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Chamber study of the Oxalyl Chloride Photodissociation in Sunlight

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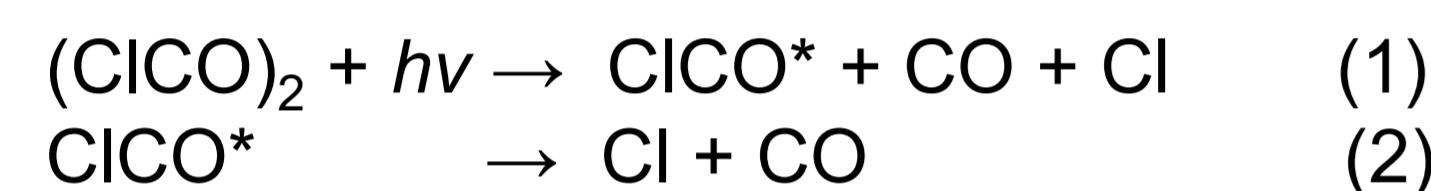
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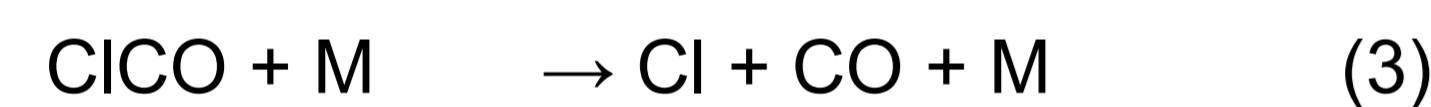
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Introduction

Oxalyl chloride, $(\text{CICO})_2$, is commonly used as a photolytic Cl atoms precursor for kinetic and photochemical studies. Previous studies of the $(\text{CICO})_2$ photodissociation at 193, 248, and 351 nm suggest that UV photodissociation proceeds via a two-step mechanism involving the formation of an excited CICO^* radical (1) and prompt dissociation of a fraction of the CICO^* depending on the photolysis wavelength to $\text{Cl} + \text{CO}$ (2) [1-5]:



The CICO radical formed with the energy lower than its dissociation barrier has been found to undergo thermal unimolecular dissociation (3) on the time scale of several microseconds at room temperature and atmospheric pressure [5,6]:



An additional $(\text{COCI})_2$ dissociation pathway via molecular Cl_2 elimination has been proposed on the basis of Cl_2 detection from 248 nm photolysis of $(\text{COCI})_2$ [7]:



In this work the photodissociation of $(\text{COCI})_2$ by solar irradiation ($\lambda > 300$ nm) has been studied in the HELIOS environmental chamber of ICARE (CNRS, Orléans).

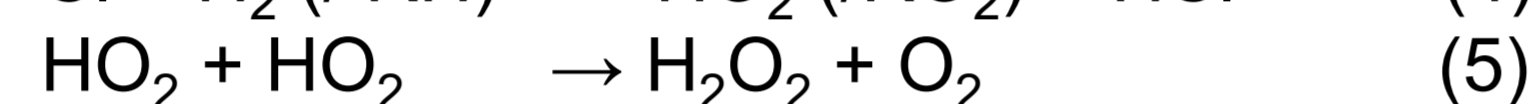
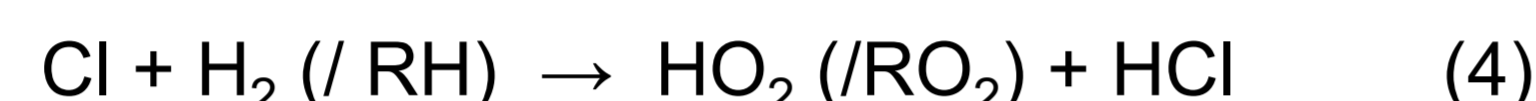
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Experimental

Solar photolysis of $(\text{COCI})_2 / \text{H}_2$ (or $\text{CH}_4, \text{C}_2\text{H}_5$) / Air mixtures in the HELIOS environmental chamber. (atmospheric pressure, 3%RH)

H_2 or other hydrocarbons ($\text{CH}_4, \text{C}_2\text{H}_5$) at high concentrations (up to 50 ppm) were used as Cl atom scavenger:



Measured species:

Actinic flux $F(\lambda)$: 2 π spectral radiometer

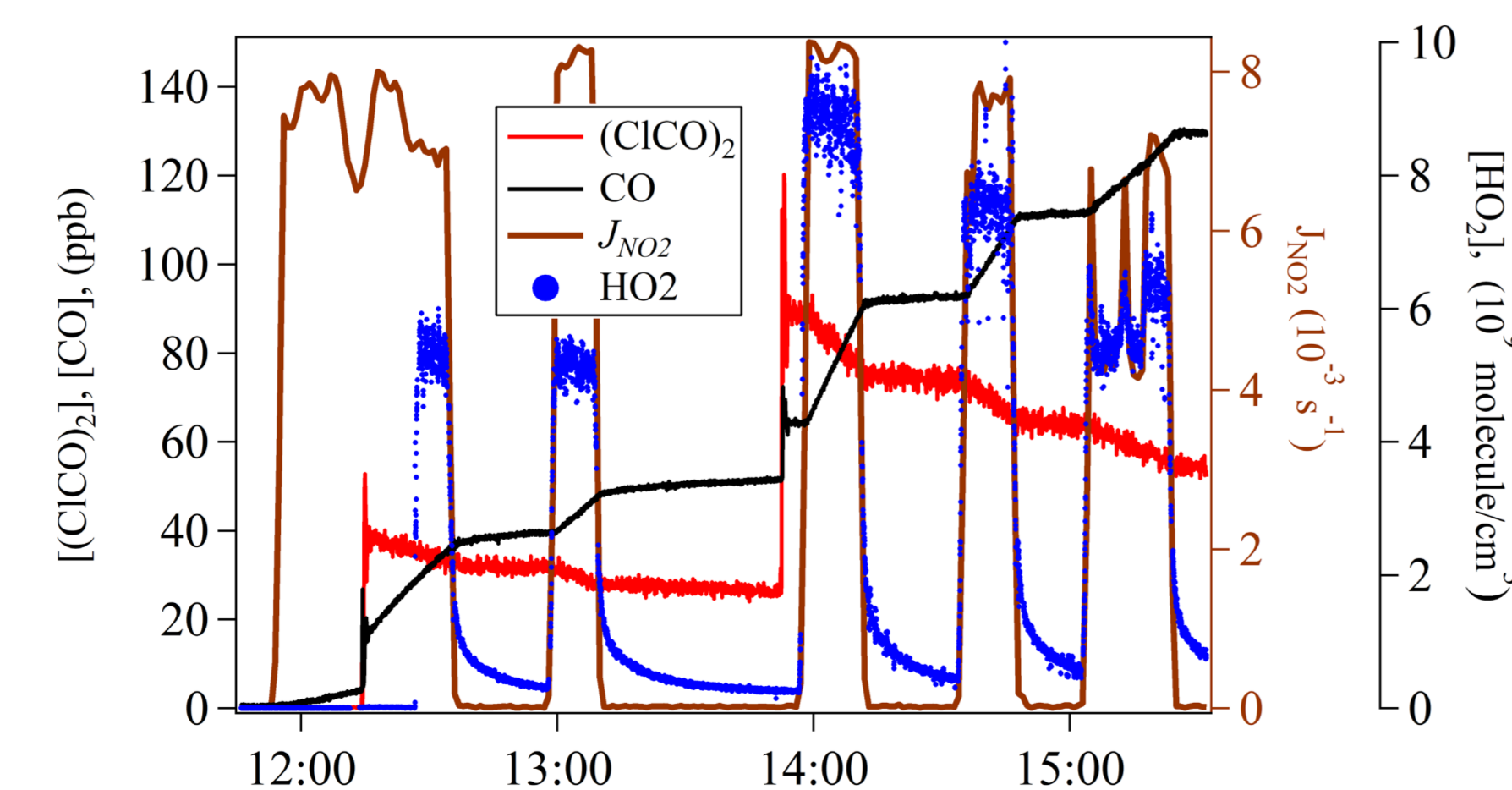
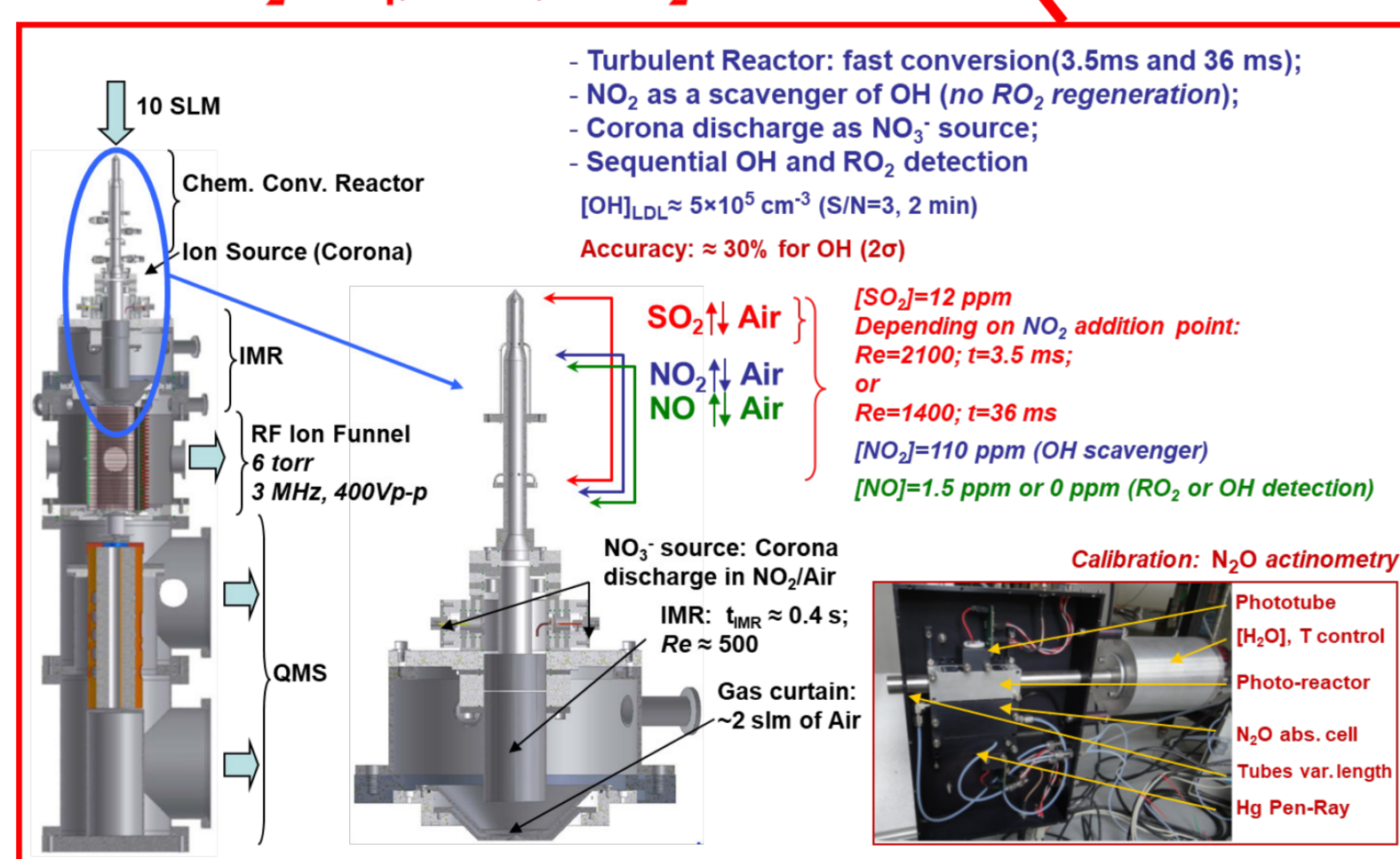
$(\text{COCI})_2$, others: PTR-TOF-MS

CO: IR absorption (SPIRIT)

RO_2, OH : CIMS



CIMS: $\text{H}_2\text{SO}_4, \text{OH}, \text{RO}_2$



Results

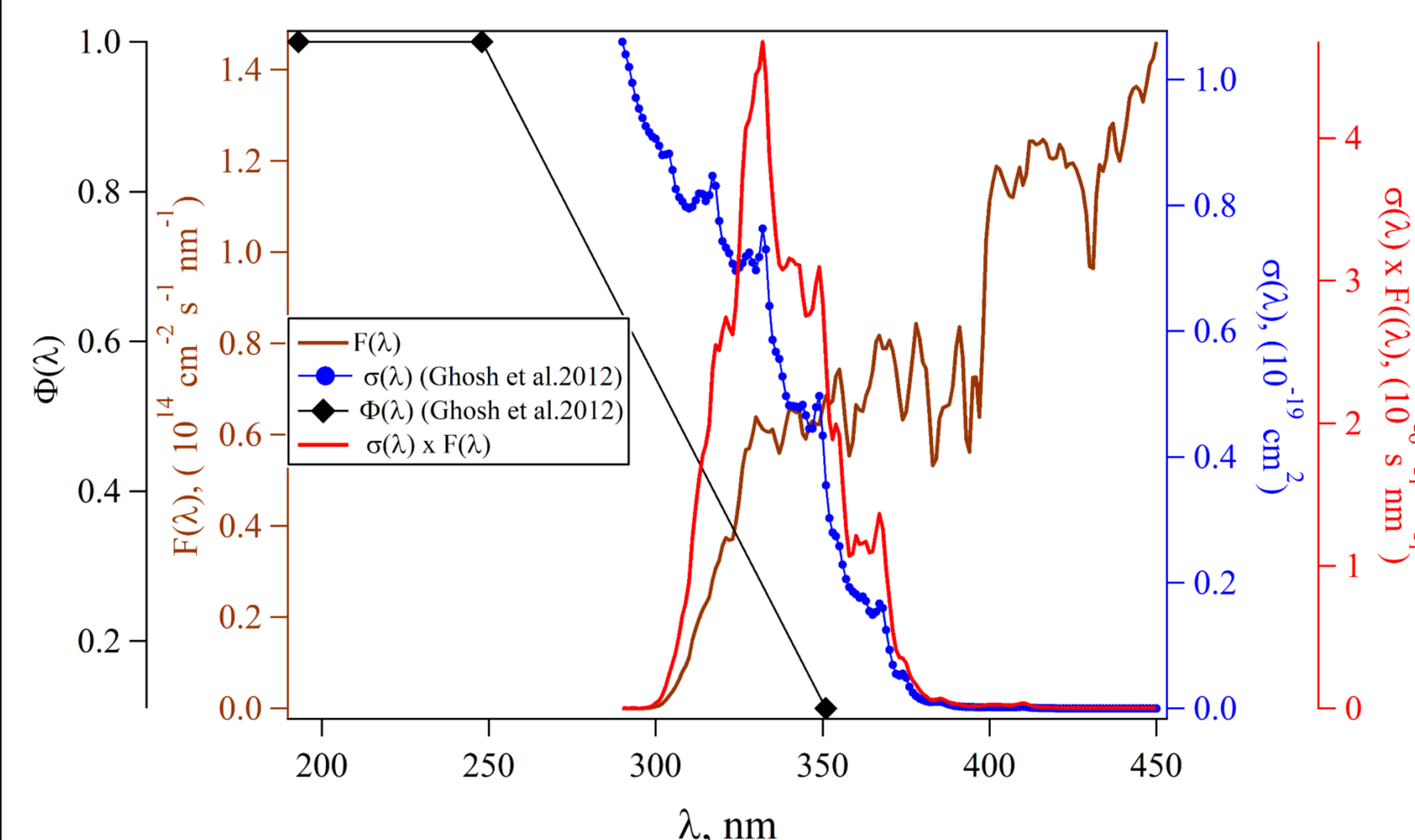
$(\text{COCI})_2$ photodissociation quantum yield

$(\text{COCI})_2$ dissociation quantum yield has been derived from the measured spectral actinic flux $F(\lambda)$ in the chamber and the observed $(\text{COCI})_2$ decay rate $L_{(\text{COCI})_2}$:

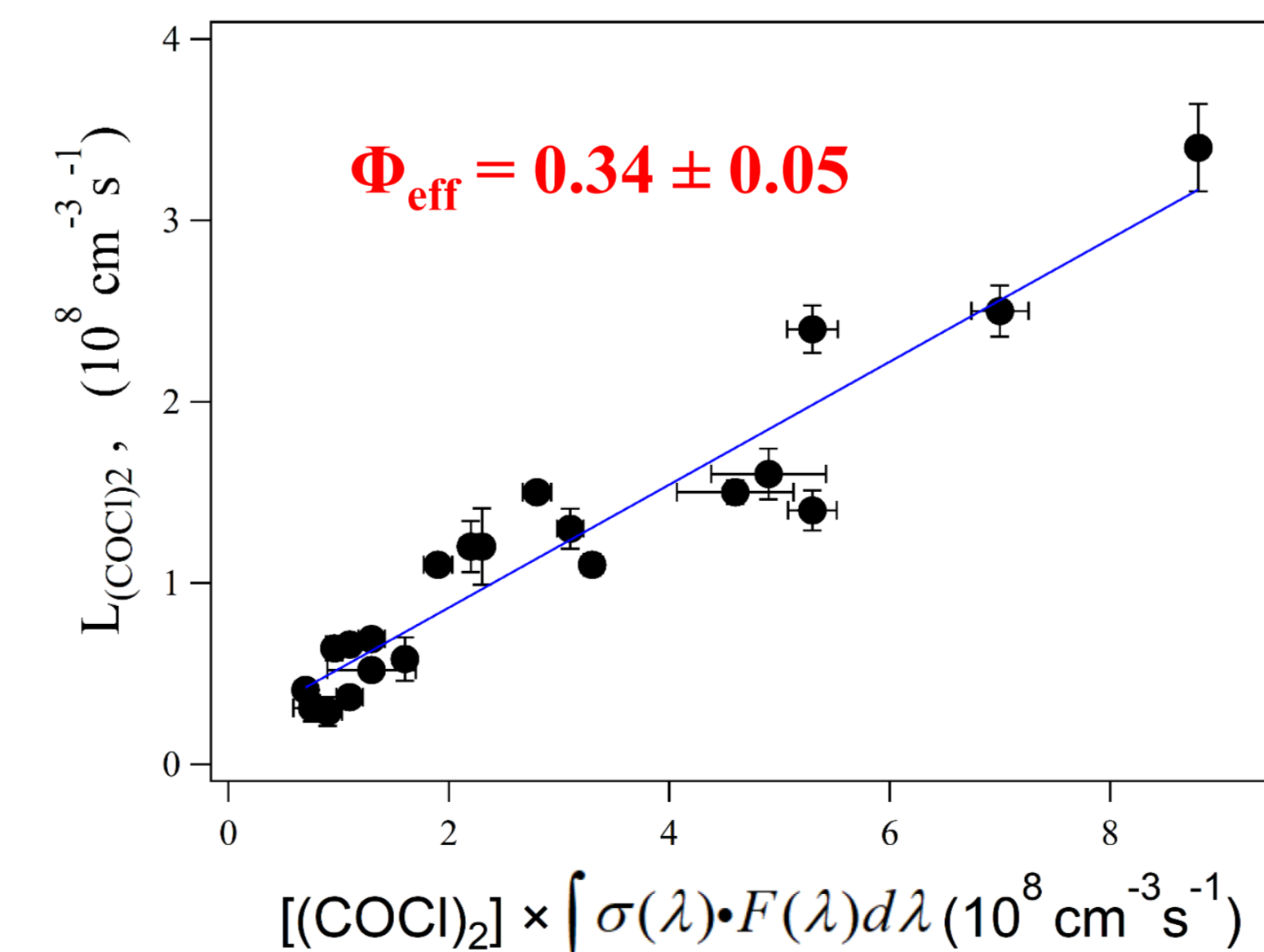
$$L_{(\text{COCI})_2} = -\frac{\delta[(\text{COCI})_2]}{\delta t} = J_{(\text{COCI})_2} \times [(\text{COCI})_2];$$

$$J_{(\text{COCI})_2} = \int \Phi(\lambda) \cdot \sigma(\lambda) \cdot F(\lambda) d\lambda = \Phi_{\text{eff}} \int \sigma(\lambda) \cdot F(\lambda) d\lambda$$

$J_{(\text{COCI})_2}$ – first order photodissociation rate coefficient;
 $\Phi(\lambda)$ – quantum yield for removal of $(\text{COCI})_2$;
 Φ_{eff} – an effective $(\text{COCI})_2$ photolysis quantum yield inside the HELIOS chamber



Measured actinic flux $F(\lambda)$ and product $F(\lambda) \times \sigma(\lambda)$ at 12:00 on 16 July, 2018. Shown also $(\text{COCI})_2$ absorption cross section $\sigma_{(\text{COCI})_2}(\lambda)$ and its photodissociation quantum yield $\Phi_{(\text{COCI})_2}(\lambda)$ (Ghosh et al., 2012)



Determination of the effective $(\text{COCI})_2$ photolysis quantum yield, Φ_{eff} , inside the HELIOS chamber

The effective quantum yield of $(\text{COCI})_2$ photolysis $\Phi_{\text{eff}} = 0.34$. This is in qualitative agreement with previous results of Ghosh, 2012 about $\Phi(\lambda)$ decreasing from 1 at 254 nm to 0.09 at 351 nm

Relative yields of CO and Cl

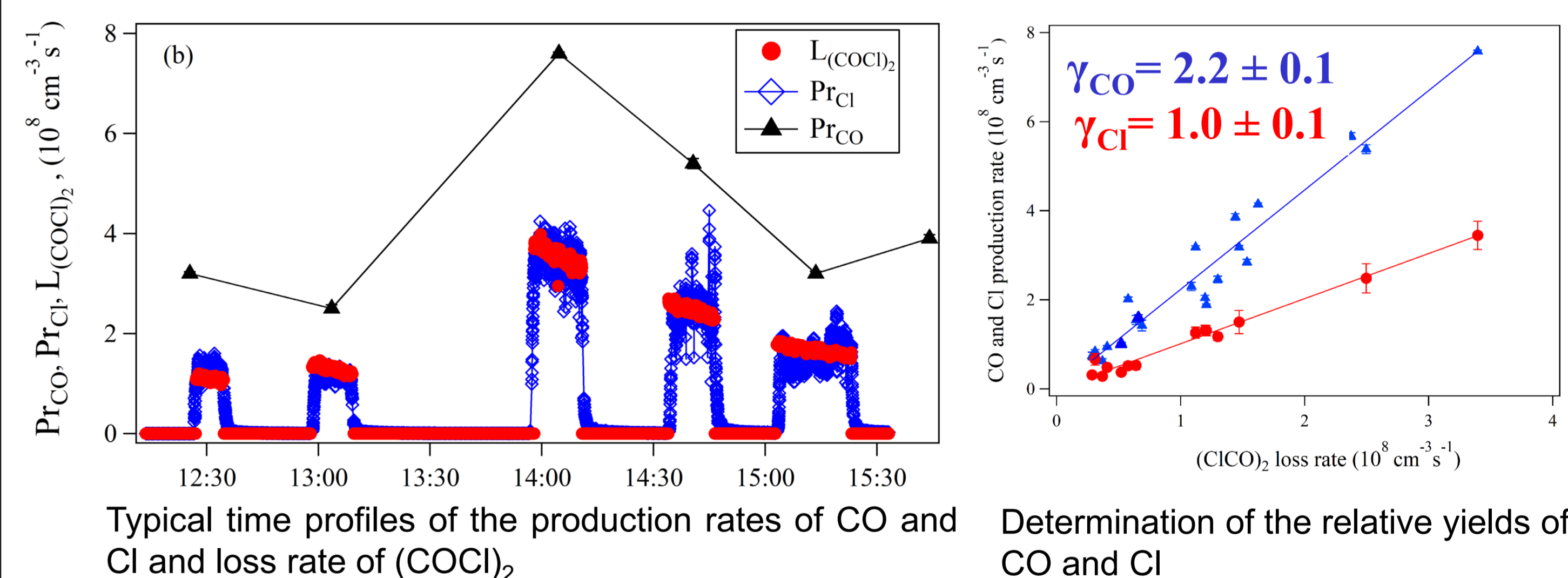
The relative yields of CO, γ_{CO} , and Cl atoms, γ_{Cl} , were derived by comparing the $(\text{COCI})_2$ loss rate $L_{(\text{COCI})_2}$ with the production rates of CO, Pr_{CO} , and Cl atoms, Pr_{Cl} .

$$Pr_{\text{CO}} = \gamma_{\text{CO}} L_{(\text{COCI})_2}$$

$$Pr_{\text{HO}_2} = \gamma_{\text{Cl}} L_{(\text{COCI})_2}$$

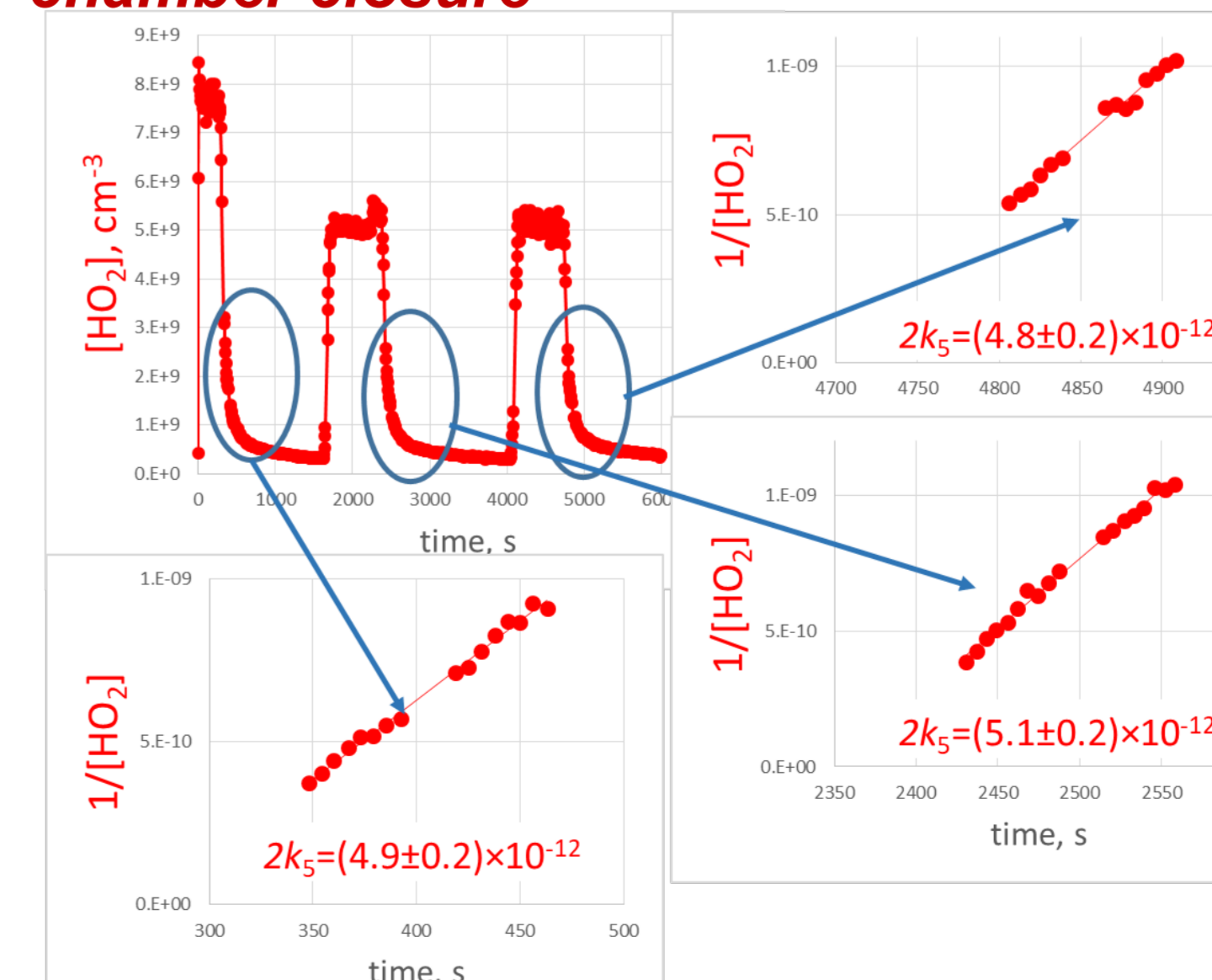
The Cl production rate was derived from the measured by CIMS steady state HO_2 or RO_2 radical concentrations generated by scavenging of Cl by H_2 or RH, respectively. Under conditions of high enough H_2 (or RH) concentrations making the reaction (4) the major pathway of Cl consumption and assuming steady state conditions for RO_2 , the production rate of Cl is equal to the production rate of RO_2 and equal to the loss rate of RO_2 :

$$Pr_{\text{Cl}} = Pr_{\text{RO}_2} = L_{\text{RO}_2} = 2k_5 [\text{RO}_2]^2$$



The obtained relative CO yield of 2.2 ± 0.1 per $(\text{CICO})_2$ loss is in agreement with previous studies. The relative yield of Cl has been found to be 1.01 ± 0.03 , 2 times lower, per $(\text{CICO})_2$ loss; this finding disagrees with previous studies and suggests potentially another mechanism of the $(\text{COCI})_2$ removal.

Test of HO_2 absolute calibration by measuring $[\text{HO}_2]$ decay rate after chamber closure



$$[\text{HO}_2]^{-1} = [\text{HO}_2]_0^{-1} + 2k_5 t$$

$$k_5(300\text{K}) = 2.45 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{JPL, 2015})$$