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Atmospheric fate and impact of perfluorinated butanone and pentanone

Yangang Ren, François Bernard, Véronique Daële, Abdelwahid Mellouki*

Affiliations

Institut de Combustion Aérothermique, Réactivité et Environnement, Centre National de la Recherche Scientifique (ICARE-CNRS), Observatoire des Sciences de l'Univers en région Centre (OSUC), CS 50060, 45071 cedex02, Orléans, France

Corresponding author

* mellouki@cnrs-orleans.fr

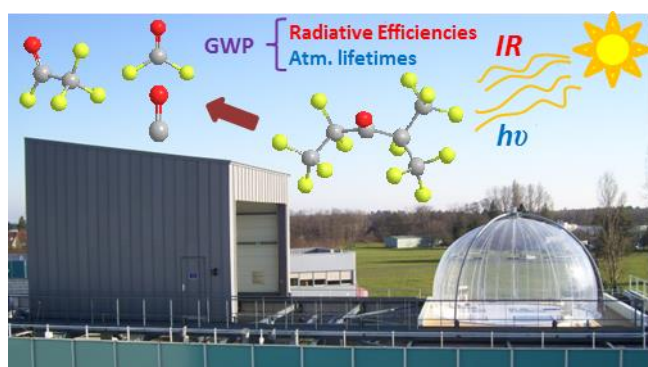
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Abstract

Perfluoroketones, used as replacement to halons and CFCs, are excluded from the Montreal Protocol because they are considered as non-ozone depleting substances. However, their chemical structure makes them possible greenhouse gases if their atmospheric lifetimes are long enough. To assess that possibility, we investigated the photolysis of perfluoro-2-methyl-3-pentanone (PF-2M3P), and perfluoro-3-methyl-2-butanone (PF-3M2B) using outdoor atmospheric simulation chambers. In addition, the photolysis of a non fluorinated pentanone (2-methyl-3-pentanone, 2M3P) was studied. The results showed that photolysis is the dominant loss pathway of PF-2M3P and PF-3M2B in the troposphere whereas 2M3P is lost by both photolysis and gas phase reaction with atmospheric oxidants. The photolysis effective quantum yields of PF-2M3P, PF-3M2B and 2M3P were estimated and some of the main products identified. The photolysis of PF-2M3P and PF-3M2B was found to have a minor impact on the atmospheric burden of fluorinated acids. The atmospheric lifetimes of PF-2M3P, PF-3M2B and 2M3P were estimated to 3-11 days, ~13 days and 1-2 days, respectively. Combining the obtained data, it has been concluded that with 100-year time horizon global warming potentials (GWP₁₀₀) equivalent to <0.21, ~0.29 and $\leq 1.3 \times 10^{-7}$ for PF-2M3P, PF-3M2B and 2M3P, respectively, these compounds will have a negligible impact on global warming.

Keywords: perfluorinated ketones, UV absorption spectrum, IR absorption spectrum, photolysis rates, natural irradiation, atmospheric lifetime, global warming potential.

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1. Introduction

Along with hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) are non-ozone depleting substances and therefore excluded from the Montreal Protocol.¹ However, they are considered as greenhouse gases due to their strong absorption in the infrared spectral region in the atmospheric window combined to their long atmospheric lifetimes.² Their atmospheric concentrations have been growing rapidly over last decades and potentially continue to grow.³ They have been widely used for the cooling of power electronics over the last decade. Perfluoroketones such as perfluoro-2-methyl-3-pentanone (PF-2M3P, $\text{C}_2\text{F}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, Novec 649/1230) and perfluoro-3-methyl-2-butanone (PF-3M2B, $\text{C}_2\text{F}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, Novec5110) are among the important replacement chemicals to halons and CFCs⁴⁻⁵. PF-2M3P and PF-3M2B are advanced heat transfer perfluorocarbons with high dielectric strength. Up to 30 t of PF-2M3P could be released into the atmosphere each year from fire-protection systems⁶. PF-3M2B is being used as versatile insulating gas for medium and high voltage applications including gas insulated lines, gas insulated switchgear and circuit breakers.⁷ The large production and usage of both chemicals are likely to induce their direct emission into the atmosphere.

Similarly to other volatile organic compounds, PF-2M3P and PF-3M2B may be potentially removed from the atmosphere through photolysis, gas phase chemical reactions with the main atmospheric oxidants, hydrolysis and deposition. The

atmospheric fate of PF-2M3P has been subject to a limited number of investigations. Photolysis studies were based on the use of artificial and natural irradiations.^{5,8,9} The atmospheric lifetime of PF-2M3P has been found to be controlled by photolysis and reported to be in the range of 4-14 days depending on latitude and period of the year.⁶ The gas phase reactions with OH radical and ozone as well as hydrolysis represent minor contribution to the total removal of PF-2M3P from the atmosphere.⁵⁻⁶ To the best of our knowledge, no experimental data on the photolysis of PF-3M2B have been reported. Hence, the present work aims at investigating the photolysis of PF-3M2B under atmospheric conditions and improving the existing data on PF-2M2B in order to evaluate their atmospheric impacts. In addition to the two perfluorinated ketones, a non-fluorinated analogue aliphatic ketone to PF-2M3P, 2-Methyl-3-pentanone (2M3P, $\text{C}_2\text{H}_5\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$) has been investigated. The UV-Visible and infrared (IR) absorption spectra of PF-2M3P, PF-3M2B and 2M3P were measured. Their photolysis rates were determined using two complementary atmospheric simulation chambers with natural sunlight irradiation. Atmospheric lifetimes and global warming potentials (GWP) for the three studied compounds are reported and discussed in terms of their atmospheric impacts.

2. Experimental Section

2.1. UV absorption spectra

The apparatus used in this work has been described in previous studies ⁸ and is briefly presented here. The UV-Visible absorption spectra of PF-2M3P, PF-3M2B, and 2M3P were measured using a spectrophotometer equipped with a 1200 grooves mm⁻¹ grating and a charge-coupled device (CCD) camera. The collimated output of a 30 W deuterium lamp passed through a 100 cm long and 2.5 cm diameter Pyrex absorption cell equipped with quartz windows and focused onto the entrance slit of the spectrometer. Measurements were made over the wavelength region 220–400 nm by recording typically three overlapping regions of about 15 nm. Typically, each measurement consisted of 8-13 scans of diode array. The wavelength scale was calibrated using the emission lines from a low-pressure Hg pen ray lamps (253.7, 313.2, and 365 nm). Absorption cross sections, $\sigma(\lambda)$ (in cm² molecule⁻¹) were obtained using the Beer's law:

$$\sigma(\lambda) = \frac{-\ln[I(\lambda)/I_0(\lambda)]}{CL} \quad \text{Eq. 1}$$

where L is the path length of absorption cell (in cm), and C is the concentration of the studied compound (in molecule cm⁻³). $I_0(\lambda)$ and $I(\lambda)$ are the light intensities in the absence and in the presence of the compound in the absorption cell, respectively. The concentration of the species of interest in the absorption cell was obtained from the measured pressure using a 0-10 Torr capacitance manometer. Measurements of the PF-2M3P, PF-3M2B and 2M3P UV absorption spectra were performed at $T = (292 \pm 1)$ K using the concentration ranges $[\text{PF-2M3P}] = (0.29 - 2.7) \times 10^{17}$, $[\text{PF-3M2B}] = (0.27 - 3.0) \times 10^{17}$ and $[2\text{M3P}] = (0.43 - 2.9) \times 10^{17}$ molecule cm⁻³.

103

104 **2.2. Atmospheric simulation chambers**

105 Photolysis studies of PF-2M3P, PF-3M2B and 2M3P were conducted in the large
106 simulation chamber HELIOS. In addition, the photolysis of PF-2M3P was also
107 investigated in a 3.4 m³ Teflon outdoor chamber. Both HELIOS and the 3.4 m³ Teflon
108 outdoor chambers allowed photolysis experiments to be performed under natural solar
109 exposure.

110

111 **2.2.1. HELIOS**

112 The facility consists of a 90 m³ hemispherical outdoor simulation chamber
113 (47°50'18.39N; 1°56'40.03E) made of FEP Teflon film. This facility has been
114 described previously.⁹ The light transmission ranges from 88 to 95% over the entire
115 solar spectrum. Two fans installed in the chamber ensure a rapid mixing of reactants
116 (within less than 90 seconds). Solar actinic flux (290-660 nm) and photolysis
117 frequencies of H₂O₂, HONO, HCHO, NO₃, NO₂ and O(¹D) were measured by a
118 spectroradiometer (Meteorologie Consult GmbH 6007). Pressure, relative humidity and
119 temperature were continuously monitored by a three-axis Ultrasonic Anemometer
120 (Delta Ohm, HD 2003) installed in the center of the chamber. The temperature
121 distribution was also measured using six thermocouples (PT-100) spatially and equally
122 distributed inside the chamber. A mobile protective housing kept the chamber under
123 the dark and can be easily moved to fully expose the chamber to sunlight within 30

seconds. The experimental duration under irradiation was between 3 and 7 hours, in which the temperature typically increased by ~ 10 °C. Between experiments, the chamber was cleaned by flushing pure air through for at least 12 hours.

Organic compounds were monitored via in situ Fourier transform infrared spectrometry (FT-IR, Bruker Vertex70 spectrometer) coupled to a White-type multipass cell (302.6 m optical path length). Infrared spectra were recorded every 3 minutes by co-adding 250 interferograms with a resolution of 0.4 cm^{-1} . The gas phase mixture was also analyzed using a gas chromatography coupled to a mass spectrometer (GC-MS, PekinElmer Clarus 600 C). Gas samples were collected from the chamber at low temperature (-30°C) onto Air Toxics tubes and analyzed through a thermal desorber (TurboMatrixTM 150 ATD), with split mode, followed by a thermal desorption at 300°C (5 min) delivering the sample to a 60-m column (GasPro diameter 0.320mm). The O_3 and NO-NO_x concentrations were continuously monitored by UV absorption (HORIBA, APOA 370) and chemiluminescence analyzer (HORIBA, APNA 360), respectively. PF-3M2B was also monitored by PTR-TOF-MS (Proton Transfer Reaction - Time of Flight-Mass Spectrometer, IONICON 8000). The fragment CF_3^+ (m/z 68.986) and $(\text{CF}_3)_2\text{CF}_3^+$ (m/z 168.970) were used to monitor the temporal behavior of PF-3M2B during the photolysis.

PF-2M3P and 2M3P were introduced into the chamber by placing known volumes of liquid in a bubbler and then, flushed by purified air. Their concentrations were derived based on the volume of the liquid introduced, the pressure and the temperature

in the chamber using the ideal gas law. PF-3M2B and SF₆ were introduced into the chamber by streaming purified air through a calibrated stainless steel cylinder (4.87 L) equipped with capacitance manometers. To compensate sampling flows from analytical instruments and chamber leaks, a flow of purified air (15-25 L/min) was added continuously during all experiments enabling a slight overpressure to be maintained, thus avoiding any contamination from outside air. Dilution of the gas volume in the chamber was determined by monitoring the decay of introduced amount of SF₆ (monitored by FT-IR). This decay under dark conditions was found to be in the range of $(5 - 20) \times 10^{-6} \text{ s}^{-1}$.

Background concentrations in the chamber were systematically found to be below the detection limits of analytical instruments (e.g., [NO_x] < 2.5 × 10¹⁰, [O₃] < 2.5 × 10¹⁰, [VOC] < 1.3 × 10⁸ molecule cm⁻³).

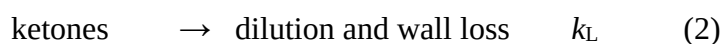
2.2.2. 3.4 m³ outdoor chamber

Photolysis studies of PF-2M3P were also performed in the 3.4 m³ ICARE outdoor atmospheric simulation chamber made of ethylene tetrafluoroethylene (ETFE) foil. The light intensity was continuously monitored using a filter radiometer measuring the photolysis frequency of NO₂, *J*_{NO₂} (Meteorologie consult GmbH, Germany). The temperature and the relative humidity were also continuously measured using a combined probe (Vaisala HMT330 series transmitters). Chemical analysis of the gas mixture was characterized by an infrared spectrometer (Nicolet 550 Magna FT-IR

spectrometer) coupled to a White-type multi-pass mirror cell (optical path length 10 meters). Infrared spectra were recorded every 5 minutes by co-adding 130 interferograms at a resolution of 1 cm^{-1} . Rapid mixing of reactant was insured using a fan made of Teflon mounted into the chamber. The dilution rate was estimated by monitoring the loss of SF_6 . IR reference spectrum of PF-2M3P was obtained by introducing a known volume of liquid in the chamber. During dark experiments, the chamber was covered by a black and opaque curtain to protect it from sunlight radiation. The curtain could be removed very quickly for exposure to solar radiation, thus initiating the photolysis process. Experiments were performed at 1013 mbar of purified air and in the temperature range of 306 to 319 K. Initial concentrations of PF-2M3P were in the range of $(0.89\text{-}2.7) \times 10^{14}\text{ molecule cm}^{-3}$. The gas mixture was exposed to solar irradiation for up to 4 hours.

2.3. Photolysis experiments

Under sunlight conditions, the investigated ketones, PF-2M3P, PF-3M2B and 2M3P may be removed by photolysis, dilution and wall loss processes following the reactions:



187 where J (in s^{-1}) is their photolysis rate while k_L (in s^{-1}) is their decay rates under the
 188 dark including dilution and wall loss. Under irradiation, the total decays of the
 189 investigated ketones are expressed as follows:

$$190 \quad \ln([\text{ketone}]_0/[\text{ketone}]_t) = k_{\text{tot}} \times t \quad \text{Eq. 2}$$

191 with $[\text{ketone}]_0$ and $[\text{ketone}]_t$ are the concentrations of PF-2M3P or PF-3M2B or 2M3P
 192 at times t_0 and t , respectively. k_{tot} (in s^{-1}), the total decay rate of the studied compound
 193 under irradiation, is formulated as:

$$194 \quad k_{\text{tot}} = J_{\text{meas}} + k_{\text{d,light}} + (k_L - k_{\text{d,dark}}) \quad \text{Eq. 3}$$

195 J_{meas} is the photolysis rate obtained from the experiment measurement. $k_{\text{d,dark}}$ and
 196 $k_{\text{d,light}}$ (in s^{-1}) are, respectively, the dilution decay rates obtained from SF_6 decay in the
 197 dark and during irradiation.

198 The atmospheric photolysis rate coefficient was calculated, J_{calc} , as follows:

$$199 \quad J_{\text{calc}} = \int \sigma(\lambda) \Phi(\lambda) F(\lambda) d\lambda \quad (\lambda = 290\text{-}400 \text{ nm}) \quad \text{Eq. 4}$$

200 where $\sigma(\lambda)$, $\Phi(\lambda)$ and $F(\lambda)$ are the absorption cross-section, the quantum yield of
 201 dissociation and the actinic flux over the absorption 290 to 400 nm, respectively. The
 202 actinic flux was directly measured by the spectroradiometer placed inside the chamber.
 203 Assuming a quantum yield of unity for the photodissociation process along the
 204 absorption region of PF-2M3P or PF-3M2B or 2M3P, the maximum photolytic rate
 205 coefficient can be calculated, $J_{\text{max}} = J_{\text{cal}}$ using Eq. 4. As a result, an effective
 206 photodissociation quantum yield can derived:

$$\Phi_{\text{eff}} = J_{\text{meas}}/J_{\text{max}} \quad \text{Eq. 5}$$

2.4. Chamber loss correction

The concentrations of the products formed from the photolysis of PF-2M3P, PF-3M2B and 2M3P were corrected to account for dilution and possible photolysis/OH reactions under irradiation using the following equation:¹⁰

$$[\text{Product}]_{\text{corrected}} = [\text{Product}]_{\text{measured}} \times F \quad \text{Eq. 6}$$

with F being the correction factor: $F = 1 + \Delta[\text{Product}]/[\text{Product}]_{\text{measured}}$

The amount of product lost, $\Delta[\text{Product}]$ due to secondary reactions, i.e., dilution, reaction with OH radical and photolysis processes is calculated from:

$$\Delta[\text{Product}] = \int (k_{\text{d,light}} + J_{\text{product}} + [\text{OH}] \cdot k) \times [\text{Product}]_{\text{measured}} \times dt \quad \text{Eq. 7}$$

The losses of CF_3COF , COF_2 and CO were only due to dilution and were corrected using $F < 1.2$. For HCHO , CH_3CHO and CH_3COCH_3 , photolysis, reaction with OH radical and dilution were considered and $F_{\text{HCHO}} < 1.52$, $F_{\text{CH}_3\text{CHO}} < 1.35$ and $F_{\text{CH}_3\text{COCH}_3} < 1.30$ were used for the corresponding corrections. J_{HCHO} measured by the spectroradiometer and $J_{\text{CH}_3\text{CHO}}$ and $J_{\text{CH}_3\text{COCH}_3}$ were calculated using Eq. 4; corresponding $\sigma(\lambda)$ and $\Phi(\lambda)$ values for CH_3CHO and CH_3COCH_3 were taken from IUPAC database¹¹. The OH rate coefficients of CO , HCHO , CH_3CHO and CH_3COCH_3 were extracted from IUPAC kinetic database¹¹ as 1.65×10^{-13} , 8.5×10^{-12} , 1.5×10^{-11} and $1.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 298 \text{ K}$.

2.5 Infrared absorption spectra

The spectra of PF-2M3P, PF-3M2B, and 2M3P were measured at 295 ± 1 K using Fourier transform infrared (FTIR) spectroscopy. Absorption spectra were recorded in 250 co-adds between 700 and 4000 cm^{-1} at 1 cm^{-1} resolution (Happ-Genzel apodization). A Whyte-type multi-pass absorption cell with 10 meters optical path length (KBr windows) was used in the course of these measurements. Absorption spectra, $A(\nu)$ (base e), (or integrated band strengths) were determined using Beer's law:

$$A(\nu) = \sigma(\nu) \times L \times [\text{Ketones}] \quad \text{Eq. 8}$$

where $\sigma(\nu)$ is the infrared absorption cross section of the ketones at wavenumber ν , L is the absorption path length, and $[\text{ketones}]$ is the PF-2M3P, PF-3M2B, and 2M3P concentration. Measurements were performed using the following concentration ranges (in units of molecule cm^{-3}): $(1.2\text{-}10.8) \times 10^{14}$ for PF-2M3P, $(1.6\text{-}9.9) \times 10^{14}$ for PF-3M2B and $(0.6\text{-}4.8) \times 10^{14}$ for 2M3P. Over the course of the study, replicate measurements were performed using independently prepared gas mixtures with helium as bath gas. The absorption spectra (band strengths) were obtained from a linear least-squares fit of A versus $[\text{Ketones}]$ that included at least 6 individual spectrum measurements.

2.6. Chemicals

The chemicals used in this work and their stated purities were as follows: perfluoro-2-methyl-3-pentanone (99%, 3M Belgium N.V, Chemical Group-EBC), 2-

248 methyl-3-pentanone (97%, Sigma-Aldrich), perfluoro-3-methyl-2-butanone (98%,
249 Ugarit Chimie), SF₆ (99.9995%, Air Liquide) and O₂ (99.9995%, Air Liquide), Helium
250 (99.9995%, Air Liquide). PF-2M3P, PF-3M2B and 2M3P samples were further
251 purified by using several freeze-pump-thaw cycles. GC-MS analysis of the samples did
252 not show any observable impurities.

254 3. Results and Discussion

255 3.1. UV absorption cross section

256 To test the accuracy of the measurement methodology used in this work, the UV
257 absorption spectrum of acetone has been measured and compared to the recommended
258 UV spectrum from NASA/JPL evaluation.¹² As shown in SI (Figure S1), the level of
259 agreement between both measured and recommended spectra is high, within the
260 measurement accuracy of the recommended UV-Vis absorption spectra ($\approx 8\%$). This
261 excellent agreement provides confidence in the reliability of the absorption cross
262 section measurement conducted in this work.

263 The measured UV-Visible absorption spectra of PF-2M3P, PF-3M2B and 2M3P
264 between 220 and 400 nm at (300 ± 2) K are depicted in Figure 1 and absorption cross
265 sections are provided in Table S1. The quoted uncertainties originated from 2 standard
266 deviation (2σ) of the average of individual measurements. The measurements satisfied
267 Beer's law over a wide concentration range (an order of magnitude). The measured
268 absorbance, A (base e) ranged from 0.2 to 1.7 for PF-2M3P, 0.1 to 1.0 for PF-3M2B,

0.3 to 2.0 for 2M3P. Corresponding graphical representations of Beer's law fits are given in Figure S2.

2M3P shows a maximum absorption at 284 nm ($\sigma_{(284 \text{ nm})} = (6.99 \pm 0.28) \times 10^{-20}$ cm² molecule⁻¹) while PF-2M3P shows a maximum around 305 nm ($\sigma_{(305 \text{ nm})} = (6.50 \pm 0.28) \times 10^{-20}$ cm² molecule⁻¹) and PF-3M2B exhibits a maximum absorption at 300 nm ($\sigma_{(300 \text{ nm})} = (3.46 \pm 0.15) \times 10^{-20}$ cm² molecule⁻¹). The UV absorption spectra obtained in this work are compared with those reported in literature when possible and are presented in Figure 1. The absorption spectrum of PF-2M3P is in agreement with the reported one by Taniguchi et al.,⁵ within 5%. The absorption cross sections of 2M3P obtained in the present work is higher than that reported by Díaz-de-Mera, et al.¹³ by 18% (σ_{max}). To the best of our knowledge, the experimental UV spectrum of PF-3M2B is reported for the first time here. Prior to this study, the UV spectrum of PF-3M2B was also determined using a theoretical approach and found to be higher compared to this work, within 27% at the maximum cross section.¹⁴

The absorption band of ketones is caused by the dipole forbidden n- π^* transition of the C=O group. The maximum absorption of PF-2M3P is red-shifted, i.e. around 20 nm, compared to 2M3P caused by the electronegative substituents in α - α' -positions.¹⁵⁻¹⁷ In addition, the maximum absorption of PF-2M3P is about ~2 times higher than that of PF-3M2B, which is consistent with the results of Mu and Mellouki⁸ who observed that the peak UV cross section increased for larger aliphatic ketones.

The actinic flux in HELIOS at 13:00 (± 5 min, local time) on 7th of September

2013 is also displayed on Figure 1. The integrated absorption cross sections over the actinic flux region for PF-2M3P, 2M3P and PF-3M2B were determined to be 2.61×10^{-18} , 1.22×10^{-18} and 1.25×10^{-18} cm² molecule⁻¹, respectively, indicating that one could expect $J_{\text{PF-2M3P}} > J_{\text{2M3P}} \approx J_{\text{PF-3M2B}}$.

3.2. Photolysis of perfluoro-2-methyl-3-pentanone

Photolysis rate measurements. Experiments in the 3.4 m³ outdoor chamber were conducted in June-July 2010 at (306-319) K and RH<1%. Temporal profiles of PF-2M3P and SF₆ concentrations were monitored under the dark for about 4 hours. No discernible loss other than dilution has been observed; the first order decay rates of PF-2M3P and SF₆ were in the order of $(6.6 - 8.1) \times 10^{-6}$ s⁻¹. The chamber was then exposed to solar radiation, thus starting the photolysis. The photolysis rate of PF-2M3P, $J_{\text{PF-2M3P}}$, was obtained by considering the total loss of PF-2M3P (k_{tot}) and that from dilution which was obtained from the loss rate of SF₆ (k_d) under irradiation. Experimental details and results derived from the four runs conducted are displayed in Table 1. For all experiments, the photolysis rates of NO₂ were in the range of $(4.4-5.5) \times 10^{-3}$ s⁻¹. The consumed fractions of PF-2M3P from photodissociation were between 2.1 and 3.7 % and the derived photolysis rates were $(1.7-2.8) \times 10^{-6}$ s⁻¹ under our experimental conditions ($J_{\text{NO}_2} = (4.4-5.5) \times 10^{-3}$ s⁻¹). The quoted error corresponds to 2σ obtained from the least square analysis applied on the experimental data. The estimated error on $J_{\text{PF-2M3P}}$ was in the range of 7-14 %.

HELIOS experiments were performed during September 2013 at $T = 298 - 317\text{ K}$ and $RH < 1\%$. SF_6 and PF-2M3P concentrations were monitored by FT-IR and ATD-GC-MS for typically 2 hours in the dark and under natural irradiation for typically 4 to 7 hours. The loss rates of SF_6 and PF-2M3P were found to be similar in the dark, equivalent to $(4.8-6.0) \times 10^{-6}\text{ s}^{-1}$, indicating a minor loss on the chamber wall of PF-2M3P. During irradiation, both FT-IR and ATD-GC-MS instruments showed a slightly higher disappearance rate of PF-2M3P than SF_6 which indicated a possible photolysis loss of PF-2M3P (ranging from 1.7 to 7.7 %) under our experimental conditions. The photolysis rate of PF-2M3P, $J_{\text{PF-2M3P}}$ was determined to be $(1.1-3.8) \times 10^{-6}$ and $(1.1-3.6) \times 10^{-6}\text{ s}^{-1}$ using Eq. 3, from FTIR and GC-MS measurements, respectively, with a recommended range of $(1.1-3.8) \times 10^{-6}\text{ s}^{-1}$ (with $J_{\text{NO}_2} = (3.0-5.6) \times 10^{-3}\text{ s}^{-1}$).

Table 2 summarizes the photolysis rates of PF-2M3P obtained in this work and those reported in the literature. The values from this work were lower than those reported by D'Anna, et al.¹⁸ Díaz-de-Mera, et al.¹³ who also conducted experiments under natural irradiation in Spain. In contrast, the experiments conducted under artificial irradiation using black lamps or sunlamps led to lower photolysis rate values⁵. It should be noted that the measured photolysis rate from this work agreed with the result from the TUV model¹⁹ run at different seasons of the year (Table S2).

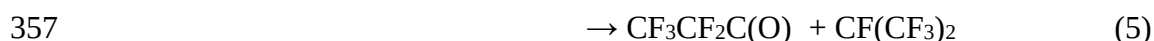
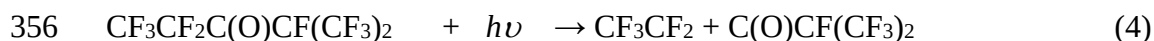
The maximum photolysis rate of PF-2M3P, $J_{\text{max-PF-2M3P}}$, was estimated using absorption cross sections and the actinic flux measured in this work (Eq. 4) and found to be in the range of $(0.7-1.2) \times 10^{-4}\text{ s}^{-1}$. Therefore, the observed photolysis rate

corresponds to an effective quantum yield of $\phi_{\text{eff}} = 0.015\text{--}0.035$, which is in agreement with the values reported by D'Anna, et al.¹⁸ and Díaz-de-Mera, et al.¹³, 0.043 ± 0.011 and 0.044 ± 0.006 , respectively.

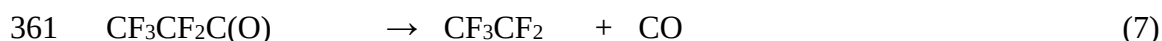
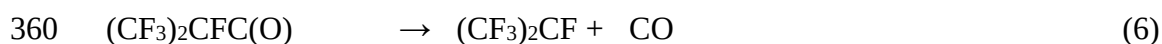
Products and mechanism. Typical IR spectra obtained from the photolysis of PF-2M3P/SF₆/air mixture in HELIOS are displayed in SI (Figure S3). CF₃COF, COF₂ and CO were identified as photolysis products by FTIR analysis from 3.4 m³ chamber and HELIOS experiments. Perfluoro-propionic acid (CF₃CF₂C(O)OH, PFPrA) and trifluoro-acetic acid (CF₃COOH, TFA) were also identified (m/z 69) among the photolysis products, using the NIST GC-MS library (Figure S4). Temporal profiles of PF-2M3P and its photolysis products are depicted in Figure 2.

The formation yields of products (COF₂, CF₃COF and CO) were obtained from a linear least-square fit applied to the experimental data as shown in Figure S5 (HELIOS) and Figure S6 (3.4 m³ chamber) and summarized in Table S3. The recommended formation yields of products ($\pm 2\sigma$) from the photolysis of PF-2M3P are: $(74 \pm 18)\%$, $(193 \pm 84)\%$, and $(204 \pm 68)\%$ for CF₃C(O)F, COF₂, and CO, respectively. The carbon and fluorine budgets were estimated to $(90 \pm 28)\%$ and $(57 \pm 18)\%$, respectively. This suggests a large fraction of unidentified fluorine-containing products. Indeed, Taniguchi, et al.⁵ identified CF₃O₃CF₃ and CF₃OH as photolysis products that were not identified in the present work.

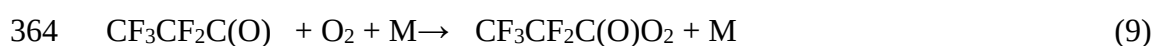
352 A proposed mechanism leading to the formation of the observed products from the
 353 photolysis of PF-2M3P is shown in Figure S7. The photodissociation of PF-2M3P may
 354 occur through a C-C bond cleavage in the α -position of the carbonyl group to produce
 355 perfluoroalkyl and perfluoroacetyl radicals:



358 Perfluoroacetyl radicals are expected to either decompose to give CO and
 359 perfluoroalkyl radical:



362 or react with O₂ leading to the corresponding peroxy radicals:



365 The high formation yield of CO (204±68)% indicates that the thermal
 366 decomposition is an important pathway in the fate of perfluoroacetyl radical over the
 367 reaction with O₂.

368 CF₃COF and COF₂, identified among the photolysis products (74±18)% and
 369 (193±84)%, respectively, might originate from the reactions of CF₃CF₂O₂ and
 370 (CF₃)₂CFCO₂ radicals with RO₂ radicals present in the system leading to the
 371 corresponding RO radicals as (CF₃)₂CFCO and CF₃CF₂O radicals, which would

thermally decompose to form CF_3 radicals and the corresponding fluorinated carbonyls $\text{CF}_3\text{C}(\text{O})\text{F}$ and COF_2 .²⁰ In addition, $\text{CF}_3\text{CF}_2\text{OH}$ and CF_3OH , formed from $\text{CF}_3\text{CF}_2\text{O}$ and CF_3O radicals reaction with hydrogen-containing compounds present in the chamber (e.g., HCHO desorbing from the chamber walls, impurities in the air diluent, or water), were also reported to transform rapidly into COF_2 .²¹⁻²²

3.3. Photolysis of 2-methyl-3-pentanone

Photolysis rate measurements. Mixtures of 2M3P/ SF_6 /air were added into HELIOS and left in the dark typically for 2 hours before irradiation by solar light. The loss rates of SF_6 and 2M3P in the dark were determined to be $(4.8\text{-}6.2) \times 10^{-6}$ and $(5.2\text{-}6.8) \times 10^{-6} \text{ s}^{-1}$, respectively. The chemical mixture 2M3P/ SF_6 /air was then exposed to solar irradiation for typically 5-6 hours. Under these experimental conditions, the measured loss of 2M3P ranged from 3.9 to 6.3%. The determination of $J_{2\text{M3P}}$ from FTIR and GC-MS measurements were in good agreement, within (3-7) %. The experimental conditions and the obtained values of $J_{2\text{M3P}}$ are summarized in Table 1.

All the experiments were performed in the absence of OH radical scavenger to avoid spectral interferences in the mid-infrared region with the studied compounds. Therefore, the gas phase removal of 2M3P during solar exposure might also due to the reaction of OH radicals with 2M3P in addition to its photolysis. Indeed, when the chamber was only filled with purified air and exposed to solar irradiation, separate measurements using a chemical ionization mass spectrometer (CIMS) have shown the

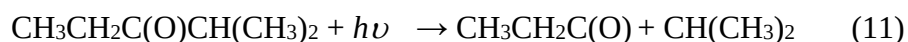
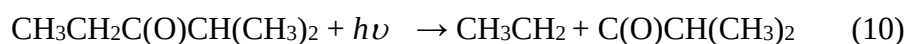
presence of OH radicals at concentration ranging from $(2.1 \pm 0.9) \times 10^5$ occasionally up to 2×10^6 molecule cm^{-3} could be observed. This implied that under these conditions, the OH reaction contribution to the total loss of 2M3P would have contributed from 30% to 100%. However, it has been also observed that the disappearance rate of 2M3P during solar exposure during this study was very comparable to those of PF-2M3P and PF-3M2B (Table 1), suggesting that the OH concentration level during these experiments was very low. Therefore, in the absence of OH radical direct measurement during this study, we preferred to be conservative and thus, recommend an upper limit for the photolysis rate of 2M3P, equivalent to $(2.6 \pm 1.4) \times 10^{-6} \text{ s}^{-1}$ (with $J_{\text{NO}_2} = 5.6 \times 10^{-3} \text{ s}^{-1}$).

Based on the integrated UV absorption spectrum over the actinic flux region, the derived maximum photolysis rate constant of 2M3P, $J_{\text{max-2M3P}}$, was found to be $(6.5\text{--}9.6) \times 10^{-6} \text{ s}^{-1}$. Therefore, the effective photolysis quantum yield is estimated to be $\phi_{\text{eff}} \leq 0.28$ under tropospheric sunlight conditions.

Products and mechanism. Products were identified and quantified using FT-IR spectroscopy. The Figure S8 displays the typical spectra acquired before and after the photolysis of 2M3P. Comparison of measured calibrated IR spectra shows the presence of CH_3CHO , CO , CH_3COCH_3 and HCHO among the oxidation products where an example of time-concentration profiles of 2M3P and its products is shown in Figure S9. These products have been observed to be of primary origin when 2M3P was exposed

to natural irradiation (Figure S10). As explained previously, derived formation yields of products, possibly accounted for both contributions of photolysis and OH reactions, were estimated to (81±18)%, (25±6)%, (90±16)% and (98±10)% for CH₃CHO, HCHO, CH₃COCH₃ and CO, respectively. Therefore, due to unquantified contribution of OH reaction to the formation yields of products during this photolysis study, we prefer to conclude qualitatively on the formation of CH₃CHO, HCHO, CH₃COCH₃ and CO among the photolysis products from the irradiation of 2M3P.

Figure S11 shows the proposed mechanistic pathways leading to the formation of the observed products. The photolysis of 2M3P may occur via C-C bond cleavage associated with C=O group to form an alkyl and the corresponding acetyl radical:



CH₃CH₂C(O) and C(O)CH(CH₃)₂ radicals, are expected to either decompose to alkyl radicals (CH₃CH₂ and (CH₃)₂CH) leading to CO elimination or react with O₂ to form the corresponding acetyl peroxy radicals ((CH₃)₂CHC(O)O₂ and CH₃CH₂C(O)O₂). CO formation indicating the occurrence of at least one of the decomposition channels 12 and 13:



The reaction of CH₃CH₂C(O)O₂ with HO₂ radical has been reported to lead to the formation of CH₃CH₂C(O)OH and O₃.²³ However, the absence of the carboxylic

acid and O₃ among the photolysis products indicates that the reaction of acetyl peroxy radicals with HO₂ was insignificant under our experimental conditions. CH₃CH₂C(O)O and (CH₃)₂CHC(O)O radicals are expected to decompose to form the corresponding alkyl radicals, CH₃CH₂ and (CH₃)₂CH, respectively.²³⁻²⁴

As shown in Figure S11, the subsequent reaction of CH₃CH₂ and (CH₃)₂CH with O₂ would form the corresponding peroxy radicals, CH₃CH₂O₂ and (CH₃)₂CHO₂. The self-reaction of CH₃CH₂O₂ radical would lead to the formation of CH₃CH₂O radical (60%) and CH₃CHO + CH₃CH₂OH (40%).¹² In addition, the (CH₃)₂CHO₂ radical self-reaction would lead to the formation of (CH₃)₂CHO radical (60%) and CH₃C(O)CH₃ + (CH₃)₂CHOH (40%). CH₃CH₂O and (CH₃)₂CHO alkoxy radicals are expected to react with O₂ to form HCHO, CH₃CHO and CH₃C(O)CH₃.

3.4. Photolysis of perfluoro-3-methyl-2-butanone

PF-3M2B/SF₆/air mixtures were monitored for 2 hours in the dark in HELIOS. The dark loss rates of SF₆ and PF-3M2B were similar and found to be (1.1-1.3) × 10⁻⁵ s⁻¹. The gas mixture PF-3M2B /SF₆/air was exposed to solar irradiation for typically 5-6 hours. PF-3M2B was monitored by FTIR and PTR-TOF-MS (CF₃⁺ and (CF₃)₂CF₃⁺ ions at *m/z* 68.986 and *m/z* 168.970, respectively). The observed loss of PF-3M2B ranged from 1.3 to 2.0% depending on the solar light intensity. The obtained photolysis rate was $J_{\text{PF-3M2B}} = (9 \pm 5) \times 10^{-7} \text{ s}^{-1}$ with $J_{\text{NO}_2} = (4.2-7.7) \times 10^{-3} \text{ s}^{-1}$. The experimental conditions and the corresponding results are summarized in Table 1. The TUV model

was also used to calculate the PF-3M2B photolysis loss rates at the different period of year, ranging from $2 \times 10^{-7} \text{ s}^{-1}$ to $1.2 \times 10^{-6} \text{ s}^{-1}$. No detectable formation of products was observed from the photolysis of PF-3M2B due to its low photolysis rate and to the detection limits of the analytical techniques used.

The maximum photolysis rate constant of PF-3M2B, $J_{\text{max-PF-3M2B}}$, was estimated using the integrated UV absorption spectrum over the actinic flux region and found to be $J_{\text{max-PF-3M2B}} = (2.9\text{-}5.6) \times 10^{-5} \text{ s}^{-1}$. The measured photolysis rate led to an effective photolysis quantum yield estimated to $\phi_{\text{eff}} \leq 0.037$ under tropospheric sunlight conditions.

3.5 Infrared absorption and global warming potential (GWP)

The infrared absorption spectra of the PF-2M3P and PF-3M2B measured in this work are characterized by broad diffuse vibrational bands as shown in Figure 3, (digitized absorption spectra are provided in SI as .txt format). The spectra are characterized by strong absorption features in the C-F stretch regions, $1200\text{-}1400 \text{ cm}^{-1}$. Overall, the larger perfluorinated ketones have greater peak cross sections in this region due, in part, to the greater overlap of vibrational bands. The infrared spectrum of 2M3P is also characterized by broad vibrational band, due to absorption features of C-H stretch regions. The IR spectrum of 2M3P is also characterized by a sharp absorption at 1700 cm^{-1} , corresponding to C=O stretch vibration (Figure 3). Corresponding graphical representations of Beer's law fits are given in Figures S12, S13 and S14.

477 The integrated band strengths over the 700-2000 cm^{-1} region were determined
478 to be 3.68×10^{-16} , 3.03×10^{-16} and $1.0 \times 10^{-16} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$ (base *e*) for PF-2M3P,
479 PF-3M2B and 2M3P, respectively. Integrated band strengths of PF-2M3P over the 700-
480 2000 cm^{-1} IR spectral region reported by Díaz-de-Mera, et al. ¹³ ($3.94 \times 10^{-16} \text{ cm}^2$
481 $\text{molecule}^{-1} \text{ cm}^{-1}$) and D'Anna, et al. ¹⁸ ($4.05 \times 10^{-16} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$) are in
482 agreement with the present results, within 7% and 9%, respectively. To the best of our
483 knowledge, IR spectra of PF-3M2B and 2M3P are reported for the first time in this
484 work.

485 The radiative efficiencies (RE) for the investigated ketones were calculated
486 using the experimentally measured spectra and the method given in Hodnebrog, et al.
487 ²⁵. The RE values obtained in this work are 0.357, 0.304 and $1.78 \times 10^{-6} \text{ W m}^{-2} \text{ ppbv}^{-1}$
488 for PF-2M3P, PF-3M2B and 2M3P, respectively for atmospherically well-mixed
489 conditions and + 10% stratospheric temperature correction.

490 However, the radiative forcing for the present ketones is expected to be minor
491 due to their expected short atmospheric lifetimes, < 13 days, and low atmospheric
492 abundances. Therefore, lifetime-adjusted RE, accounting for non-uniform horizontal
493 and vertical mixing for very short-lived compounds, was preferred and calculated to be
494 0.012-0.036, ~ 0.036 and $\leq 4 \times 10^{-8} \text{ W m}^{-2} \text{ ppbv}^{-1}$ for PF-2M3P, PF-3M2B and 2M3P,
495 respectively. Corresponding GWPs (for 100 years horizon) were found to be <0.21,
496 ~ 0.29 and $\leq 1.3 \times 10^{-7}$ for PF-2M3P, PF-3M2B and 2M3P, respectively, showing a
497 minor contribution of the studied ketones to the global warming potential. As shown in

Table S4, GWP of PF-2M3P is in good agreement with the studies of Díaz-de-Mera, et al.¹³ and Hodnebrog, et al.²⁵.

4. Atmospheric implications

The photolysis rate of PF-2M3P was measured in September 2013 and July 2010 under natural irradiation and found to be $(1.1-3.8) \times 10^{-6} \text{ s}^{-1}$ and $(1.7-2.8) \times 10^{-6} \text{ s}^{-1}$, respectively ($J_{\text{NO}_2} = (3.3-5.6) \times 10^{-3} \text{ s}^{-1}$) leading to an atmospheric lifetime of PF-2M3P with respect to photolysis in the range of 3-11 days considering that the photolysis occurs during the daytime, which is in good agreement with the literature results, i.e., 4-14 days.^{5-6, 13, 18} The hydrolysis as removal process was demonstrated to be too slow to be considered of atmospheric importance.⁵⁻⁶ Besides, due to a high air-water partition coefficient,²⁶ very low quantities of PF-2M3P will be present in the cloud droplets. Based on the upper limits for the reaction rate coefficients (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with OH radical ($< 5 \times 10^{-16}$), O_3 ($< 4 \times 10^{-22}$) and Cl atoms ($< 1.7 \times 10^{-19}$) taken from Taniguchi, et al.⁵ and typical global average tropospheric concentrations (in molecule cm^{-3}) of OH $\sim 2 \times 10^6$,²⁷ Cl $\sim 10^4$,²⁸ and $\text{O}_3 \sim 7 \times 10^{11}$,²⁹ the tropospheric lifetime towards OH, Cl and O_3 reactions is equivalent to > 30 years. Thus, it is concluded that the photolysis will be the dominant atmospheric loss process for PF-2M3P.

Based on the photolysis rate measurement of PF-3M2B under natural irradiation ($J_{\text{PF-3M2B}} = (9 \pm 5) \times 10^{-7} \text{ s}^{-1}$), an atmospheric lifetime with respect to photolysis of ~ 13 days was derived. To the best of our knowledge, this work provides the first photolysis

study of PF-3M2B. By analogy with PF-2M3P, other processes such as reactions with OH radical, Cl and O₃ and hydrolysis would not contribute significantly to the atmospheric removal of PF-3M2B.

Using the photolysis rates of 2M3P measured under natural irradiation ($J_{2M3P} = \leq (2.6 \pm 1.4) \times 10^{-6} \text{ s}^{-1}$), an atmospheric lifetime with respect to photolysis of ≥ 4 days was derived. In addition to photolysis, gas phase reactions with OH radical and Cl atom could also contribute significantly to the tropospheric loss of 2M3P. Indeed, tropospheric lifetimes towards OH and Cl reactions were derived to be ≈ 4 (OH rate coefficient estimated from SAR)³⁰ and 11 days³¹, respectively. Thus, both photolysis and gas phase loss processes will contribute to the loss of 2M3P in the troposphere. Therefore, the tropospheric lifetime, τ_{tot} , defined as $\frac{1}{\tau_{tot}} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} + \frac{1}{\tau_{hv}}$ with τ_{OH} , τ_{Cl} and τ_{hv} , the corresponding lifetimes with respect to photolysis and OH radical and Cl reactions, respectively, was estimated to be 1-2 days.

Based on the present study, the photolysis of PF-2M3P has been found to produce CF₃C(O)F, COF₂, TFA, PFPrA, and CO under natural conditions. In the atmosphere, CF₃C(O)F will mainly hydrolyze to give trifluoroacetic acid (TFA, CF₃C(O)OH). In the lower atmosphere, COF₂ will be lost through hydrolysis,³²⁻³³ whereas in the stratosphere, the photolysis is the dominant pathway producing CO₂ and HF,³⁴ leading to a local lifetime of 5-10 days.³⁵

The photolysis of 2M3P in the troposphere will lead to the formation of CH₃C(O)CH₃, CH₃CHO, HCHO and CO. The major atmospheric loss of CH₃C(O)CH₃,

CH₃CHO and HCHO is controlled by photolysis and reaction with OH radical. Their photolysis are a source of HO_x (OH, HO₂) in the upper troposphere.^{16,36}

Finally, the low GWP values and the short atmospheric lifetimes for the studied ketones may not lead to a large impact on the global warming of the Earth's atmosphere but may have some impact regarding the formation of other fluorinated species.

ASSOCIATED CONTENT

Supporting Information

UV absorption cross section of PF-2M3P, PF-3M2B and 2M3P are provided in Table S1 and Beer's law fits in Figure S2; UV absorption spectra of acetone is displayed in Figure S1; Seasonal dependence of the photolysis rate of PF-2M3P, PF-3M2B and 2M3P simulated using TUV Model is tabulated in Table S2; Figures S3 and S4 represents the FTIR spectra and GC-MS spectrum, respectively and were used to obtain the products yield as shown in Figures S5 and S6. Formation yields from the photolysis of PF-2M3P are summarized in Table S3. Corresponding photolysis pathway is proposed in Figure S7; Figure S8 presents the FTIR spectra from irradiation of 2M3P. Figure S10 presents the data used to derive the formation yield of products from the loss of 2M3P (Figure S9). Corresponding proposed photolysis pathway is given in Figure S11. Infrared absorption cross sections of 2M3P, PF-2M3P and PF-3M2B (.txt format) used to calculate radiative efficiencies (RE) and GWPs (100 years) (Table S4) and the fitting according to Beer's law (Figure S12, Figure 13 and Figure S14).

AUTHOR INFORMATION

Corresponding Author

*Tel: 33 (0)2 38 25 76 12; e-mail: mellouki@cnrs-orleans.fr.

ORCID

Yangang Ren: 0000-0001-5770-5050

François Bernard: 0000-0002-6116-3167

Véronique Daële: 0000-0003-2509-4077

Abdelwahid Mellouki: 0000-0002-6594-5262

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Table 1. Experimental conditions and obtained results for the photolysis of perfluoro-2-methyl-3-pentanone (PF-2M3P), perfluoro-3-methyl-2-butanone (PF-3M2B) and 2-methyl-3-pentanone (2M3P).

[ketone]	J_{NO_2}	Photolysis loss	Irradiation period	J (10^{-6} s^{-1})			
($10^{13} \text{ molecule cm}^{-3}$)	(10^{-3} s^{-1})	(%)	(h:mm)	FT-IR	GC-MS ^b / PTR-TOF-MS ^c	Rec ^a	
PF-2M3P	3.4 m ³ outdoor chamber						
	18	4.4±1.1	3.7	4:23	2.3±0.2	-	2.3±0.4
	18	4.9±0.9	3.7	4:18	2.8±0.2	-	2.8±0.4
	27	4.4±1.5	2.1	3:39	1.7±0.2	-	1.7±0.4
	8.9	5.5±0.6	2.8	4:13	1.9±0.3	-	1.9±0.6
	HELIOS						
	3.8	3.0±0.4	1.7	4:32	1.1±0.1	1.1±0.1 ^b	1.1±0.4
	3.0	5.3±1.0	7.7	5:01	3.8±0.3	3.5±0.5 ^b	3.8±1.0
	3.6	4.6±1.2	6.1	7:11	2.2±0.3	2.3±0.4 ^b	2.2±0.8
	3.5	5.6±0.7	7.4	7:08	3.7±0.5	3.6±0.5 ^b	3.6±1.0
2M3P	3.3	2.9±1.2	5.7	6:00	1.6±0.7	1.5±0.4 ^b	1.6±1.0
	3.4	2.2±0.3	3.9	5:49	1.2±0.2	1.3±0.4 ^b	1.2±0.8
	3.4	2.4±1.1	3.9	6:14	1.5±0.2	1.7±0.3 ^b	1.6±0.6
	3.3	5.6±0.5	6.3	5:26	2.7±0.7	2.6±0.7 ^b	2.6±1.4
	3.4	5.1±0.5	5.3	6:01	2.1±0.7	2.0±0.4 ^b	2.0±1.0
	3.4	5.1±0.7	4.8	4:58	2.0±0.6	2.0±0.4 ^b	2.0±1.2
PF-3M2B	0.09	7.6±1.3	< 0.2%	5:30	< 1%	-	
	0.05	7.7±1.4	< 0.2%	5:17	< 1%	-	
	1.5	4.2±1.8	2.0	5:07	1.1	-	1.1
	4.2	5.8±1.1	1.3	5:30	0.67	0.28 ^c	0.48±0.28
	3.9	6.3±1.4	1.7	6:08	0.8	1.2 ^c	0.98±0.50

^a Recommended value obtained from the weighted average of each individual measurement: $J_{\text{av}} = (w_1 J_1 + w_2 J_2 + \dots) / (w_1 + w_2 + \dots)$, where $w = 1/\sigma^2$, etc. The error, is given by: $2\sigma_{\text{av}} = (\sigma_1^2 + \sigma_2^2 + \dots)^{0.5}$

^b measured using GC-MS

^c measured using PTR-TOF-MS

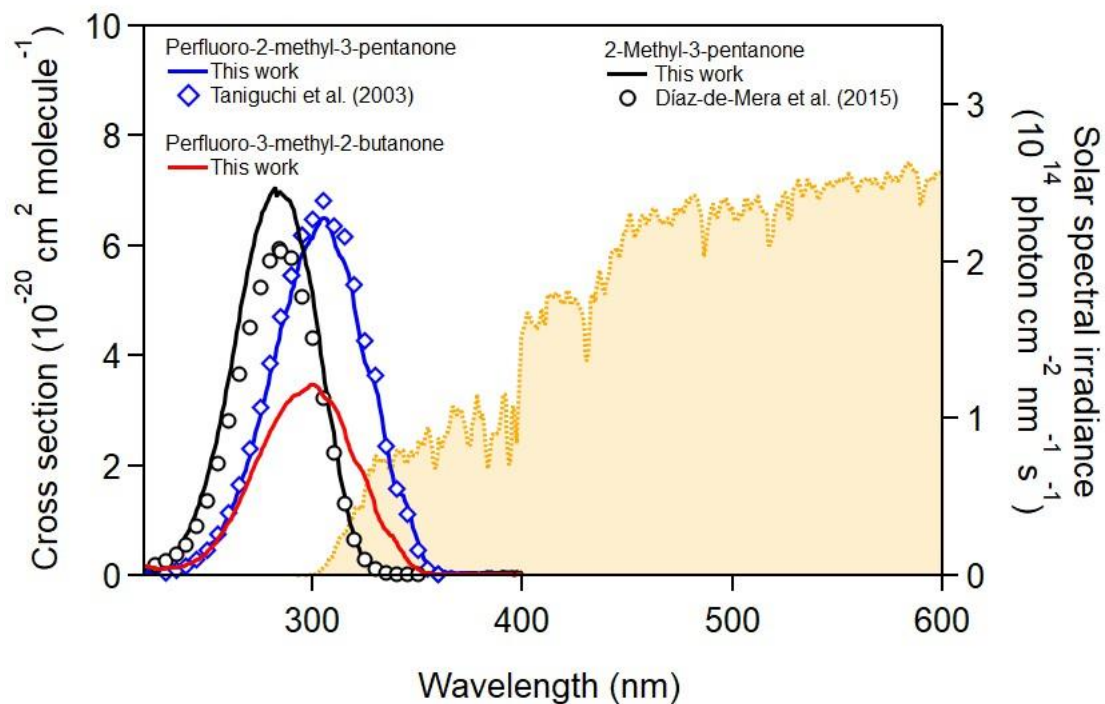
708 **Table 2.** Photolysis rate of perfluoro-2-methyl-3-pentanone (PF-2M3P), perfluoro-3-methyl-2-butanone (PF-3M2B) and 2-methyl-3-
709 pentanone (2M3P) obtained in this work and compared to the reported data from the literature.
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Ketone	[Ketone] ₀ (10 ¹³ molecule cm ⁻³)	Chamber	Date	Irradiation	<i>J</i> (s ⁻¹)	<i>J</i> _{NO2} (s ⁻¹)	Atmospheric Lifetime (days)	Reference
PF-2M3P	3.0-3.8	HELIOS	Sept 2013	Solar irradiation	(1.1-3.8)×10 ⁻⁶	(3.0-5.6)×10 ⁻³	3-11	This work
	8.9-27	3.4 m ³ chamber	July 2010	Solar irradiation	(1.7-2.8) ×10 ⁻⁶	(4.4-5.5)×10 ⁻³	4-7	This work
	8-64	Toledo, Spain	June-July 2013/2014	Solar irradiation	(6.8±0.8)×10 ⁻⁶		5.5±1.9	Díaz-de-Mera, et al. ¹³
	2.5	Euphore	July 2003	Solar irradiation	(6.4±0.3)×10 ⁻⁶	7.85×10 ⁻³	~7	D'Anna, et al. ¹⁸
	(0.55-6.5)×10 ³	140-L Pyrex reactor		14 blacklamps	(1.0±0.1)×10 ⁻⁷		7-14	Taniguchi, et al. ⁵
				8 sunlamps	(6±2)×10 ⁻⁷			
2M3P	47° N and 1° E ^a		a	TUV model	(0.4-2.8)×10 ⁻⁶			This work
	39.9° N and 4° W ^a		a	TUV model	(2.1±0.8)×10 ⁻⁶		5.5±1.9	Díaz-de-Mera, et al. ¹³
	Different latitude ^a		a	TUV model	(0.82-3.1)×10 ⁻⁶		4-14	Jackson, et al. ⁶
PF-3M2B	3.0-3.4	HELIOS	Oct 2013	Solar irradiation	≤(2.6±1.4)×10 ⁻⁶	(2.2-5.6)×10 ⁻³	1-2	This work
	47° N and 1° E ^a		a	TUV model	(0.3-2.8)×10 ⁻⁶			This work
PF-3M2B	3.0-3.4	HELIOS	July 2017	Solar irradiation	(9±5)×10 ⁻⁷	(4.2-7.7)×10 ⁻³	~13	This work
	47° N and 1° E ^a		a	TUV model	(0.2-1.2)×10 ⁻⁶			This work

711 ^a yearly average;

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Figure 1. UV absorption spectra of perfluoro-2-methyl-3-pentanone (PF-2M3P), perfluoro-3-methyl-2-butanone (PF-3M2B) and 2-methyl-3-pentanone (2M3P) and compared with those from literature. The shaded area in yellow represents the solar spectral irradiance measured inside HELIOS (13:00 local time, 27 September 2013).

721

The figure 1 has been replaced

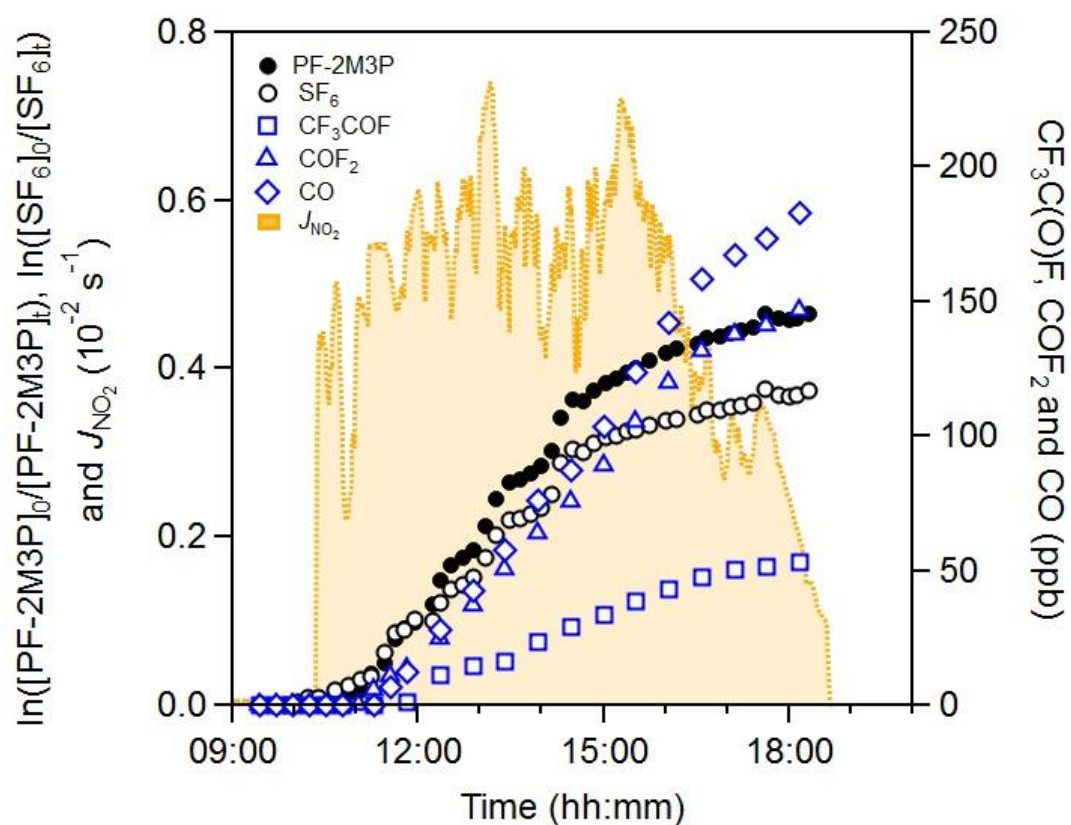


Figure 2. Perfluoro-2-methyl-3-pentanone (PF-2M3P) and its products during the photolysis experiment under natural irradiation in HELIOS (27 September 2013).

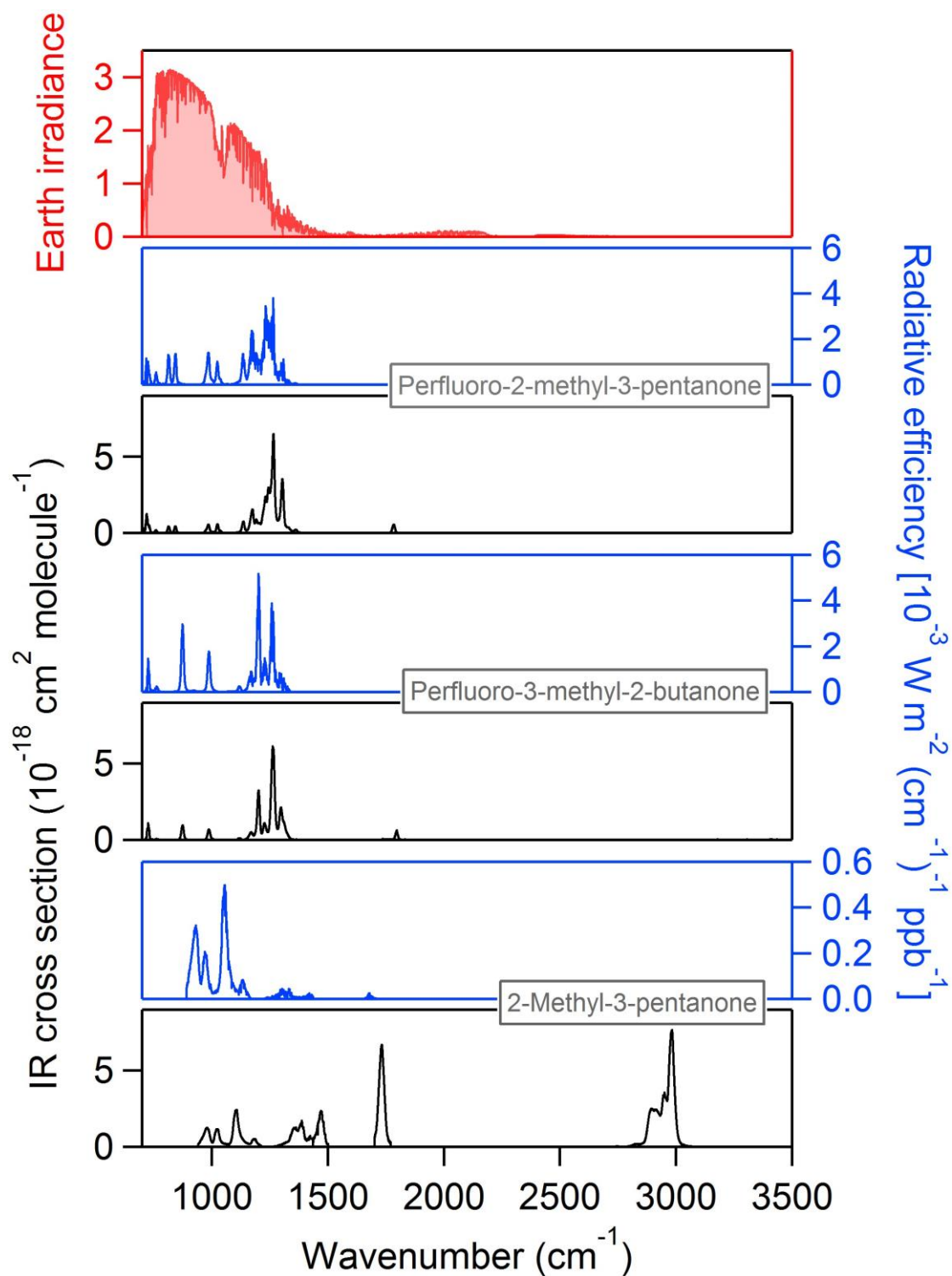


Figure 3. Infrared absorption of perfluoro-2-methyl-3-pentanone, perfluoro-3-methyl-2-butanone and 2-methyl-3-pentanone and their contributions to the radiative efficiency. Earth's irradiance spectrum (top panel) is reported by Hodnebrog, et al.²⁵ (in units of $10^{-3} \text{ W m}^{-2} (\text{cm}^{-1})^{-1} \text{ ppb}^{-1}$ ($10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$)⁻¹). The infrared absorption spectra measured in this work are showed in black, lower panel (in units of $10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$, base e) and the radiative efficiency spectra are displayed in blue, upper panel (in units of $\text{W m}^{-2} (\text{cm}^{-1})^{-1} \text{ ppb}^{-1}$).