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Kinetic measurements by Laser Photolysis/Infrared diode laser absorption: rate constants of $\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$ and $\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$

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Kinetic measurements by Laser Photolysis/Infrared Diode Laser absorption : rate constants of $\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$ and $\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$

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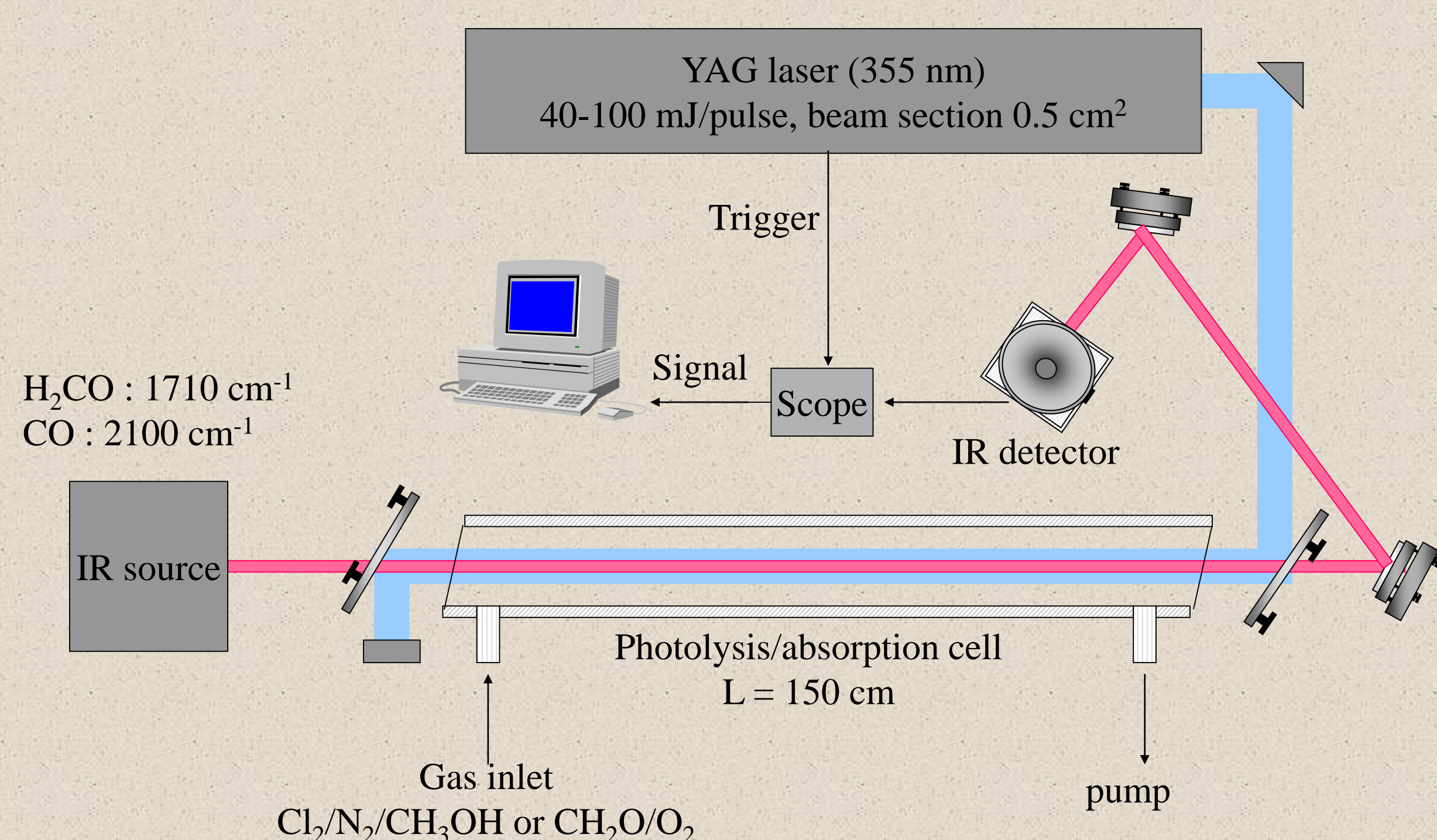
UMR CNRS 8522 « Physicochimie des Processus de Combustion »
Centre d'Études et de Recherches Lasers et Applications
Bâtiment C11 - Université des Sciences et Technologies de Lille
59655 Villeneuve d'Ascq - France

Introduction

Thanks to their narrow emission width ($\approx 10^{-4} \text{ cm}^{-1}$), cw diode lasers provide an excellent source to monitor very selectively stable and radical species via their infrared absorption bands, provided the absorption feature is not significantly broadened. The time resolution of infrared detectors (typically 1 μs or better) is sufficient for most kinetic studies.

We have recently completed a new experimental setup for gas-phase kinetics and photochemical studies based on such lasers, coupled to a pulsed laser for the photolytic initiation of the reaction. The emission frequency of the infrared laser is tuned to a single ro-vibrational absorption line. Stabilization was found not to be necessary.

We present here two sets of experiments : the reaction with O_2 of CH_2OH and HCO radicals at room temperature, produced by reaction of Cl atoms with ethanol and formaldehyde.



Results

Experimental conditions and sample signals, converted into either absorption or molecule concentration, are given for the two systems under investigation.

After a few microseconds that allow for the Cl -initiated conversion of the precursor to the reactant radical, and before diffusion can occur, the rise of the stable product can be fitted by a simple exponential law.

k_{obs} vs. $[\text{O}_2]$ plots are linear and yield values for the rate constant in agreement with the recommended data. However, as shown in the $k_{\text{obs}}/[\text{O}_2]$ vs. $[\text{O}_2]$ plots, for low O_2 concentrations ($< 2 \cdot 10^{15} \text{ molec.cm}^{-3}$ for CH_2OH , $< 1 \cdot 10^{16} \text{ molec.cm}^{-3}$ for HCO) reactions of the radical with itself and/or with other species cannot be neglected. We therefore prefer to derive the rate constants from these latter plots, as the average of the values at high O_2 concentrations.

Conclusion

The agreement between the rate constants obtained in this work and the recommended values validates our instrument.

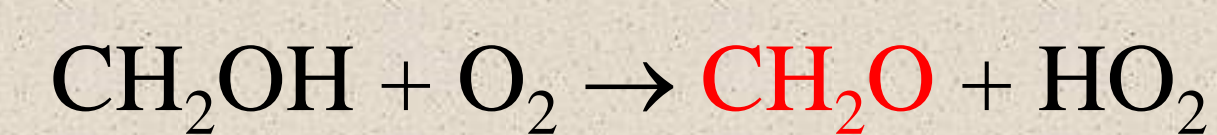
Individual results demonstrate the sensitivity of our setup, and its adequacy for the study of fast reactions (k_{obs} up to $200,000 \text{ s}^{-1}$, limited by the response time of the detection chain).

Since the technique is applicable to radicals and stable species, it can be used for kinetic and photolytic investigations (rate constants and reaction yields).

Future study will include monitoring of the rise of the HO_2 radical produced in these two reactions, as well as the decay of the reactant radicals, at temperature up to 900 K.

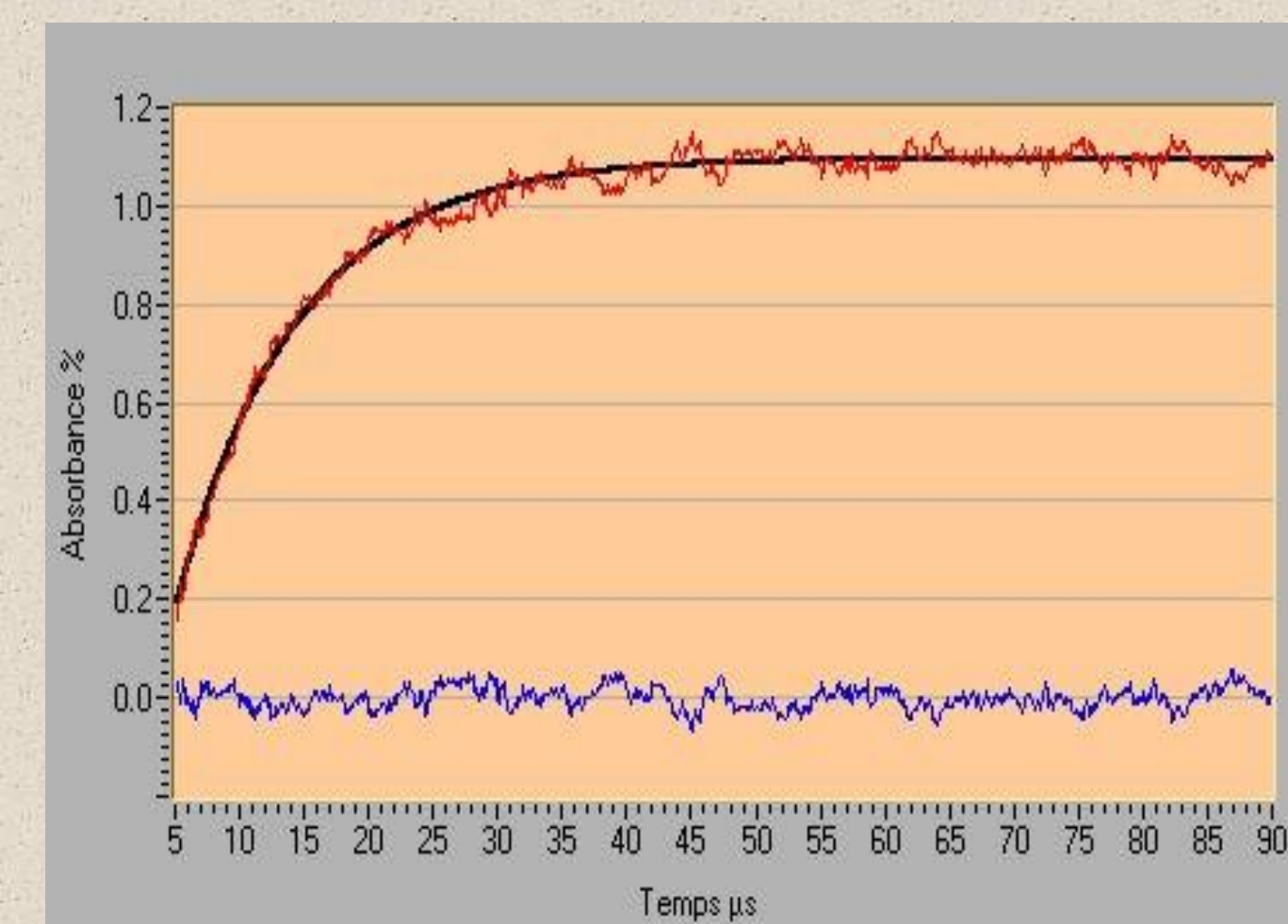
References

DeMore W.B. et al., JPL Publication 97-4, 1997
Atkinson R. et al., *J. Phys. Chem. Ref. Data* **26**, 521-1011, 1997

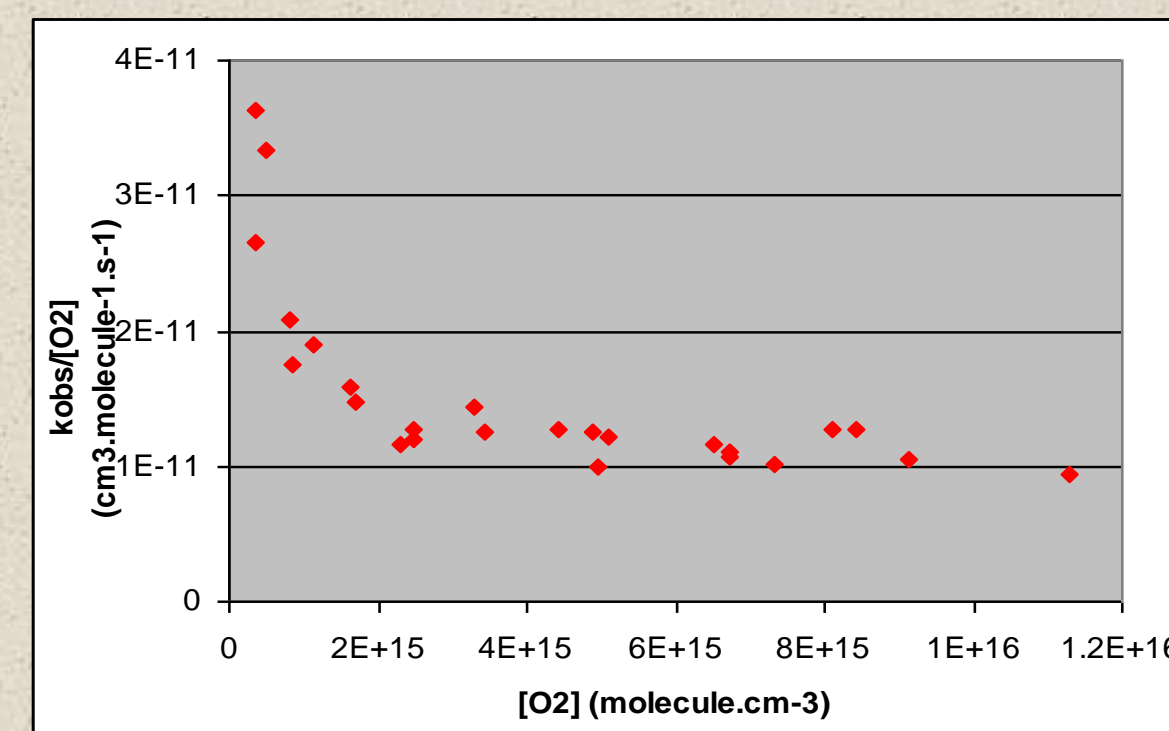
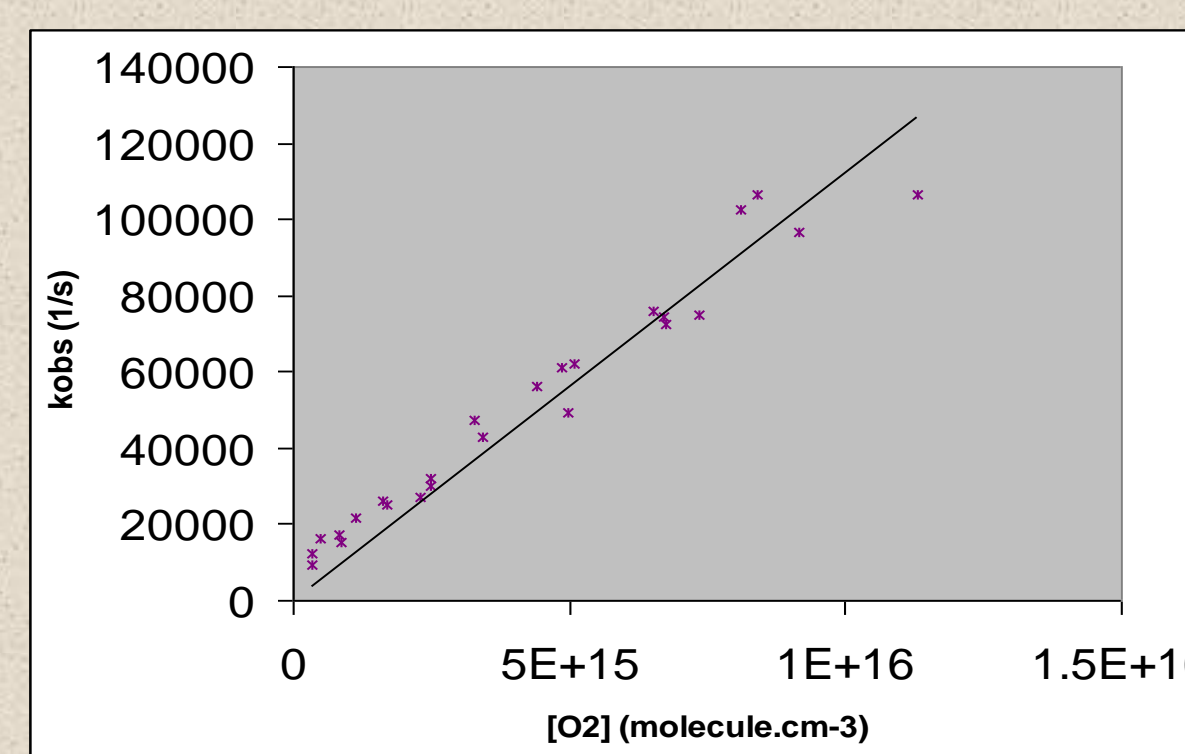


Experimental conditions

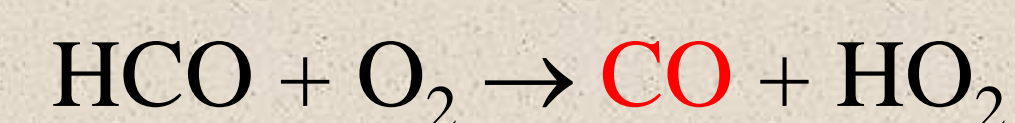
- $[\text{CH}_2\text{OH}]$: $1.6\text{-}50 \cdot 10^{15} \text{ molecule.cm}^{-3}$ (by pumping on liquid methanol or by flowing nitrogen through it)
- $[\text{Cl}_2]$: $5\text{-}20 \cdot 10^{14} \text{ molecule.cm}^{-3}$
- $[\text{Cl}]$: $0.1 [\text{Cl}_2]$
- $[\text{O}_2]$: $3\text{-}120 \cdot 10^{14} \text{ molecule.cm}^{-3}$
- total pressure : 6 or 15 Torr



CH_2O apparition signal (red curve), fit to exponential rise (black) and residuals (blue).
Experimental conditions: $[\text{CH}_2\text{OH}] = 3.4 \cdot 10^{15}$, $[\text{Cl}_2] = 2 \cdot 10^{15}$, $[\text{O}_2] = 11.3 \cdot 10^{15}$, $P = 6.5 \text{ Torr}$, 30 YAG shots.

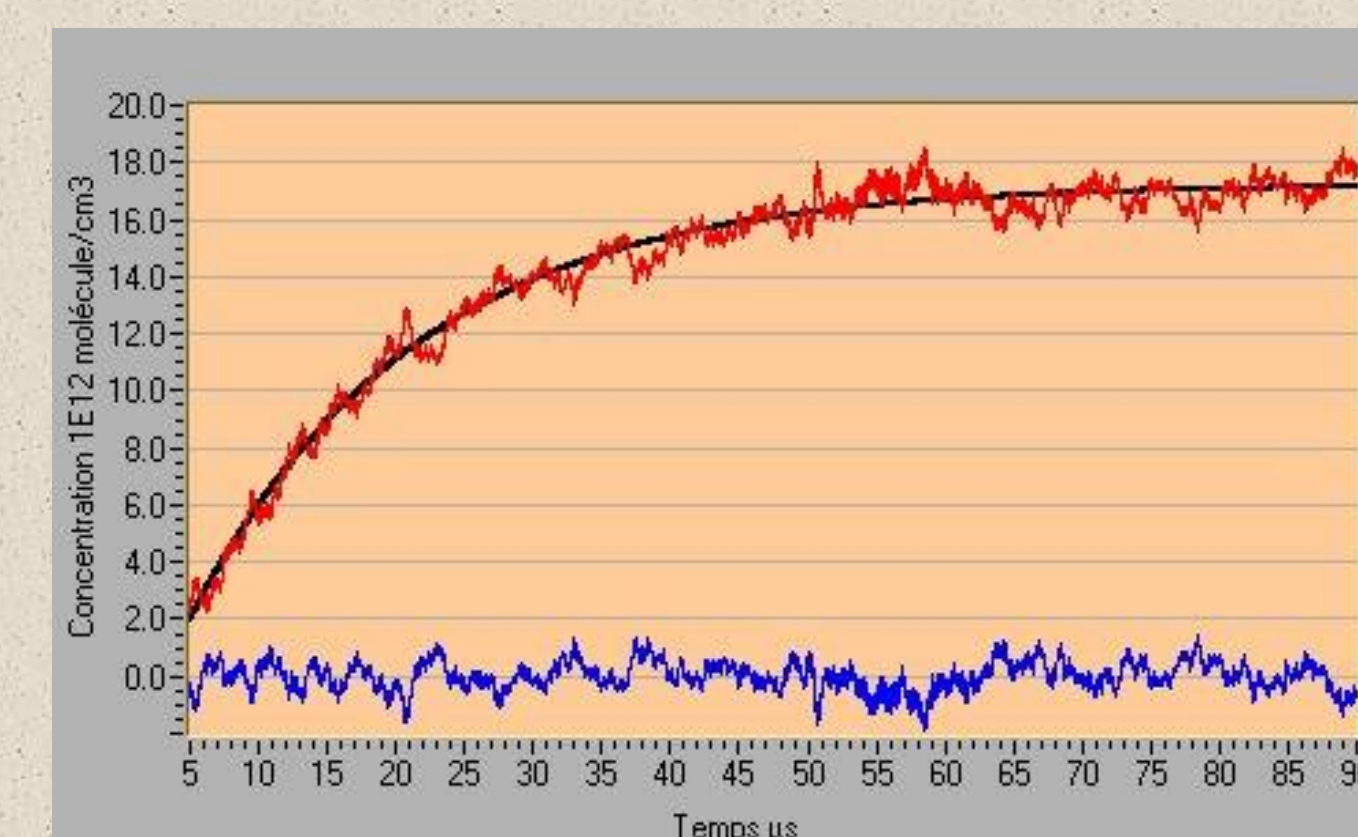


k (cm ³ molecule ⁻¹ s ⁻¹)	reference
11.3 ± 1.7	this work
11.4 ± 1.7	this work
9.1	DeMore 1997
9.4	Atkinson 1997

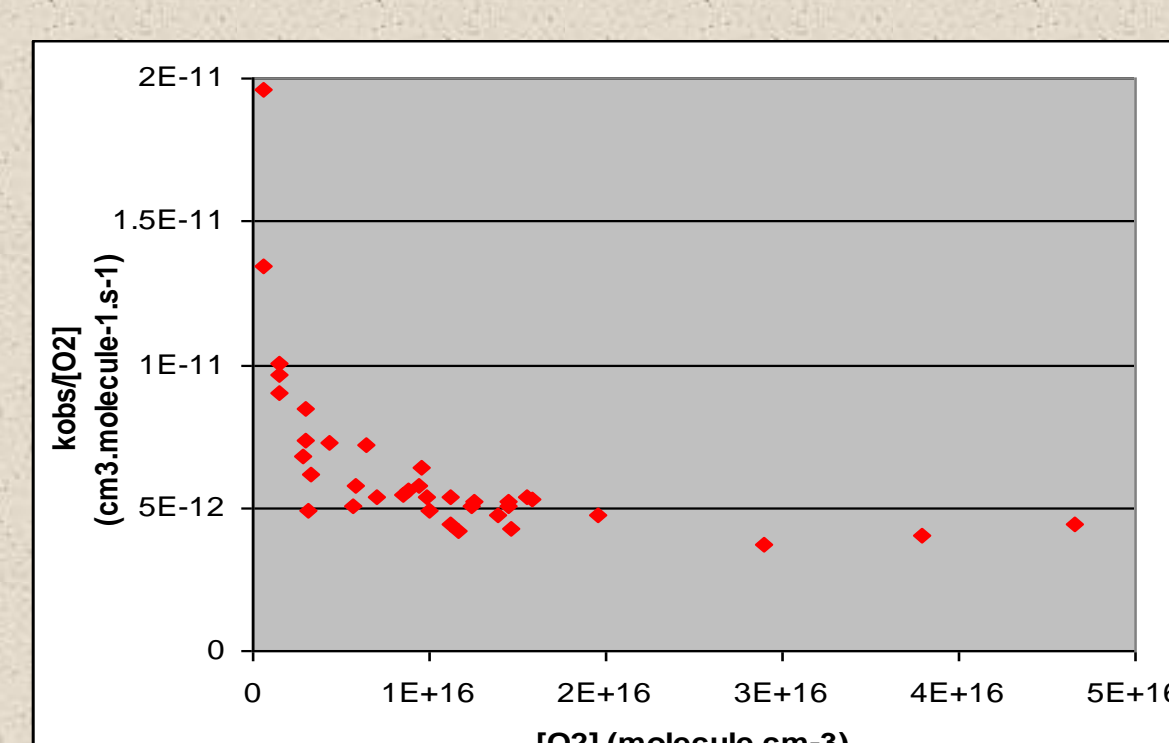
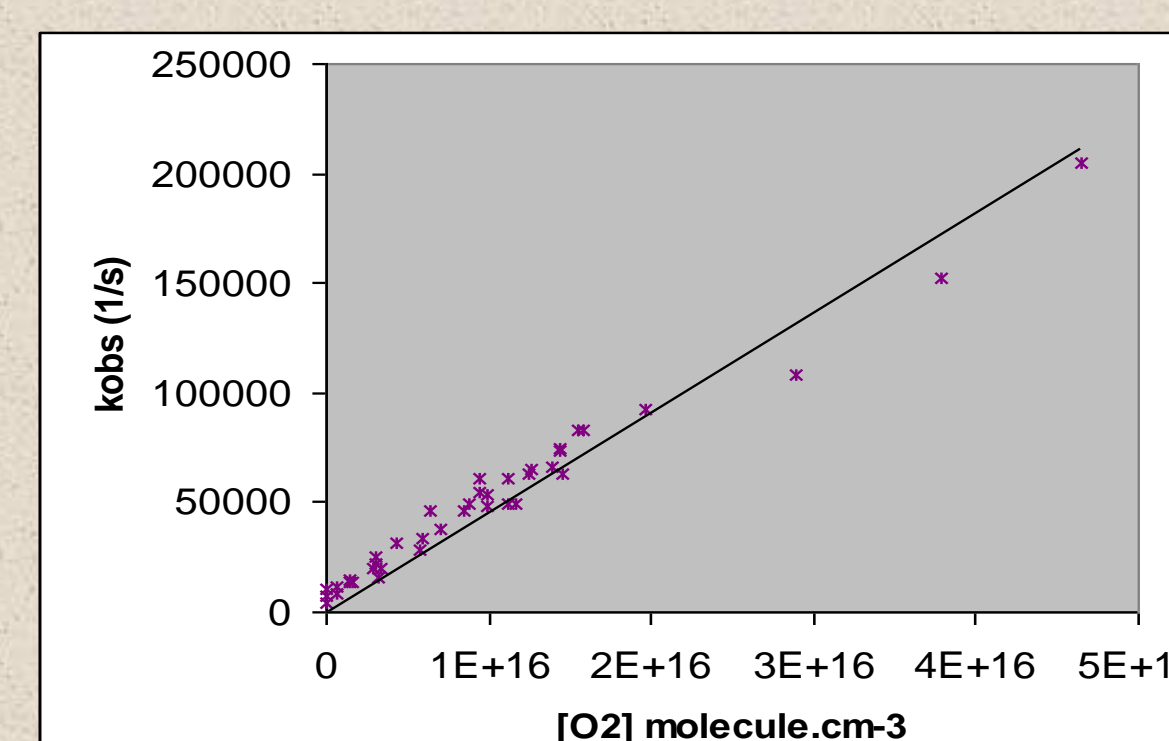


Experimental conditions

- $[\text{H}_2\text{CO}]$: $3\text{-}10 \cdot 10^{15} \text{ molecule.cm}^{-3}$ (from thermal depolymerization of paraformaldehyde)
- $[\text{Cl}_2]$: $2\text{-}10 \cdot 10^{14} \text{ molecule.cm}^{-3}$
- $[\text{Cl}]$: $0.1 [\text{Cl}_2]$
- $[\text{O}_2]$: $6\text{-}500 \cdot 10^{14} \text{ molecule.cm}^{-3}$
- total pressure : 5-20 Torr



CO apparition signal (red curve), fit to exponential rise (black) and residuals (blue).
Experimental conditions: $[\text{H}_2\text{CO}] = 3.2 \cdot 10^{15}$, $[\text{Cl}_2] = 10^{15}$, $[\text{O}_2] = 9.5 \cdot 10^{15}$, $P = 7 \text{ Torr}$, 30 YAG shots.



k (cm ³ molecule ⁻¹ s ⁻¹)	reference
4.6 ± 0.7	this work
4.9 ± 0.7	this work
5.6	DeMore 1997
5.5	Atkinson 1997