

Preliminary results,
please do not share
outside of workshop
attendees



***EXPERIMENTAL STUDIES OF VIBRATIONAL
RELAXATION AND FORMATION OF WEAKLY BOUND
COMPLEXES IN COLD UNIFORM SUPERSONIC FLOWS***

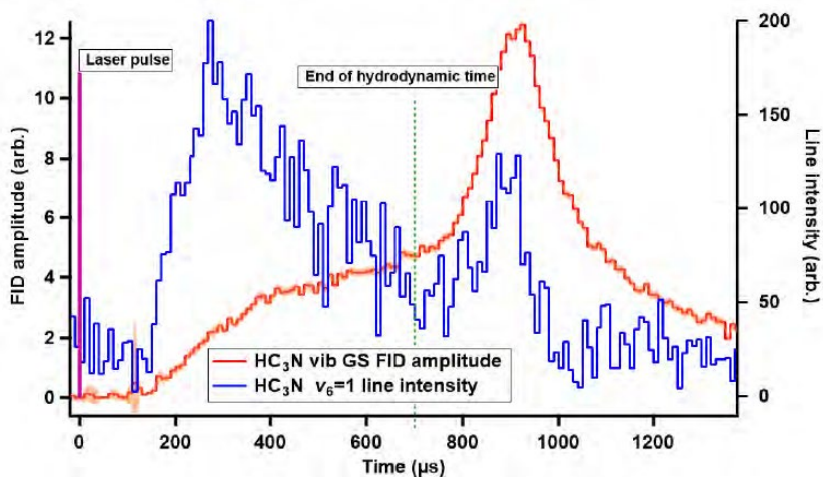
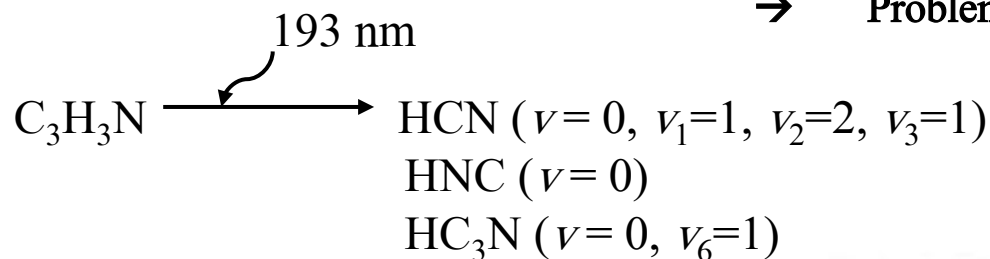
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*Institut de Physique de Rennes (IPR) – UMR 6251 du CNRS, Université de
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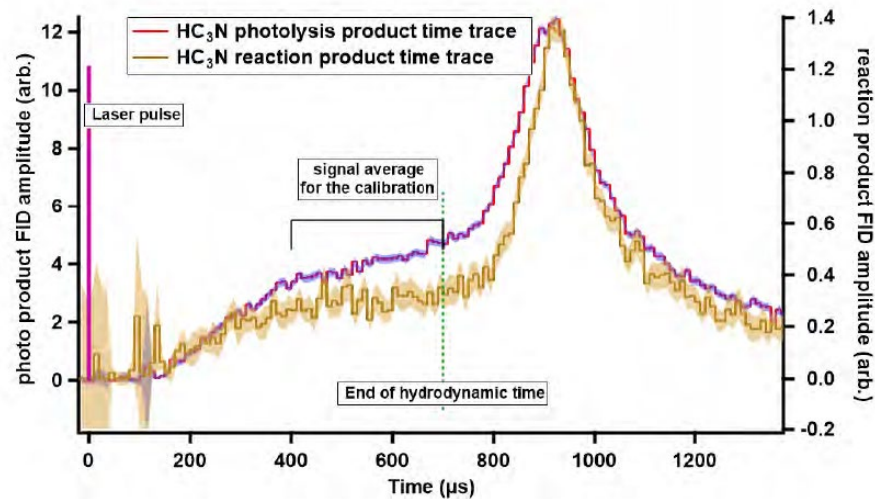
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INTRODUCTION

- ↻ Vibrational Energy Transfer (VET) → Vibrationally excited products
→ Problem in reaction product branching studies

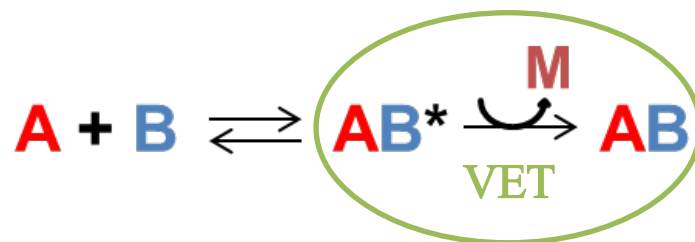


Incomplete vibrational relaxation



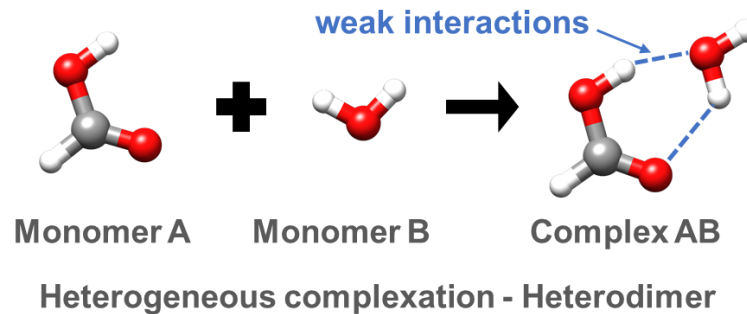
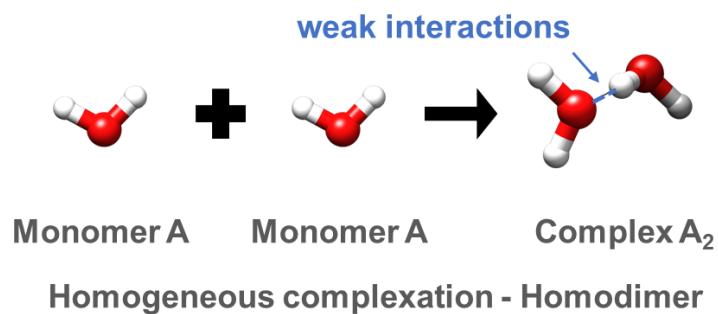
INTRODUCTION

↻ Vibrational Energy Transfer (VET) → Termolecular association



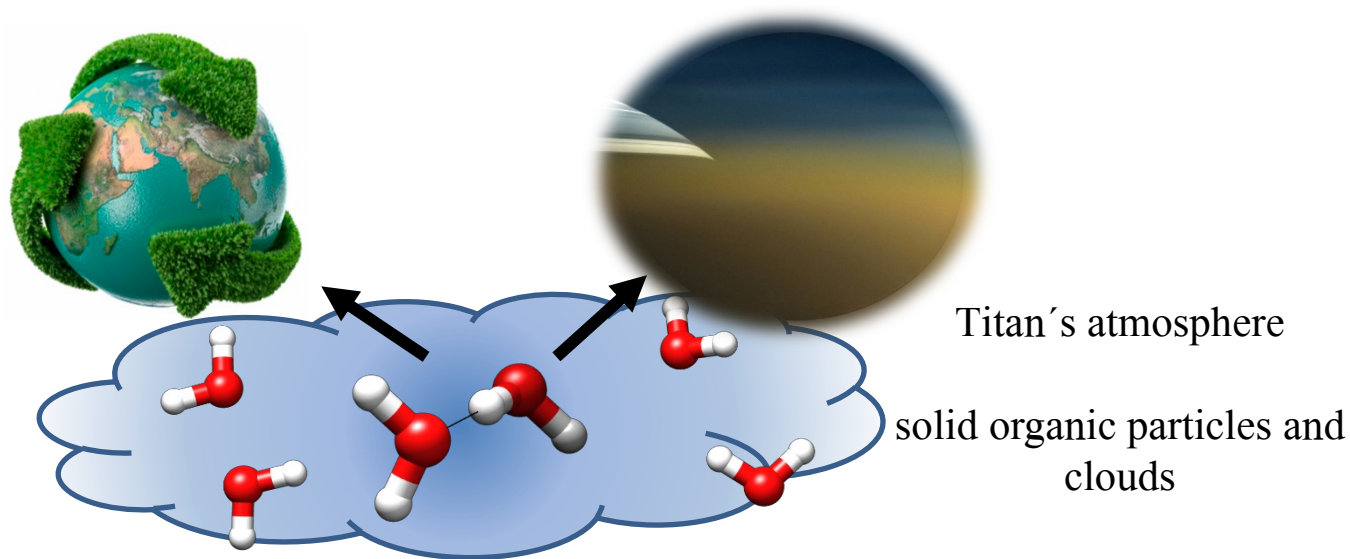
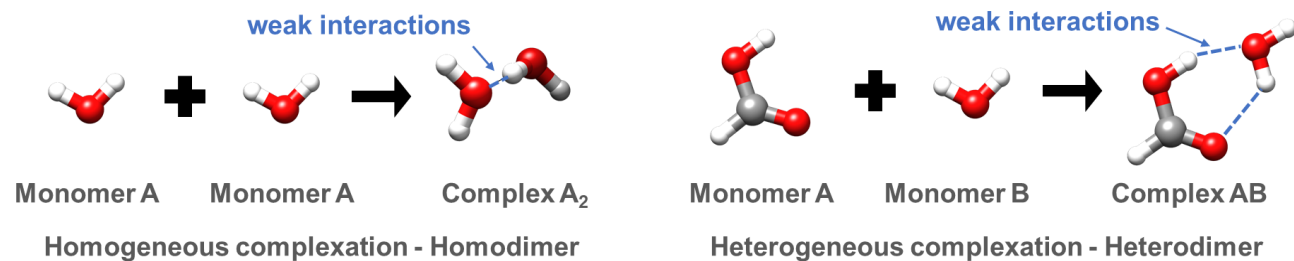
Lindemann mechanism

↻ A-B weak non-covalent interaction → Complexation process



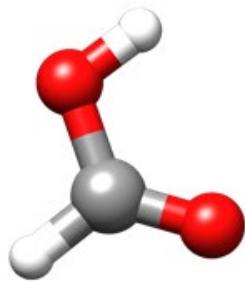
INTRODUCTION

Nucleation

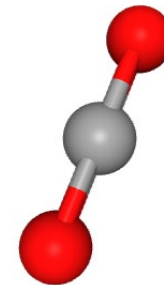


INTRODUCTION

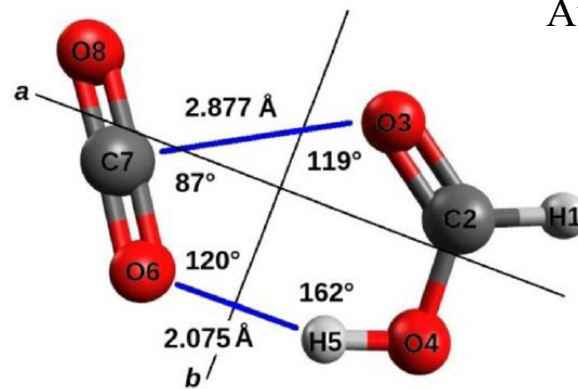
☞ Formic acid – CO₂ complex



Atmospheric importance
Cloud formation
CCU technologies



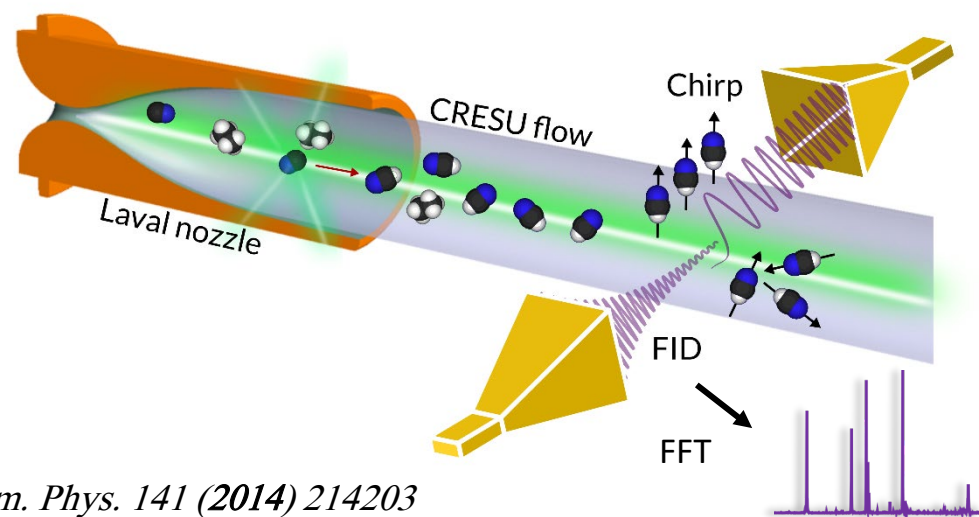
Atmospheric importance
Greenhouse effect



Atmospheric aerosol growth, cloud evolution and environmental impact

EXPERIMENTAL METHOD

Chirped-Pulse microwave spectroscopy in Uniform supersonic Flow (CPUF)

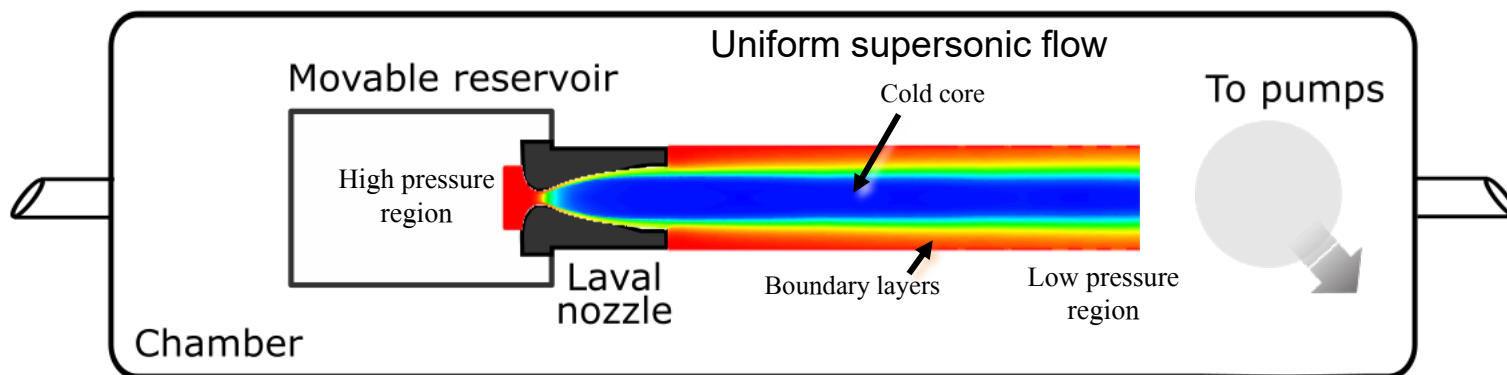


C. Abeysekera *et al.* *J. Chem. Phys.* 141 (2014) 214203

C. Abeysekera *et al.* *J. Phys. Chem. Letts.* 6 (2015) 1599

EXPERIMENTAL METHOD

☞ Uniform supersonic Flows → CRESU technique



Convergent-Divergent nozzle to create supersonic flow

$$C_p T_{\text{res}} = C_p T_{\text{flow}} + \frac{v_{\text{flow}}^2}{2}$$

Wall-less cooling reactor

Uniform supersonic flow

Length = 10 – 70 cm $T = 10 - 220 \text{ K}$ $\rho = 10^{16} - 10^{18} \text{ cm}^{-3}$

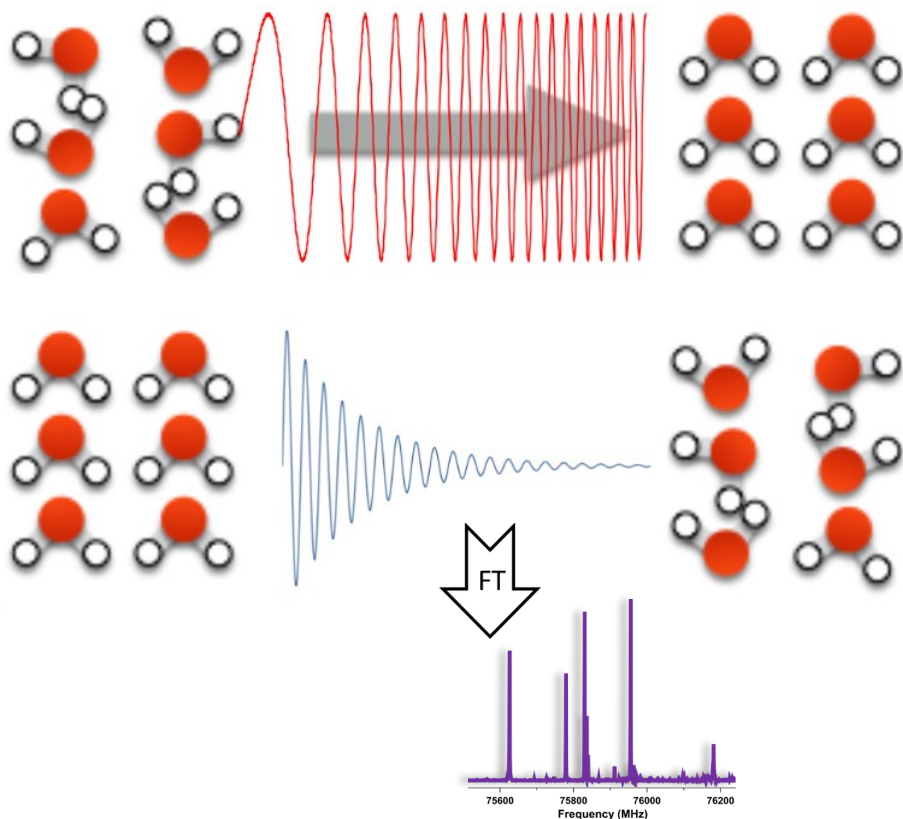
Frequent enough collisions

local thermodynamic equilibrium

a sufficient extent of chemical reaction to take place to follow the kinetics

EXPERIMENTAL METHOD

☞ Chirped-Pulse microwave spectroscopy



High specificity

Distinguish **simultaneously** between different species

Conformers, isomers, vibrational excited states, isotopologues ...

EXPERIMENTAL METHOD



Ka Band Spectrometer 24-40 GHz

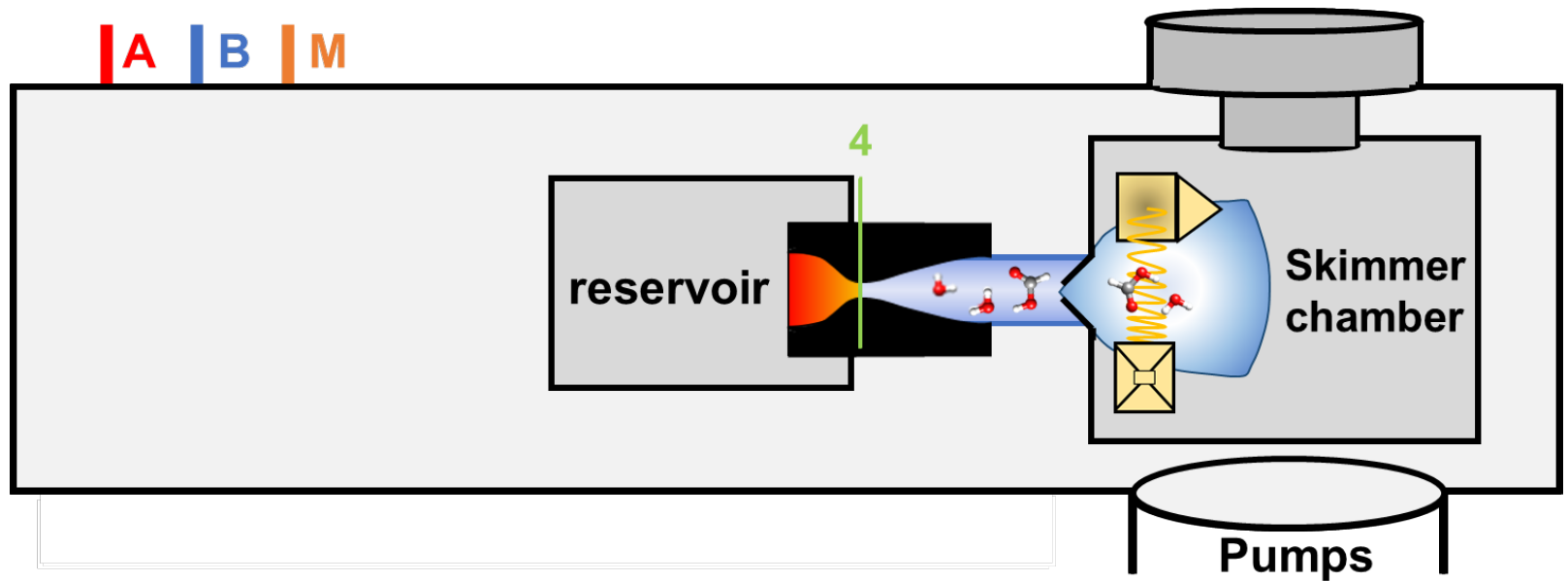
T. S. Hearne *et al. J. Chem Phys.* 153 (2020) 084201

E Band Spectrometer 60-90 GHz

B. M. Hays *et al. J. Quant. Spectrosc. Radiat. Transf.* 250 (2020) 107001

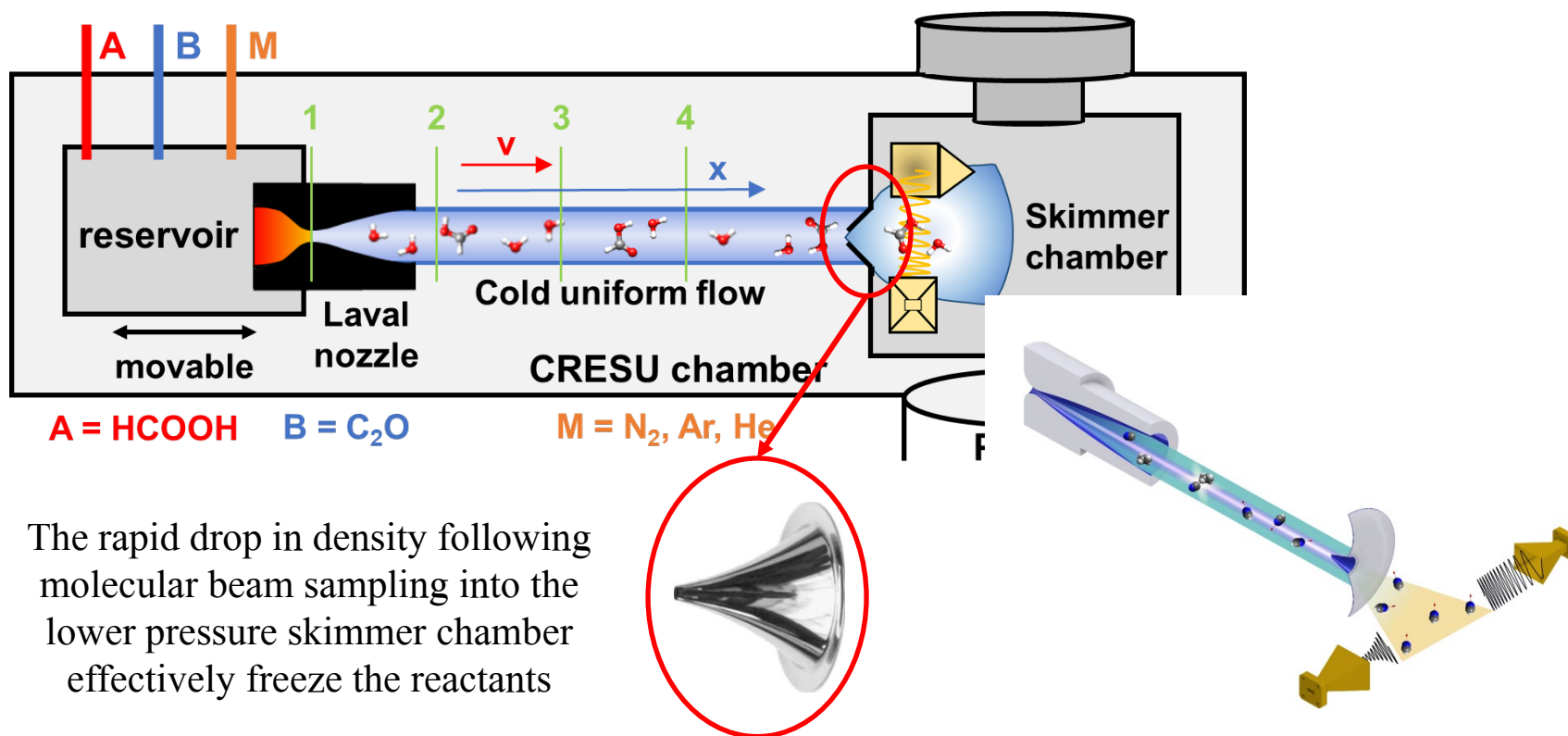
EXPERIMENTAL METHOD

☞ Acquisition procedure → Time dependence

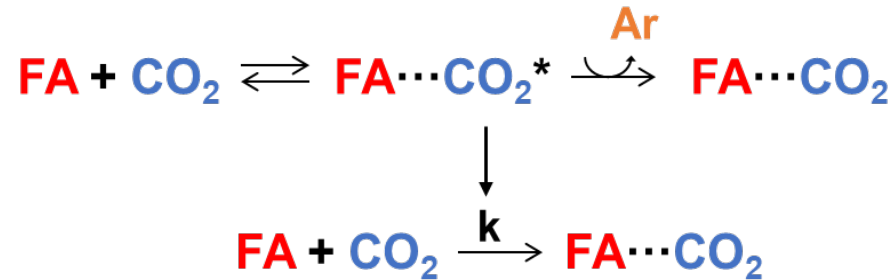


EXPERIMENTAL METHOD

Acquisition procedure → Importance of the skimmer chamber

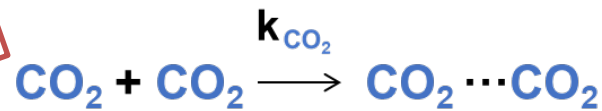


REACTION KINETICS



$$r = k [\text{FA}][\text{CO}_2] \xrightarrow{[\text{CO}_2] \gg [\text{FA}]} r = k' [\text{FA}]$$

Avoid

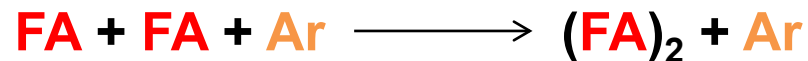


$$k \gg k_{\text{CO}_2}$$

$$k \gg k_{\text{FA}}$$

PRELIMINARY RESULTS

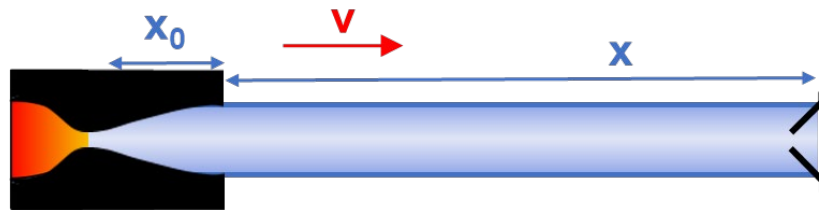
☞ Formic acid homodimer formation → Termolecular reaction



$$-\frac{1}{2} \frac{d[\text{FA}]}{dt} = k [\text{FA}]^2 [\text{Ar}] \xrightarrow{k' = k [\text{Ar}]} \frac{d[\text{FA}]}{dt} = -2k' [\text{FA}]^2$$

$$\frac{1}{[\text{FA}]_t} - \frac{1}{[\text{FA}]_{t_0}} = 2k't \xrightarrow{t = \frac{x + x_0}{v}} \frac{1}{[\text{FA}]_x} - \frac{1}{[\text{FA}]_{x_0}} = \frac{2k'x}{v}$$

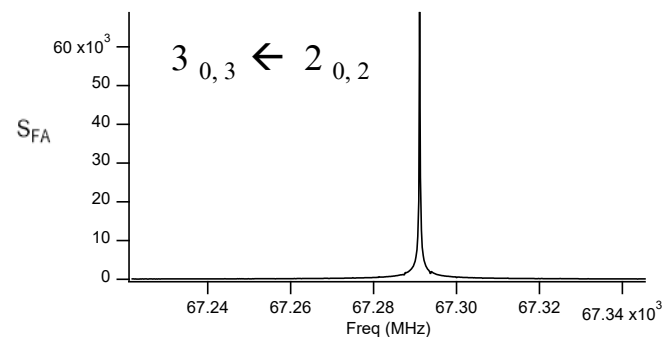
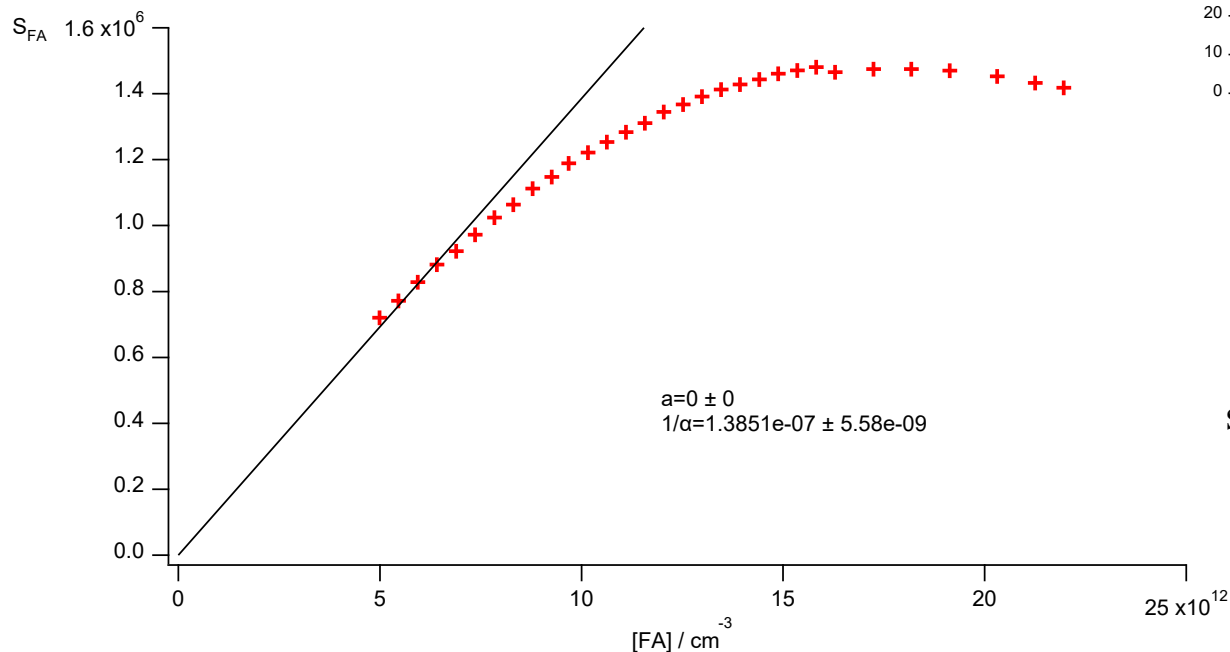
Absolute density value



PRELIMINARY RESULTS

☞ Formic acid homodimer formation → Termolecular reaction

$$S_{FA} = \frac{1}{\alpha} [FA]$$



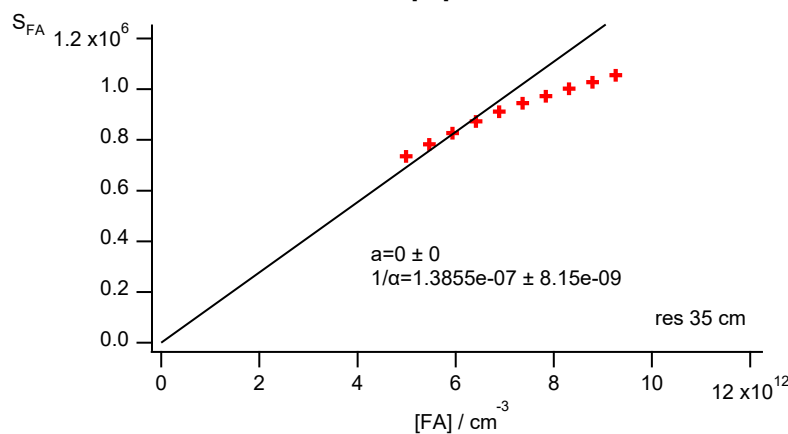
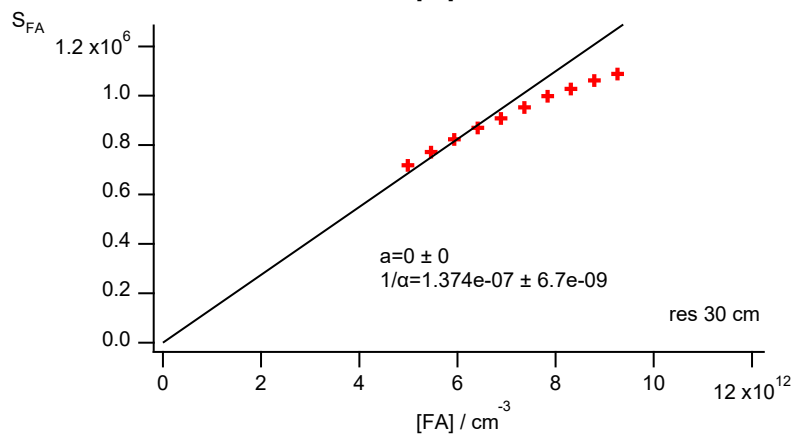
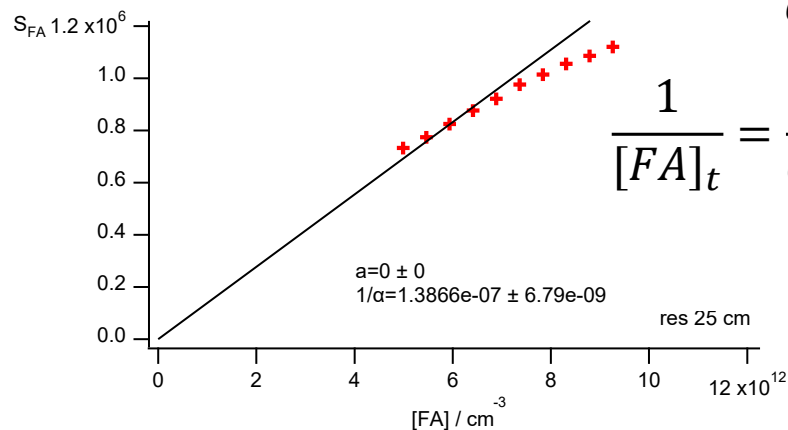
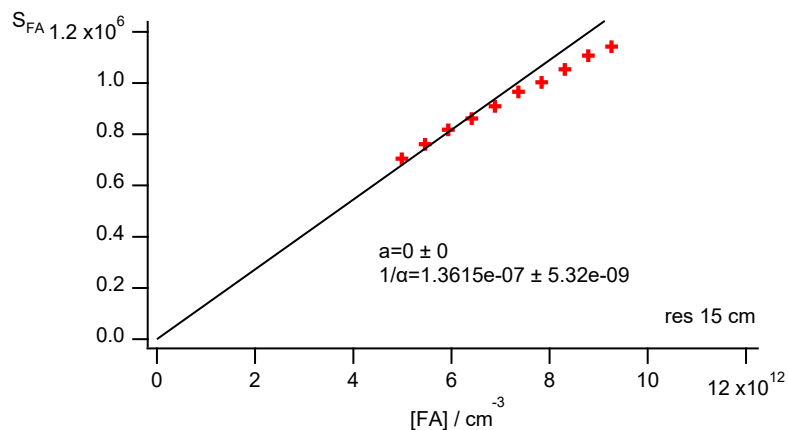
small removal fraction of the monomer (20-30%)

PRELIMINARY RESULTS

☞ Formic acid homodimer formation → Termolecular reaction

$$S_{FA} = \frac{1}{\alpha} [FA]$$

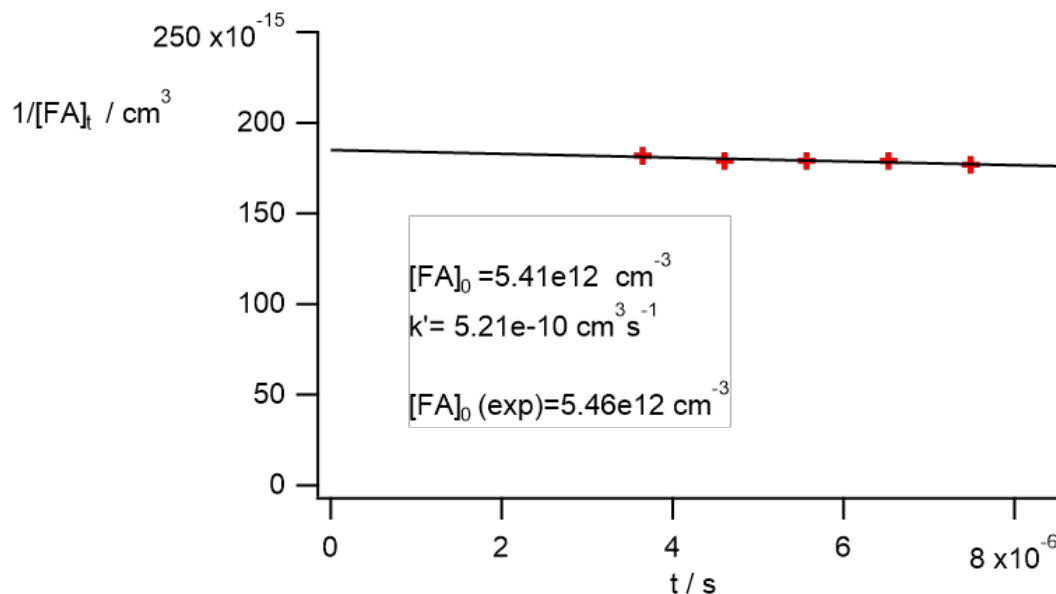
$$\frac{1}{[FA]_t} = \frac{1}{\alpha \cdot S_{FA}}$$



PRELIMINARY RESULTS

☞ Formic acid homodimer formation → Termolecular reaction

$$\frac{1}{[FA]_t} = \frac{1}{[FA]_{t_0}} + 2k't$$



☞ Determination of apparent rate constant of the formic acid dimer formation

PRELIMINARY RESULTS

Formic acid + CO₂ formation → Heterodimer formation reaction

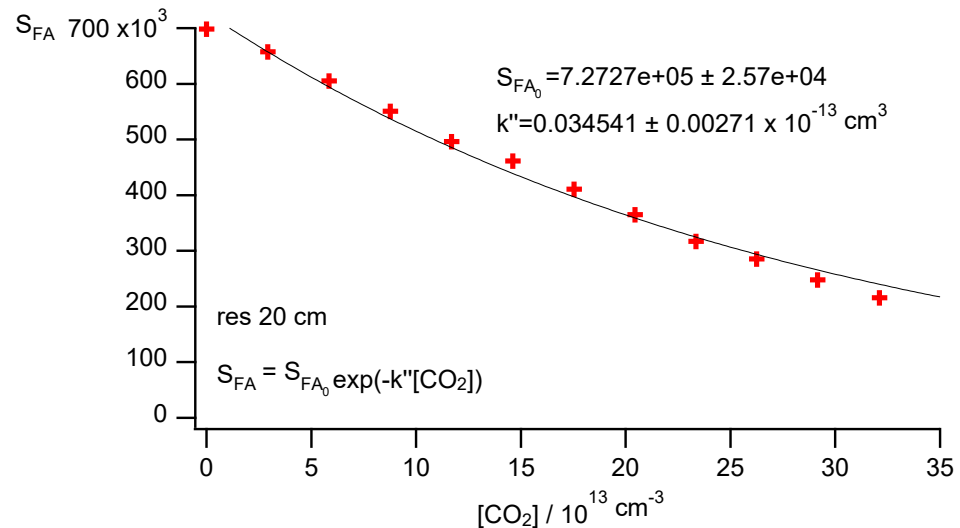


$$-\frac{d[\text{FA}]}{dt} = k'[\text{FA}][\text{CO}_2] \longrightarrow [\text{FA}]_t = [\text{FA}]_{t_0} \exp(-k' t [\text{CO}_2])$$

$$k'' = k' t$$

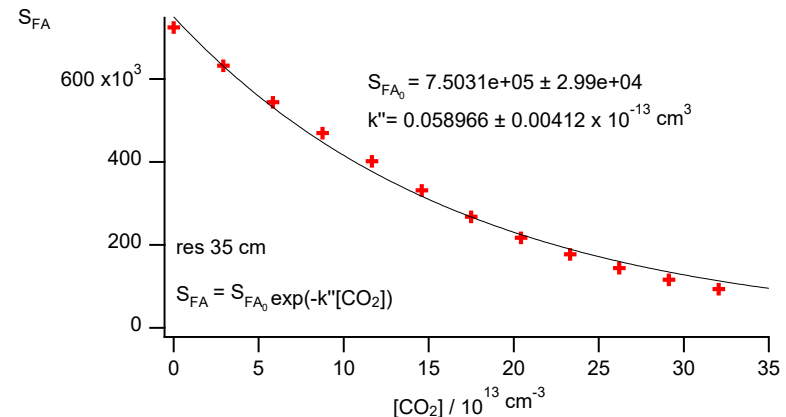
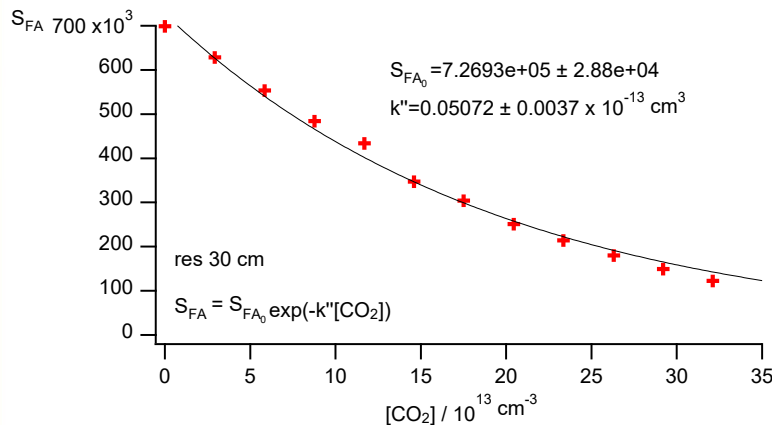
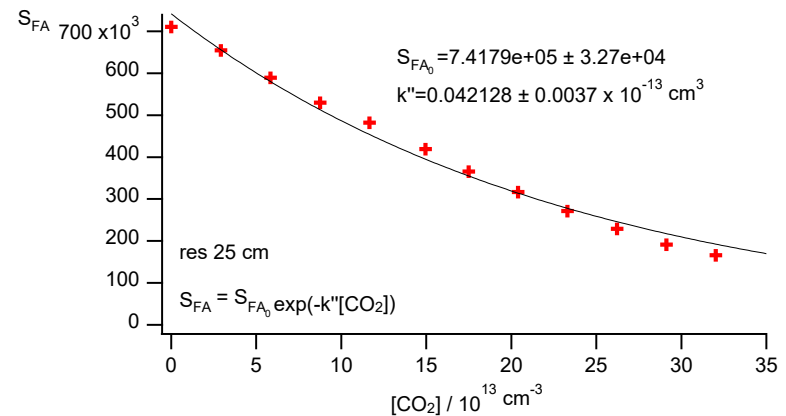
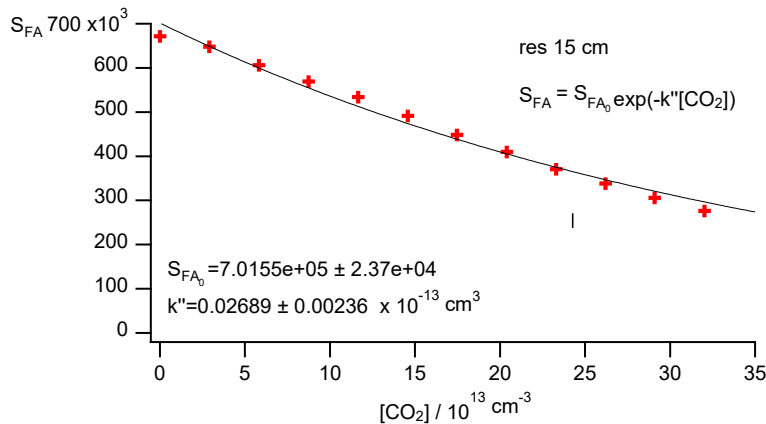
$$[\text{FA}]_t = [\text{FA}]_{t_0} \exp(-k'' [\text{CO}_2])$$

$$S_{\text{FA}} = S_{\text{FA}_0} \exp(-k'' [\text{CO}_2])$$



PRELIMINARY RESULTS

☞ Formic acid $\bullet\bullet\bullet$ CO₂ formation \rightarrow Heterodimer formation reaction

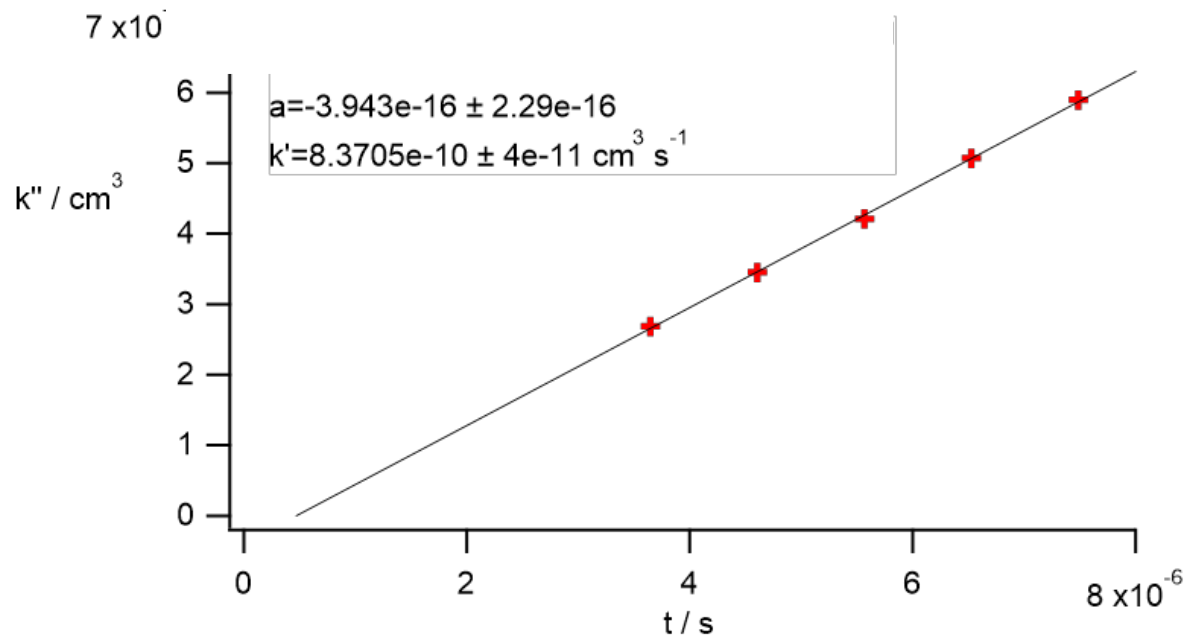


PRELIMINARY RESULTS

☞ Formic acid•••CO₂ formation → Heterodimer formation reaction

$$k'' = k' t$$

$$t = \frac{x + x_0}{v}$$



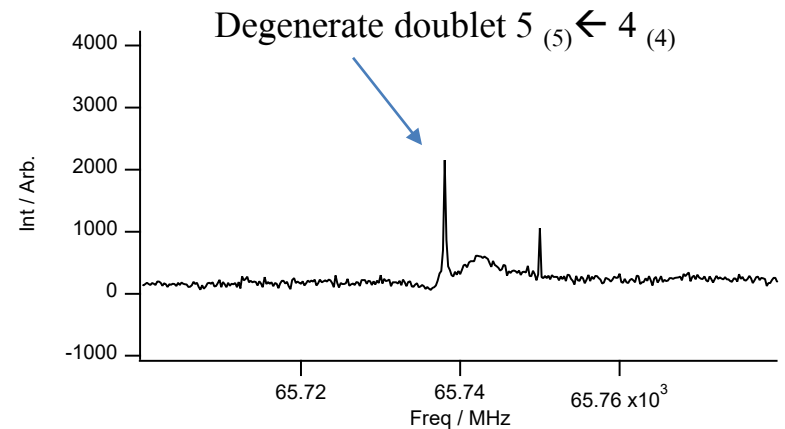
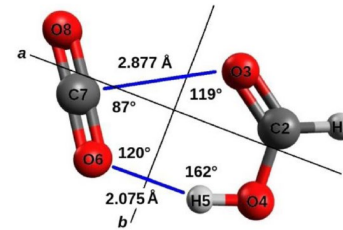
☞ First direct determination of a weakly bound heterodimer formation rate constant

CONCLUSIONS AND NEXT STEPS

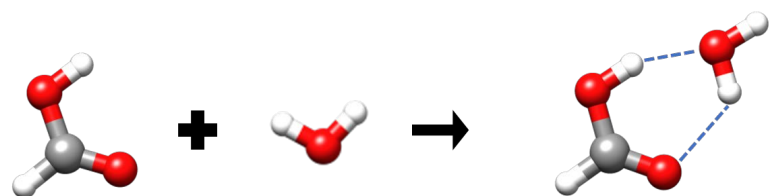
☞ More measurements

☞ Change the temperature of the flow

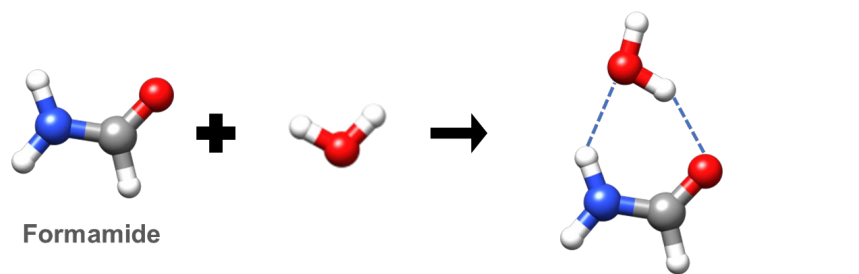
☞ Change the buffer gas



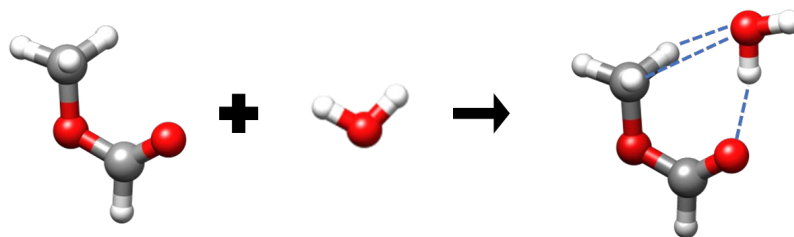
PERSPECTIVES



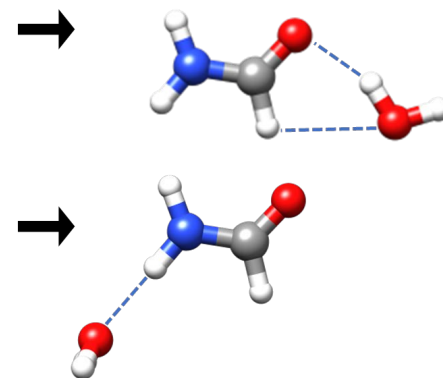
Formic Acid



Formamide



Methyl Formate



ACKNOWLEDGEMENTS

☞ Ian Sims

Myriam Drissi, Omar Abdelkader Khedaoui,
Théo Guillaume, Brian M. Hays, Divita Gupta, Ilsa R. Cooke



☞ Funding

CNRS INSU PCMI
EU FEDER
ERC CRESUCHIRP

CNRS INSU PNP
Rennes Métropole
ANR Hydrides

Université de Rennes 1
Région de Bretagne

