



Photolysis of fluorinated and non-fluorinated ketones under natural irradiation

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Outline

❖ Introduction

❖ Methodology

- Photolysis rate (J)
- Atmospheric simulation chamber

❖ Results and Discussion

- UV cross section
- Photolysis rate (J)
- Mechanism
- Global warming potential (GWP)

❖ Conclusion

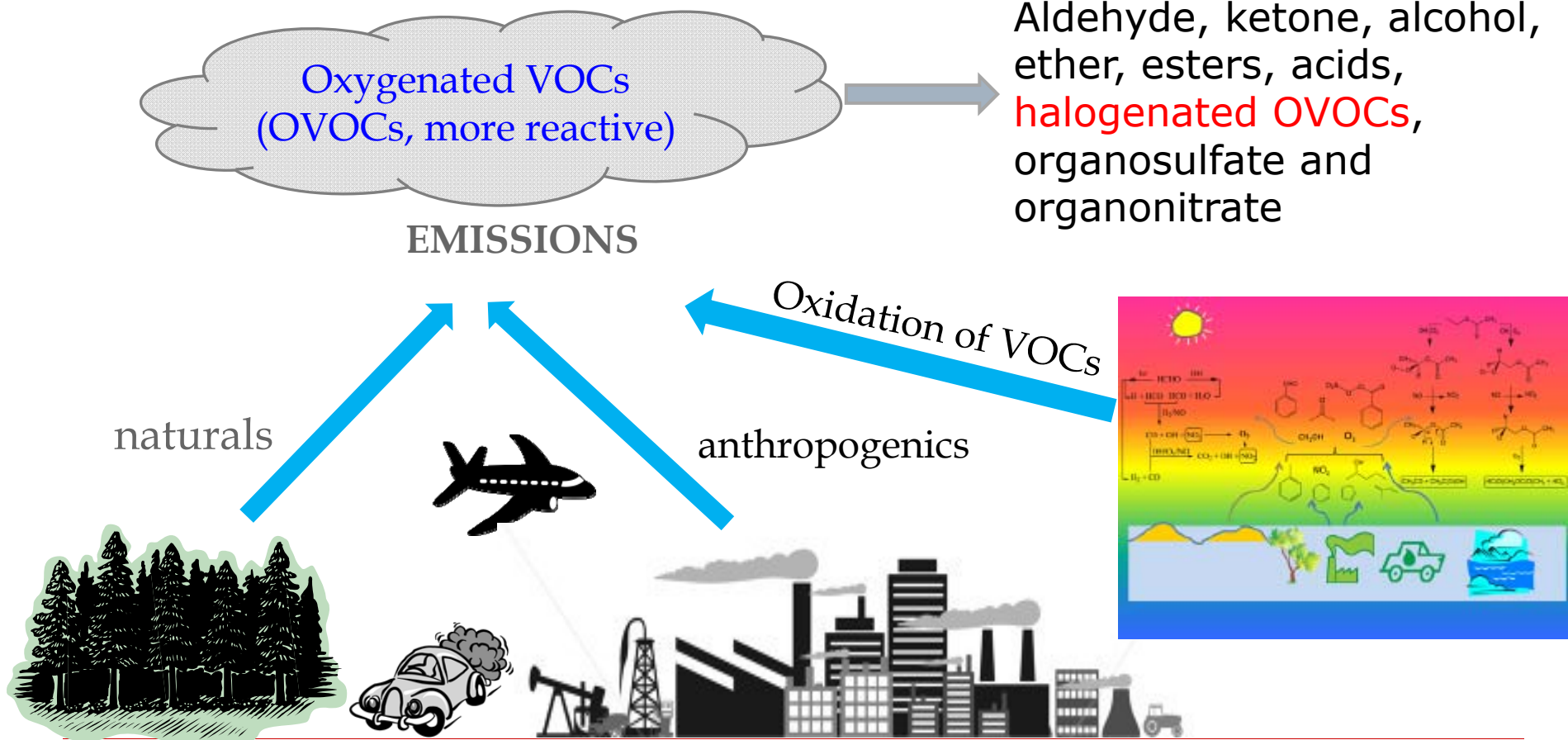
Organic content of the atmosphere

Introduction

..... 15 km

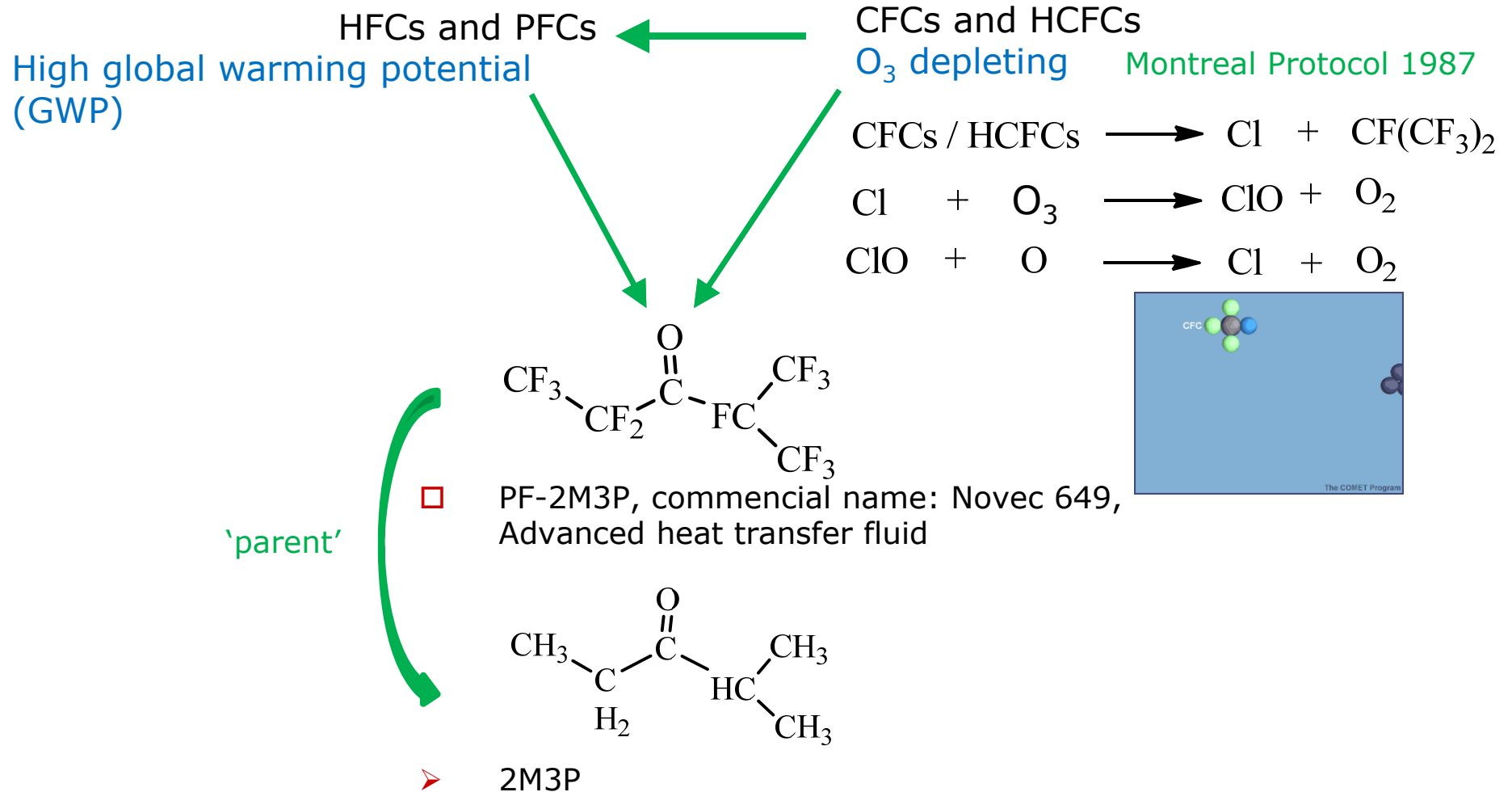
Troposphere

- ◆ Volatile Organic Compounds (VOCs) in the atmosphere:
 - ◆ 10,000 species detected
 - ◆ 100,000 species unexplored



Halogenated OVOC

Introduction



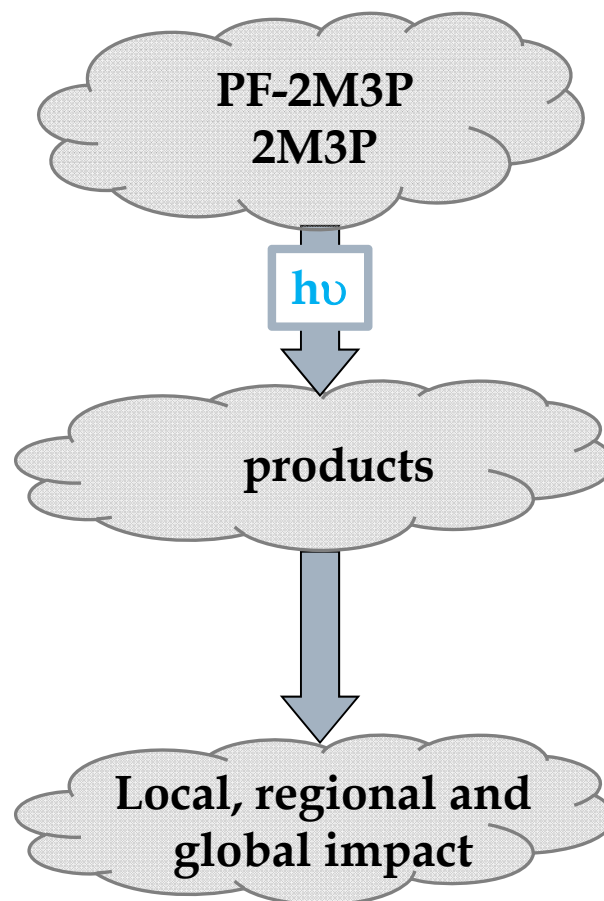
NB: **CFCs**: Chlorofluorocarbons; **HCFCs**: hydrochlorofluorocarbons; **HFCs**: hydrofluorocarbons; **PFCs**: Perfluorocarbons

Fluorinated organic compounds are less reactive toward OH radicals and have longer atmospheric lifetimes than their nonfluorinated counterparts.

✓ Atmospheric lifetimes :

$$\tau = \frac{1}{\tau_{hv}}$$

➤ **Mechanism studies:**
Identification of Products



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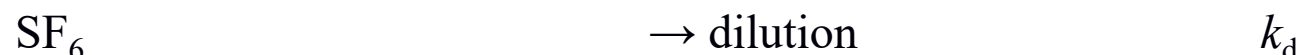
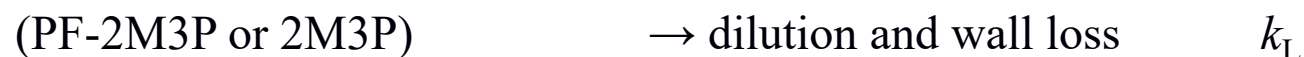
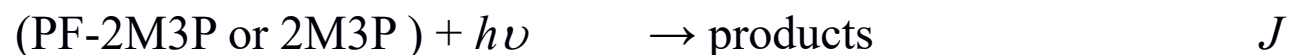
❖ Results and Discussion

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J measurement

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



Hence, the total decays of PF-2M3P and 2M3P are obtained as follows:

$$\ln([\text{Compound}]_0/[\text{Compound}]_t) = k_{\text{tot}} \times t$$

Then, photolysis rate of PF-2M3P and 2M3P are obtained as follows:

$$J_{\text{meas}} = k_{\text{tot}} - k_L$$

Photolysis rate (J)

Methodology

J calculation

$$J_{calc} = \int \sigma(\lambda)\Phi(\lambda)F(\lambda)d\lambda$$

$\sigma(\lambda)$ is the absorption cross-section;

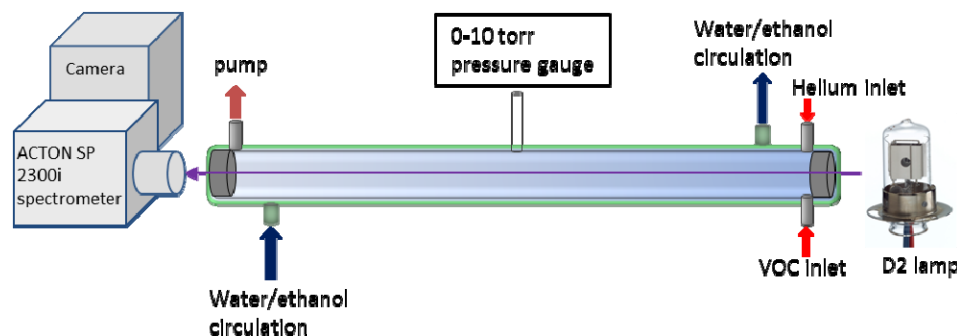
$\Phi(\lambda)$ is the quantum yield of dissociation

$F(\lambda)$ is the actinic flux over the absorption 290 to 400 nm.

$$J_{max} = J_{cal} \text{ when } \Phi = 1$$

An effective photodissociation quantum yield can then be derived from the ratio:

$$\Phi_{eff} = J_{meas}/J_{max}$$



Beer-Lambert Law:

$$I(\lambda, X) = I_0(\lambda) * 10^{-\sigma L} = I_0(\lambda) * e^{-\sigma' L}$$

$I_0(\lambda)$ is the light intensity in the absence of OVOC

$I(\lambda)$ is the light intensity in the presence of OVOC

L is the path length of absorption cell (in cm),

C is the concentration of OVOCs (in molecule cm^{-3}).

$\sigma(\lambda)$ is the UV absorption cross section

Photolysis rate (J)

Methodology

TROPOSPHERIC ULTRAVIOLET AND VISIBLE (TUV) RADIATION MODEL

```
***** changed to zout = 0.11500000
TUV inputs:
=====
inpfil = 0R0313   outfil = 0R0313   nstr = 4
lat = latitude 47.000   lon = longitude 1.000   tmzone = 2.0
iyear = 2013   imonth = 3   iday = 22
-----
zstart = 0.115   zstop = 120.000   nz = 121
wstart = 290.000   wstop = 730.000   nwint = 440
tstart = 8.000   tstop = 20.000   nt = 12
lzenit = F   alsurf = 0.150   psurf = -999.0
o3col = 370.000   so2col = 0.000   no2col = 1.000
taucl = 18.000   zbase = 5.000   ztop = 7.000
tauaer = 0.050   ssaer = 0.990   alpha = 1.000
dirsun = 1.000   difdn = 1.000   difup = 1.000
zout = 0.115   zaird = -9.990E+02   ztemp = -999.000
lirrad = T   laflux = T   lmech = F
lrates = T   isfix = 0   nms = 1
ljvals = T   ijfix = 1   nmj = 9
iwfix = 0   itfix = 1   izfix = 1
=====
Type ?variable for help on a variable, or
<enter> = keep these settings, or
Type variable name to change (lower case):
```

Surface Elevation (points to zstart)

Solar zenith angle (points to lzenit)

Total vertical O3 column (points to o3col)

Total cloud optical depth (points to taucl)

Altitude of cloud (points to ztop)

Atmospheric simulation chamber

Methodology



90 m³ HELIOS



SMPS

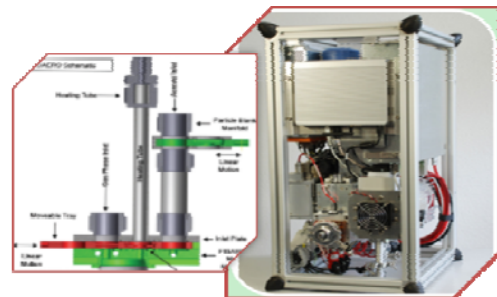


FTIR

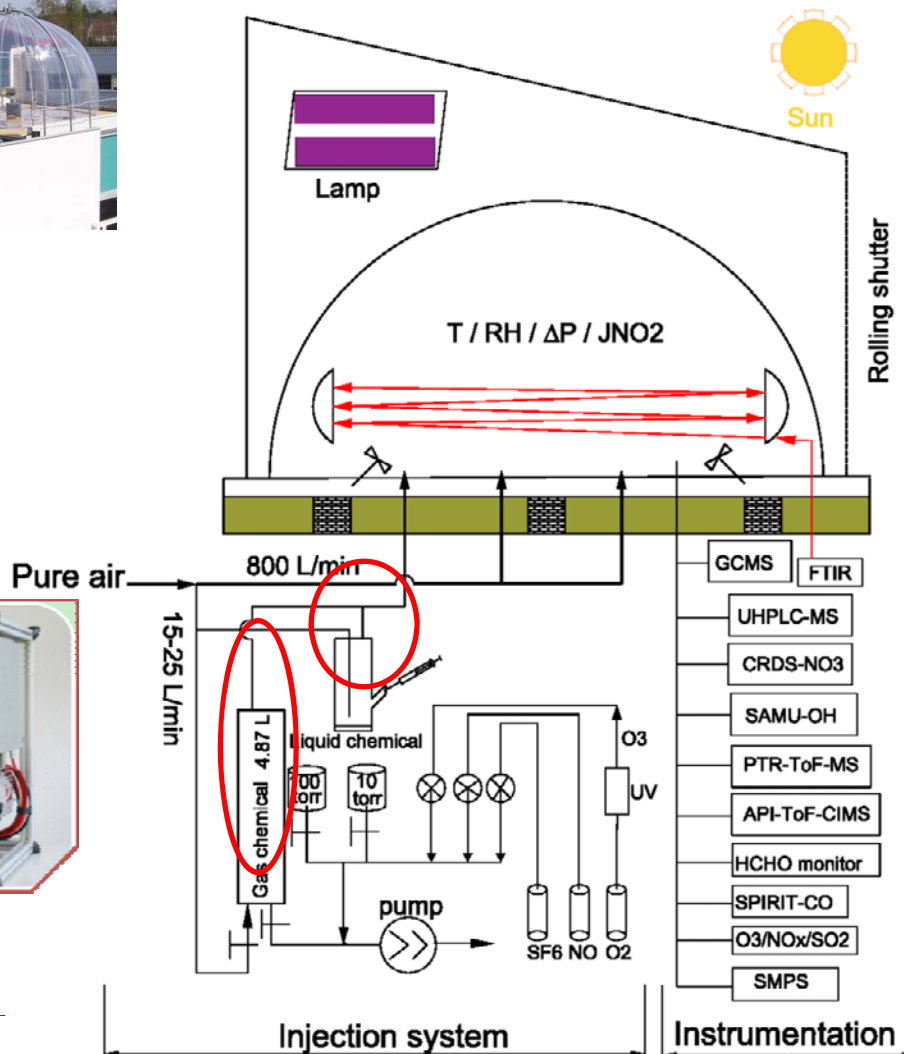
HCHO monitor



UHPLC/MS



API-ToF-CIMS



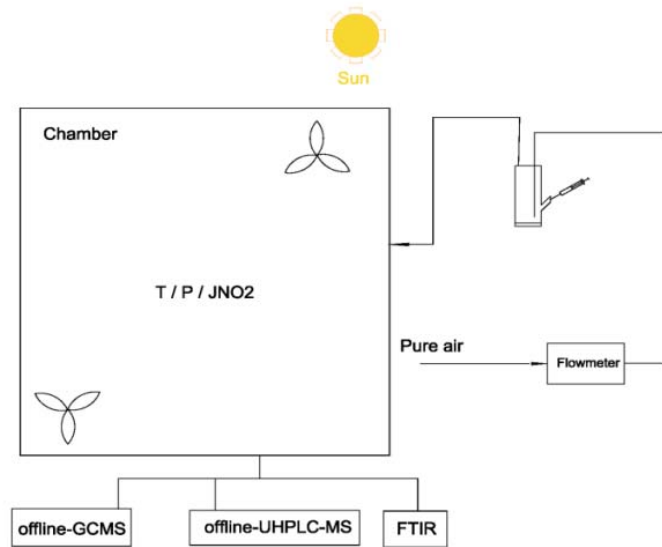
GCMS



PTR-ToF-MS

Atmospheric simulation chamber

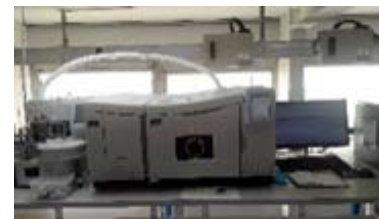
Methodology



3400 L movable chamber



Offline-FTIR



Offline-GCMS



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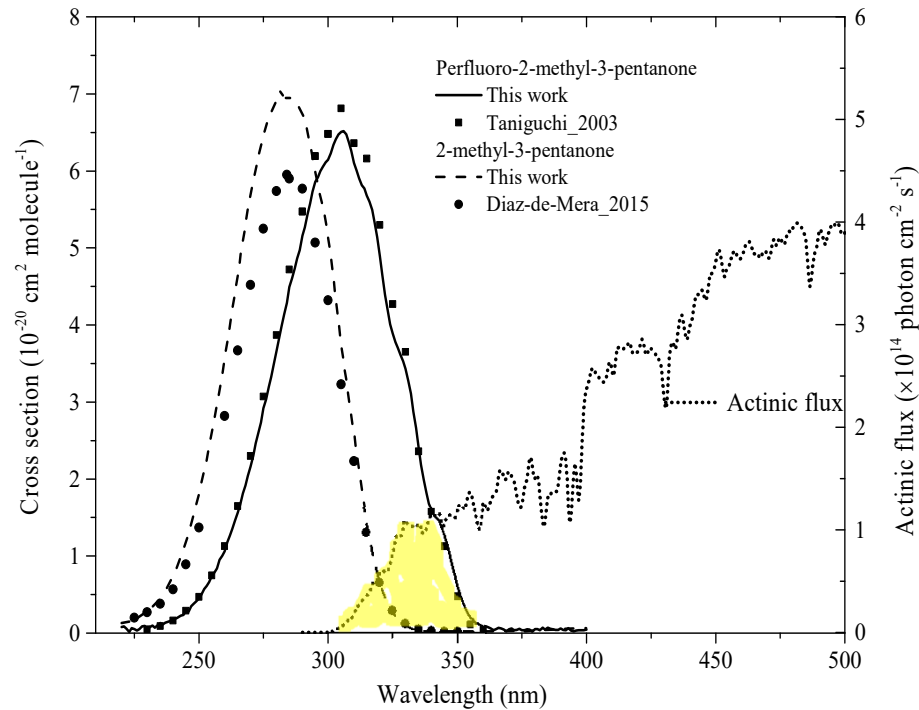
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UV cross section

Results and Discussion



UV spectra:

➤ 2M3P: 284 nm-

$$\sigma_{\max} = (6.99 \pm 0.28) \times 10^{-20}$$

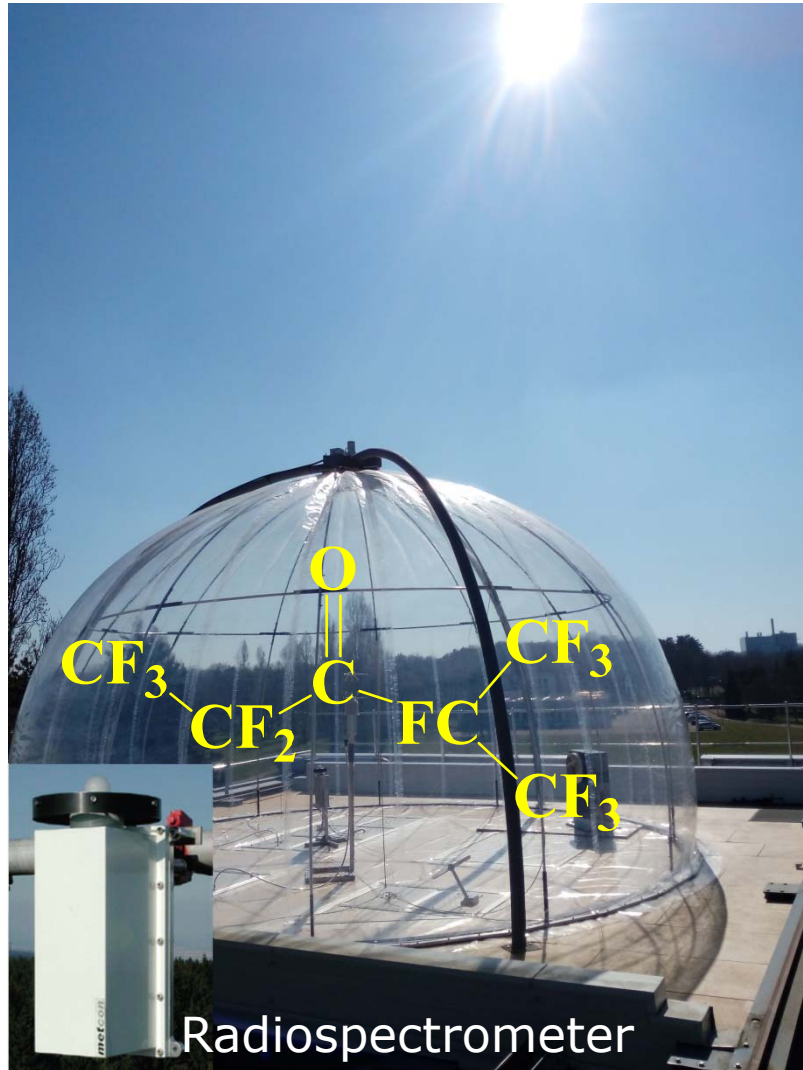
➤ PF-2M3P: 305 nm-

$$\sigma_{\max} = (6.50 \pm 0.14) \times 10^{-20}$$

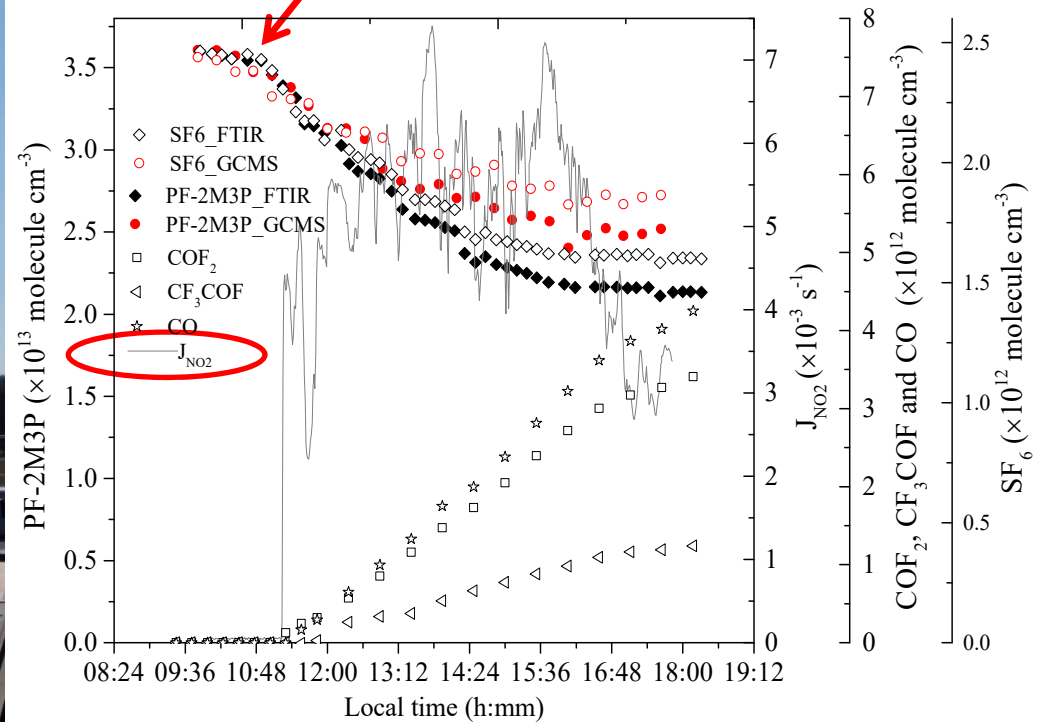
(in $\text{cm}^2 \text{ molecule}^{-1}$)

General procedure

Results and Discussion



Open the protection house



J measurement

Experimental conditions and obtained results for the photolysis of PF-2M3P

| n | [PF-2M3P] ₀ ($\times 10^{13}$ molecule cm ⁻³) | J_{NO_2} (10^{-3} s ⁻¹) | $J_{\text{O}(^1\text{D})}$ (10^{-6} s ⁻¹) | Photolysis loss (%) | Irradiation period (h:mm) | $J_{\text{PF-2M3P}}$ ($\times 10^{-6}$ s ⁻¹) | |
|--|---|--|---|---------------------------|---------------------------------|---|---------------|
| | | | | | | FT-IR | GC-MS |
| 3.4 m³ outdoor chamber | | | | | | | |
| 1A | 18 | 4.4 \pm 1.1 | a | 3.7 | 4:23 | 2.3 \pm 0.2 | |
| 2A | 18 | 4.9 \pm 0.9 | a | 3.7 | 4:18 | 2.8 \pm 0.2 | |
| 3A | 27 | 4.4 \pm 1.5 | a | 3.1 | 3:58 | | |
| $\rightarrow \Phi_{\text{eff}} = 0.008\text{-}0.017$ | | | | | | | |
| HELIOS chamber | | | | | | | |
| 1B | 3.8 | 3.0 \pm 0.4 | 7.5 \pm 2.8 | 1.7 | 4:32 | 1.1 \pm 0.1 | 1.1 \pm 0.1 |
| 2B | 3.0 | 5.3 \pm 1.0 | 11.0 \pm 4.0 | 7.7 | 5:01 | 3.8 \pm 0.3 | 3.5 \pm 0.5 |
| 3B | 3.6 | 4.6 \pm 1.2 | 10.8 \pm 3.5 | 6.1 | 7:07 | | |
| 4B | 3.5 | 5.6 \pm 0.7 | 14.5 \pm 1.5 | 7.4 | 7:08 | 3.7 \pm 0.5 | 3.6 \pm 0.5 |

$(1.7 - 2.8) \times 10^{-6} \text{ s}^{-1}$

$(1.1 - 3.8) \times 10^{-6} \text{ s}^{-1}$

J calculation

TUV model parameters and Photolysis rates of PF-2M3P based on the seasons of year from the TUV model using the quantum yield from this work.

| 47° N 1° E | Mar 22 | Jun 22 | Sept 22 | Dec 22 |
|---|---------------|---------------|---------------|----------------|
| O ₃ total vertical column (DU) ^a | 370 | 340 | 278 | 302 |
| Cloud total optical depth ^b | 18 | 22 | 20 | 31 |
| Altitude of Cloud base (km) | 5 | | | |
| Altitude of Cloud top (km) | 7 | | | |
| $J_{\text{PF-2M3P}}$ ($\times 10^{-6} \text{ s}^{-1}$) 8am-8pm average | 0.5 \pm 0.4 | 0.9 \pm 0.5 | 0.5 \pm 0.4 | 0.1 \pm 0.08 |
| $J_{\text{PF-2M3P}}$ ($\times 10^{-6} \text{ s}^{-1}$) 12am-2pm average | 1.0 \pm 0.1 | 1.4 \pm 0.1 | 1.0 \pm 0.1 | 0.2 \pm 0.01 |

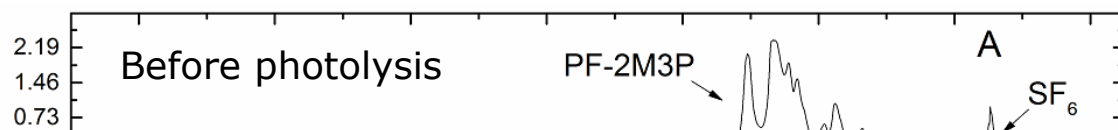
Comparison

Results and Discussion

| [PF-2M3P] ₀ (× 10 ¹³ molecule cm ⁻³) | Nature of irradiation | J _{PF-2M3P} (S ⁻¹) | J _{NO₂} (S ⁻¹) | Technique | T (K) | Reference |
|--|--|--|--|-----------|---------|-----------------------------|
| 3.0-3.8 | Solar irradiation - HELIOS chamber | (1.1-3.8) × 10 ⁻⁶ | (3.0-5.6) × 10 ⁻³ | FT-IR | 298-317 | This work |
| | | (1.1-3.5) × 10 ⁻⁶ | (3.0-5.6) × 10 ⁻³ | GC-MS | | |
| 8.9-27 | Solar irradiation - 3.4 m ³ outdoor chamber | (1.7-2.8) × 10 ⁻⁶ | (4.4-5.5) × 10 ⁻³ | FT-IR | 308-316 | This work |
| 8-64 | Solar irradiation - Toledo, Spain | (6.8 ± 0.8) × 10 ⁻⁶ | | GC-FID | | Diaz-de-Mera et al., (2015) |
| 2.5 | Solar radiation - Euphore | (6.4 ± 0.3) × 10 ⁻⁶ | 7.85 × 10 ⁻³ | FT-IR | 301-309 | D'Anna et al., (2005) |
| (0.55-6.5) × 10 ³ | 14 blacklamps 8 sunlamps | (1.0 ± 0.1) × 10 ⁻⁷ (6 ± 2) × 10 ⁻⁷ | | FT-IR | 296 | Taniguchi et al., (2003) |
| TUV model in 47° N and 1° E and times of year | | (0.2-1.4) × 10 ⁻⁶ | | | | This work |
| TUV model in 39.9° N and 4° W and times of year | | (2.1 ± 0.8) × 10 ⁻⁶ | | | | Diaz-de-Mera et al., (2015) |
| TUV model in different latitude and times of year | | (0.82-3.1) × 10 ⁻⁶ | | | | Jackson et al., (2011) |

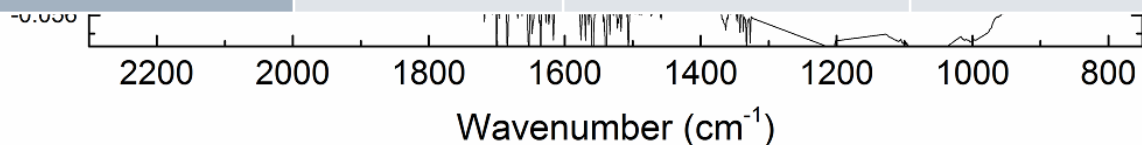
Products

Results and Discussion



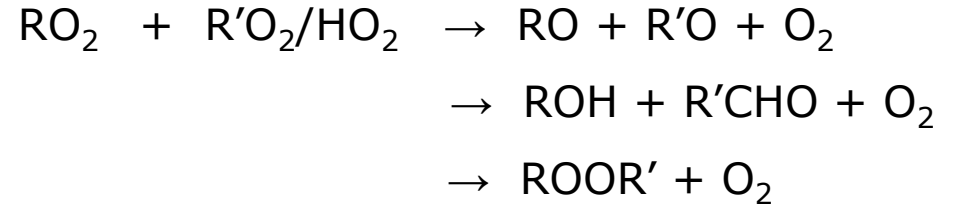
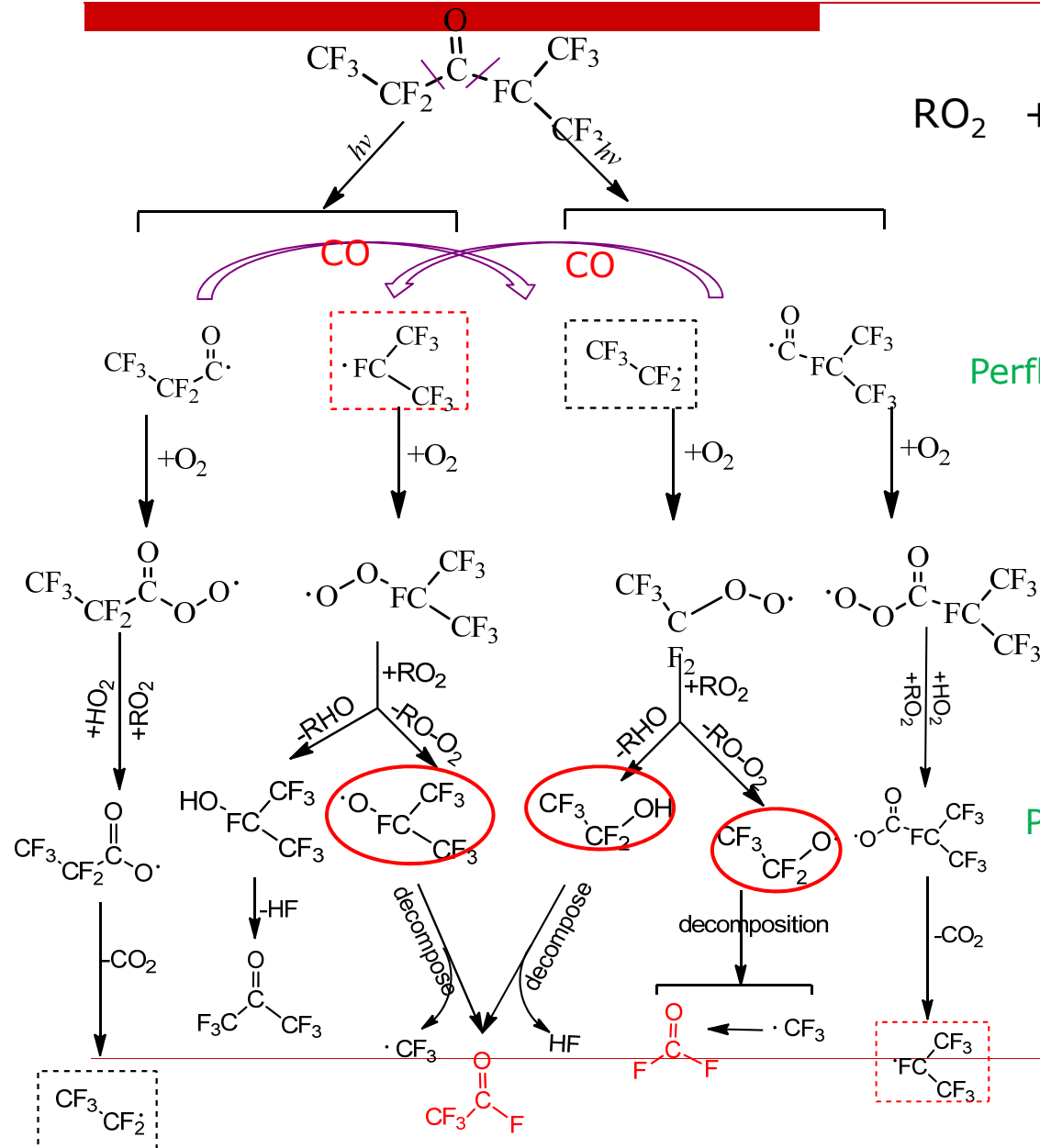
FTIR spectra

| Run | COF ₂ (%) | CF ₃ COF (%) | CO (%) | Fluorine balance (%) | Carbon balance (%) |
|--|----------------------|-------------------------|-----------------|----------------------|--------------------|
| 3.4 m ³ outdoor chamber experiments | | | | | |
| 1A | 181±5 | 77±2 | 173±9 | 56±2 | 85±3 |
| 2A | 247±13 | 81±4 | 176±7 | 68±4 | 98±5 |
| 3A | 184±13 | 74±5 | 122±9 | 61±4 | 74±5 |
| 4A | 173±8 | 63±3 | 170±9 | 50±2 | 78±4 |
| Average ± 1s | 196 ± 34 | 74 ± 8 | 160 ± 26 | 59 ± 8 | 84 ± 11 |
| HELIOS chamber experiments | | | | | |
| 1B | 165±5 | 76±3 | 264±8 | 53±1 | 97±2 |
| 2B | 224±4 | 80±1 | 244±5 | 64±2 | 105±1 |
| 3B | 164±4 | 74±3 | 190±4 | 52±2 | 84±1 |
| 4B | 188±5 | 68±2 | 225±7 | 54±1 | 92±2 |
| Average ± 1s | 185 ± 28 | 75 ± 5 | 231 ± 31 | 56 ± 6 | 94 ± 9 |
| Rec. Average ± 1s | 191 ± 8 | 74 ± 1 | 196 ± 50 | 57 ± 2 | 89 ± 7 |



Mechanism

Results and Discussion



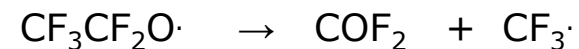
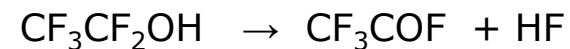
Perfluoro-acetyl or alkyl radical

Perfluoro-R(O)O₂ or RO₂

RO radical would mainly proceed:

- (1) reaction with O₂
- (2) decomposition
- (3) isomerization via a 6-membered transition state.

Perfluoro-RO and fluorinated alcohol



GWP

Results and Discussion

$AGWP_i$ is an **absolute GWP** for gas i (usually in Watts m^{-2} kg^{-1} year)

$$AGWP_i(H) = RE_i * \tau * (1 - \exp(-\frac{H}{\tau}))$$

RE_i is Radiative Efficiency for a species i ,

τ is the lifetime

GWP (Global Warming Potential) is defined as:

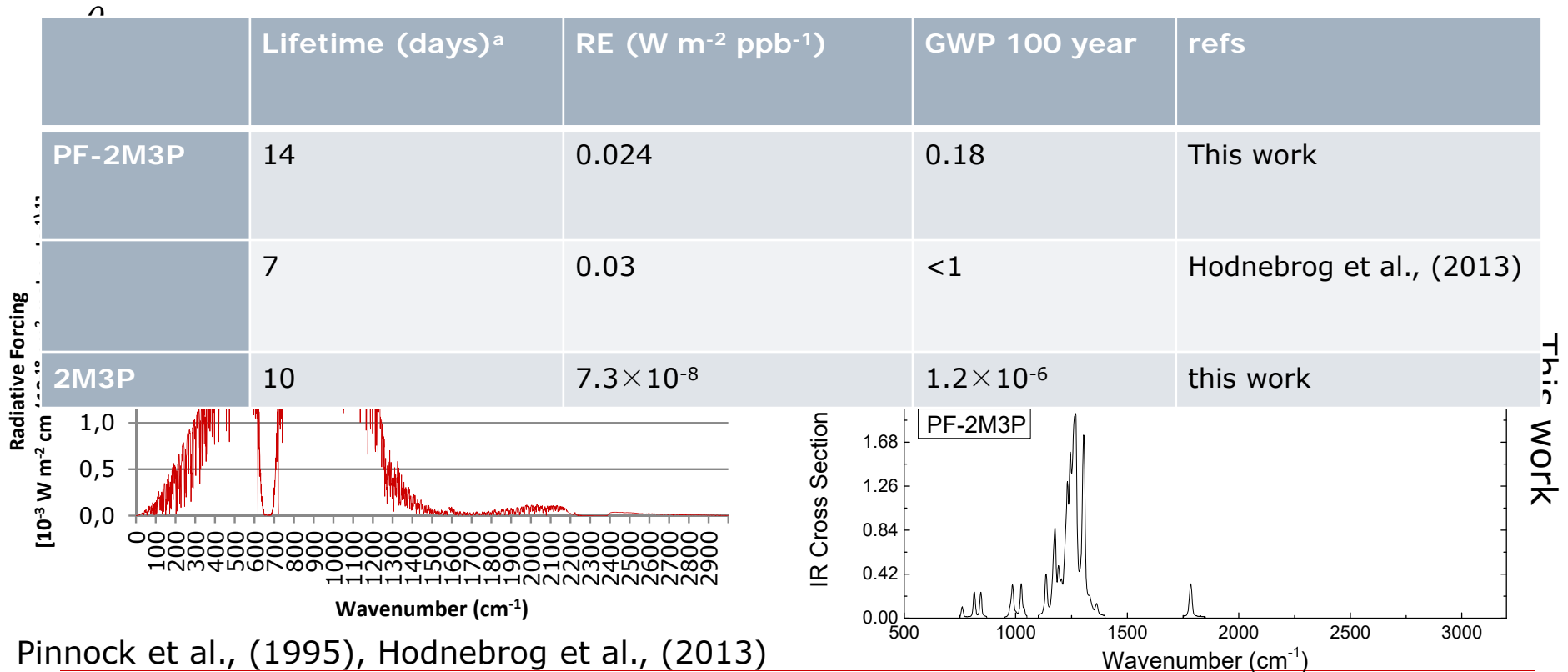
$$GWP_i(H) = \frac{\int_0^H RF_i(t) dt}{\int_0^H RF_{CO_2}(t) dt} = \frac{AGWP_i(H)}{AGWP_{CO_2}(H)}$$

H is the time horizon over which the integration is performed (IPCC presented GWP as 20, 100 and 500 years horizon and Kyoto Protocol has adapted GWP as 100 years horizon),

Pinnock et al., (1995), Hodnebrog et al., (2013)

Based on the **simple method** outlined by **Pinnock et al. (1995)**, in which RE was easily estimated as following:

$$RE = \sum_{\theta=1}^n (1) * \sigma_{av}^{\theta} * F_{\sigma}^{\theta}$$



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Conclusion

- The photolysis rate of PF-2M3P was obtained to be $(1.1-3.8) \times 10^{-6} \text{ s}^{-1}$, from HELIOS chamber (September, 2013) and 3.4 m³ chamber (July, 2010). The lifetime of PF-2M3P depending on photolysis was estimated to be **6-21 days**
- The photolysis rate of 2M3P was obtained from HELIOS chamber (October, 2013) to be $(1.9-3.4) \times 10^{-6} \text{ s}^{-1}$. The lifetime of 2M3P depending on photolysis was estimated to be **7.5-13 days**
- **CF₃C(O)F, COF₂ and CO** were identified to be the main products from the photolysis of PF-2M3P.
- Photolysis of 2M3P in the troposphere will lead to the formation of **CH₃C(O)CH₃, CH₃CHO, HCHO and CO**.
- The photolysis mechanism of PF-2M3P and 2M3P were proposed
- The TUV model shows that the photolysis of PF-2M3P and 2M3P mainly happens in the **summer**, especially the **middle of the day** (12am-2pm).

Thank you for your attention!

Photolysis of PF-2M3P and 2M3P under nature irradiation

2M3P
~~Photolysis rate~~

TUV model parameters and **Photolysis rates of 2M3P** based on the seasons of year from the TUV model using the quantum yield from this work.

| 47° N 1° E | Mar 22 | Jun 22 | Sept 22 | Dec 22 |
|--|---------|---------------|---------|----------|
| O ₃ total vertical column (DU) ^a | 370 | 340 | 278 | 302 |
| Cloud total optical depth ^b | 18 | 22 | 20 | 31 |
| Altitude of Cloud base (km) | 5 | | | |
| Altitude of Cloud top (km) | 7 | | | |
| J _{2M3P} (× 10 ⁻⁶ s ⁻¹) 8am-8pm average | 0.7±0.5 | 1.0±0.6 | 0.6±0.5 | 0.1±0.08 |
| J _{2M3P} (× 10 ⁻⁶ s ⁻¹) 12am-2pm average | 1.3±0.1 | 1.8±0.1 | 1.1±0.1 | 0.2±0.03 |

Photolysis of PF-2M3P and 2M3P under nature irradiation

2M3P
~~Photolysis rate~~

Experimental conditions and obtained results for the **photolysis of 2M3P**

$$\Phi_{\text{eff}} = \frac{J_{\text{meas}}}{J_{\text{max}}} = \frac{J_{\text{meas}}}{\int \sigma(\lambda) \Phi(\lambda) F(\lambda) d\lambda} = \frac{J_{\text{meas}}}{\int \sigma(\lambda) * 1 * F(\lambda) d\lambda}$$

$$\rightarrow \Phi_{\text{eff}} = 0.139-0.179$$

$\sigma(\lambda)$ is the absorption cross-section;

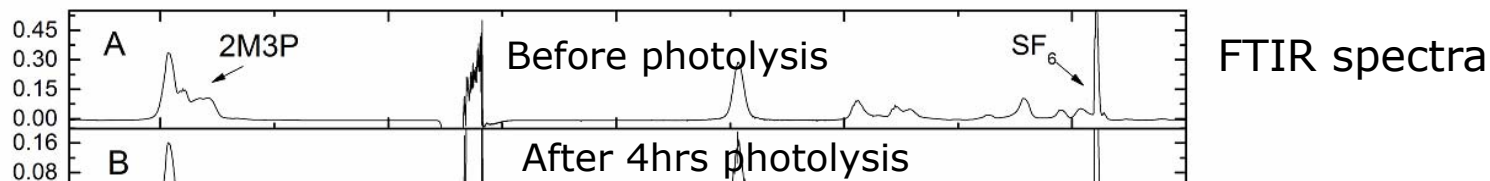
$\Phi(\lambda)$ is the quantum yield of dissociation

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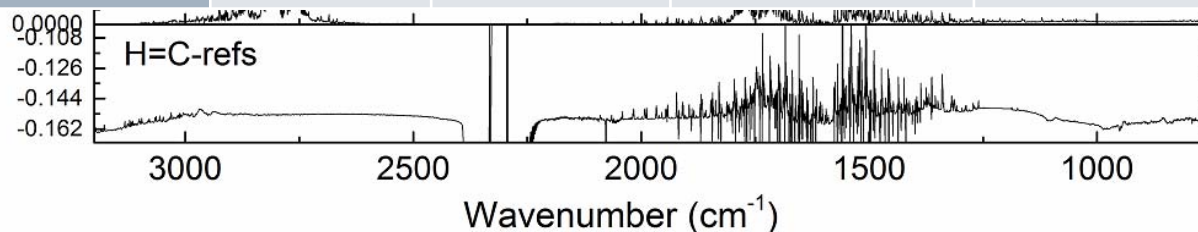
This is the first study for the photolysis of 2M3P

Photolysis of PF-2M3P and 2M3P under nature irradiation

2M3P
~~products~~

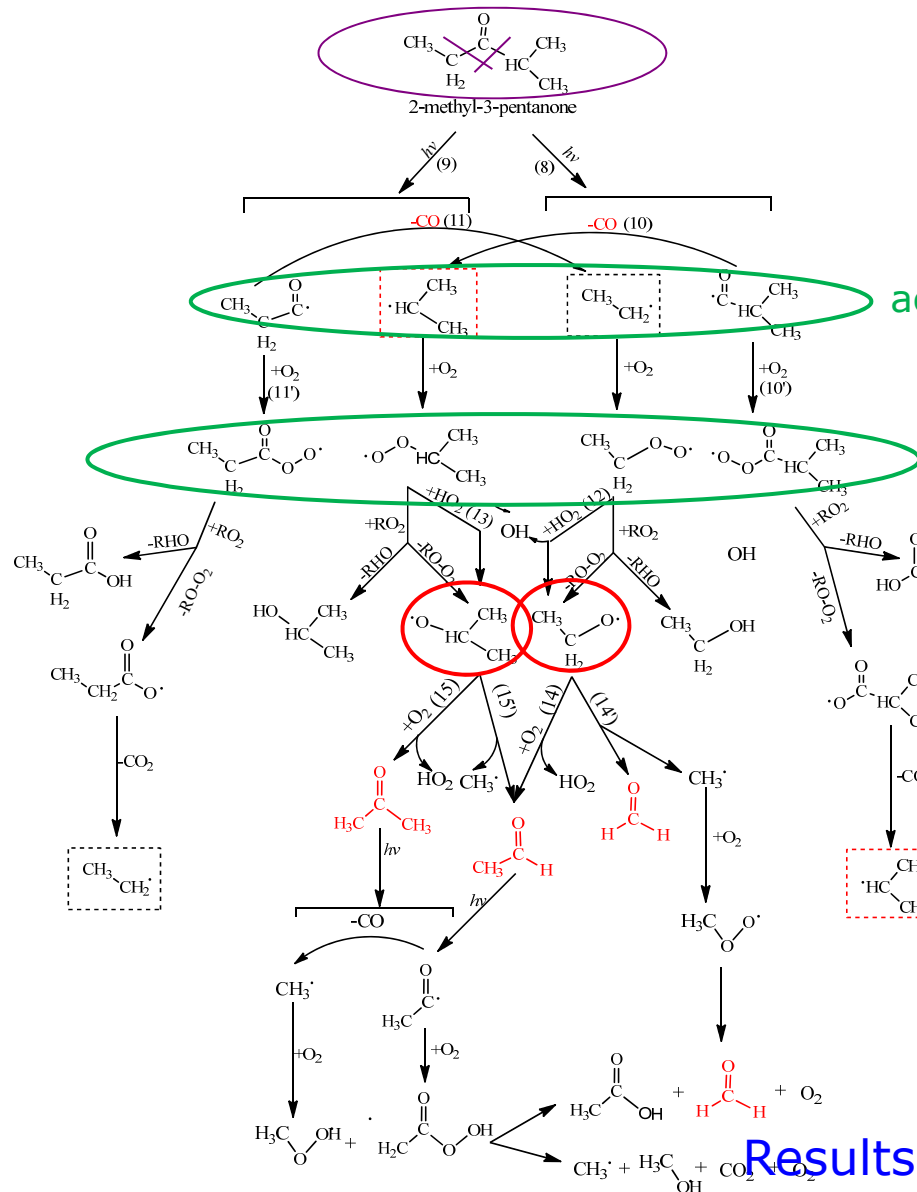


| Run | CO | HCHO | CH ₃ CHO | CH ₃ COCH ₃ | Carbon balance (%) |
|---------------------------------|---------------|---------------|---------------------|-----------------------------------|--------------------|
| I | 98±1 | 32±1 | 79±2 | 97±3 | 97±2 |
| II | 90±1 | 27±1 | 82±3 | 93±3 | 93±1 |
| III | 93±2 | 22±1 | 93±2 | 106±3 | 103±2 |
| IV | 102±4 | 28±2 | 70±3 | 90±3 | 90±2 |
| V | 104±2 | 26±3 | 74±3 | 84±2 | 88±2 |
| VI | 79±1 | 22±1 | 66±3 | 79±2 | 78±2 |
| Average ± SD^a | 97 ± 6 | 27 ± 4 | 80 ± 9 | 90 ± 6 | 94 ± 6 |



Photolysis of PF-2M3P and 2M3P under nature irradiation

2M3P
~~mechanism~~



RO radical would mainly proceed:

- (1) reaction with O₂,
- (2) decomposition
- (3) isomerization via a 6-membered transition state.

