figure 4 presents the simultaneous decay of the PFMP concentration given as a plot of  $\ln\{[\text{PFMP}]_0/[\text{PFMP}]_t\}$  versus the photolysis time, from which the total removal rate coefficient of PFMP was determined to be  $(1.258 \pm 0.013) \times 10^{-5} \text{ s}^{-1}$  ( $2\sigma$ )—in 3 h around 13% of PFMP was removed from the reactor. The data obtained (Figures 2 and 3) indicate that the total reduction in PFMP concentration during midday conditions in July was about twice the reduction in concentration of the inert tracer,  $\text{SF}_6$ . As there are no other known loss processes, the effective photolysis rate is found by correcting for dilution giving a value for  $J_{\text{obs}}$  of  $(6.4 \pm 0.3) \times 10^{-6} \text{ s}^{-1}$  ( $2\sigma$ ) at July 14 in Valencia 2003. This corresponds to a lifetime of 44 h under conditions of atmospheric pressure with  $(J_{\text{NO}_2}) = 7.85 \times 10^{-3} \text{ s}^{-1}$ . A conservative estimate of the atmospheric lifetime of PFMP with respect to photolysis is around 1 week. For comparison, Taniguchi et al. (1) estimated



**FIGURE 5.** Plot of the calculated maximal photolysis rates,  $J_{\text{max}}$ , of PFMP (1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone,  $\text{CF}_3\text{CF}_2\text{--C(O)CF(CF}_3)_2$ ) (●) and 2-pentanone,  $\text{CH}_3\text{--C(O)CH}_2\text{CH}_2\text{--CH}_3$  (○) vs time of day (GMT solar) assuming a uniform quantum efficiency. The UV-vis data for 2-pentanone are taken from ref 7.

the atmospheric photolysis lifetime of PFMP to be between 1 and 2 weeks from laboratory studies employing sunlamps. Although the integrated absorption cross section of PFMP is large, the short atmospheric lifetime makes the global warming potential of the compound negligible.

The maximum photolysis rate coefficient,  $J_{\text{max}}$  (see eq 8), during the experiment is shown in Figure 5, which also includes  $J_{\text{max}}$  for 2-pentanone for comparison—the only related ketone studied under similar conditions (8).  $J_{\text{max}}$  for PFMP varies between  $1.24$  and  $1.57 \times 10^{-4} \text{ s}^{-1}$  with a time average during the experiment of  $1.49 \times 10^{-4} \text{ s}^{-1}$ . The observed photolysis rate therefore corresponds to an effective quantum efficiency of photolysis under tropospheric sunlight conditions of  $\Phi_{\text{eff}} = 0.043 \pm 0.011$  ( $2\sigma$ ), which compares to  $0.07 \pm 0.1$  for 2-pentanone (8). As shown by Taniguchi et al. (1) nonradiative (collision assisted) relaxation processes are extremely effective following the initial  $S_0 \rightarrow S_1$  excitation. However, an effective fluorescence via the  $S_1 \rightarrow S_0$  transition similar to the situation in  $\text{CF}_3\text{CHO}$  (11) cannot be ruled out.

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## Supporting Information Available

UV-vis and infrared absorption cross sections of 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone in JCAMP format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- (1) Taniguchi, N.; Wallington, T. J.; Hurley, M. D.; Guschin, A. G.; Molina, L. T.; Molina, M. J. Atmospheric chemistry of  $\text{C}_2\text{F}_5\text{C(O)CF(CF}_3)_2$ : photolysis and reaction with Cl atoms, OH radicals, and ozone. *J. Phys. Chem. A* **2003**, *107*, 2674–2679.
- (2) Becker, K. H. *The European Photoreactor EUPHORE*; Final Report of the EC Project, Contract EV5V-CT92-0059; Wuppertal, Germany, 1996.
- (3) Magneron, I.; Thevenet, R.; Mellouki, A.; Le Bras, G.; Moortgat, G. K.; Wirtz, K. A study of the photolysis and OH-initiated oxidation of acrolein and trans-crotonaldehyde. *J. Phys. Chem. A* **2002**, *106*, 2526–2537.

- (4) Volkamer, R.; Platt, U.; Wirtz, K. Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and *p*-xylene. *J. Phys. Chem. A* **2001**, *105*, 7865–7874.
- (5) Klotz, B.; Sorensen, S.; Barnes, I.; Becker, K. H.; Etzkorn, T.; Volkamer, R.; Platt, U.; Wirtz, K.; Martin-Reviejo, M. Atmospheric oxidation of toluene in a large-volume outdoor photoreactor: In situ determination of ring-retaining product yields. *J. Phys. Chem. A* **1998**, *102*, 10289–10299.
- (6) Wenger, J. C.; Le Calve, S.; Sidebottom, H. W.; Wirtz, K.; Reviejo, M. M.; Franklin, J. A. Photolysis of chloral under atmospheric conditions. *Environ. Sci. Technol.* **2004**, *38*, 831–837.
- (7) Martinez, R. D.; Buitrago, A. A.; Howell, N. W.; Hearn, C. H.; Joens, J. A. The near UV absorption-spectra of several aliphatic-aldehydes and ketones at 300-K. *Atmos. Environ., Part A* **1992**, *26*, 785–792.
- (8) Moortgat, G. K. *Evaluation of Radical Sources in Atmospheric Chemistry through Chamber and Laboratory Studies: RADICAL*; Max-Planck-Institut für Chemie, Atmospheric Chemistry Division: 2000.
- (9) Metcalfe, J.; Phillips, D. Photophysical processes in fluorinated acetones. *J. Chem. Soc., Faraday Trans. 2*, **1976**, *72*, 1574–1583.
- (10) Ballard, J.; Knight, R. J.; Newnham, D. A.; Vander Auwera, J.; Herman, M.; Di Lonardo, G.; Masciarelli, G.; Nicolaisen, F. M.; Beukes, J. A.; Christensen, L. K.; McPheat, R.; Duxbury, G.; Freckleton, R.; Shine, K. P. An intercomparison of laboratory measurements of absorption cross-sections and integrated absorption intensities for HCFC-22. *J. Quant. Spectrosc. Radiat. Transfer* **2000**, *66*, 109–128.
- (11) Sellevåg, S. R.; Kelly, T.; Sidebottom, H.; Nielsen, C. J. A study of the IR and UV-vis absorption cross-sections, photolysis and OH-initiated oxidation of CF<sub>3</sub>CHO and CF<sub>3</sub>CH<sub>2</sub>CHO. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1243–1252.
- (12) Oyaro, N.; Sellevåg, S. R.; Nielsen, C. J. A study of the OH and Cl-initiated oxidation, IR absorption cross-section, radiative forcing and global warming potential of four C4-hydrofluoroethers. *Environ. Sci. Technol.* **2004**, *38*, 5567–5576.
- (13) Oyaro, N.; Sellevåg, S. R.; Nielsen, C. J. Atmospheric chemistry of hydrofluoroethers: Reaction of a series of hydrofluoroethers with OH radicals and Cl atoms, atmospheric lifetimes, and global warming potentials. *J. Phys. Chem. A* **2005**, *109*, 337–346.

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