



***STUDY OF COMPLEXATION KINETICS  
PROCESSES BY ROTATIONAL SPECTROSCOPY  
COUPLED WITH UNIFORM SUPERSONIC FLOWS***

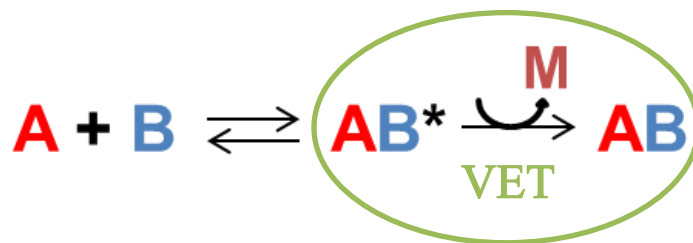
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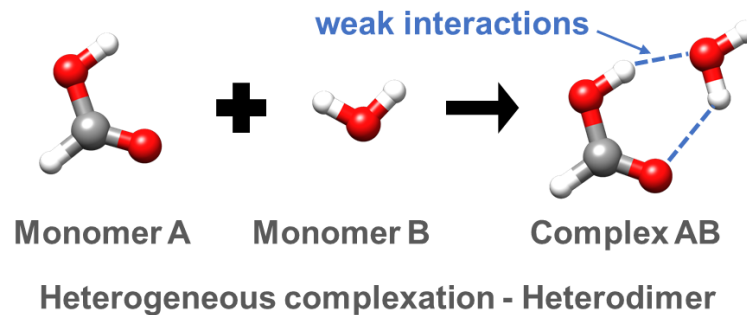
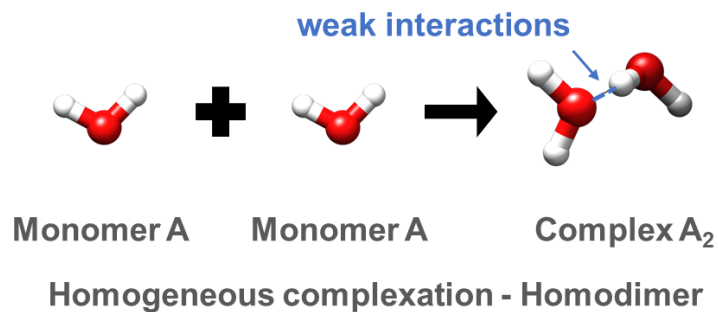
# INTRODUCTION

☞ Termolecular association reactions



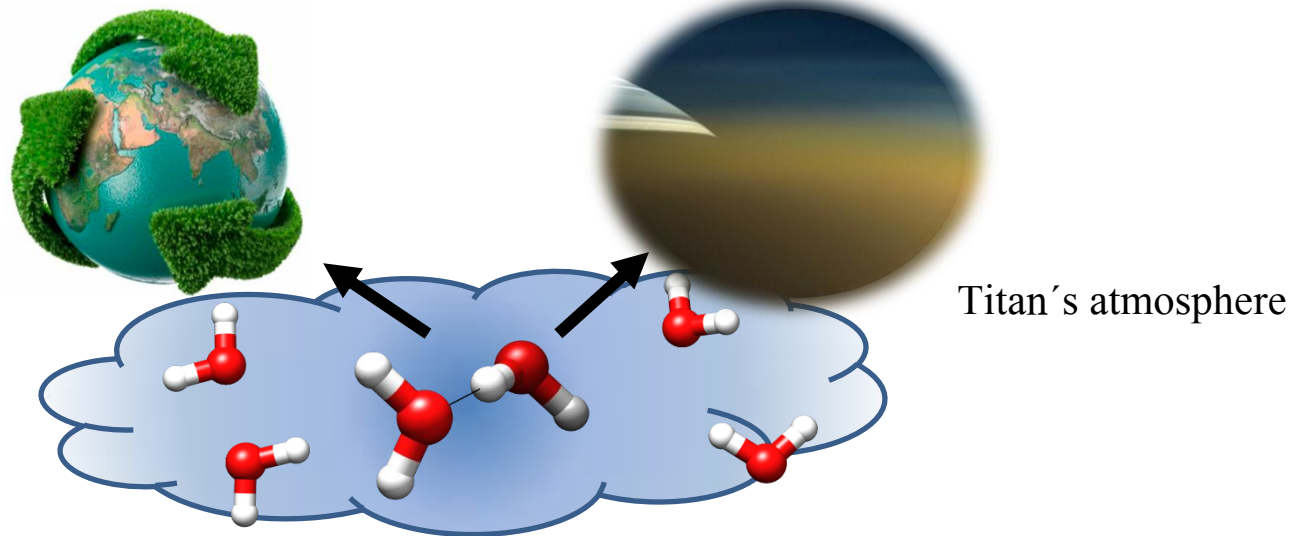
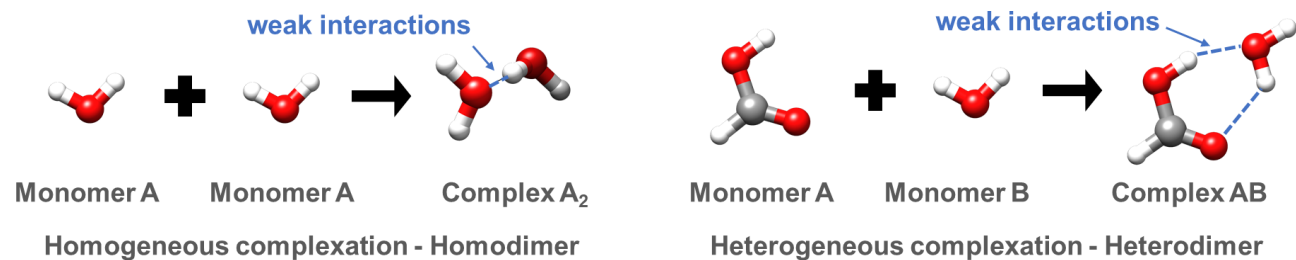
Lindemann mechanism

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



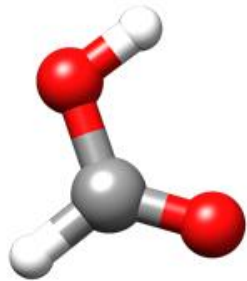
# INTRODUCTION

## Nucleation

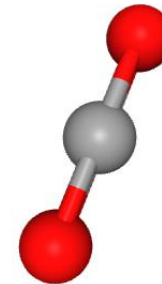


# INTRODUCTION

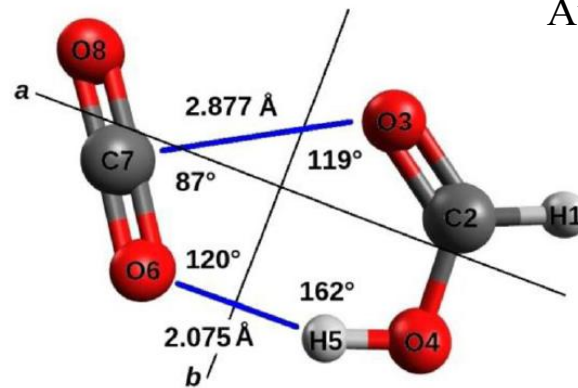
## ☞ Formic acid – CO<sub>2</sub> complex



Atmospheric importance  
Cloud formation  
CCU technologies



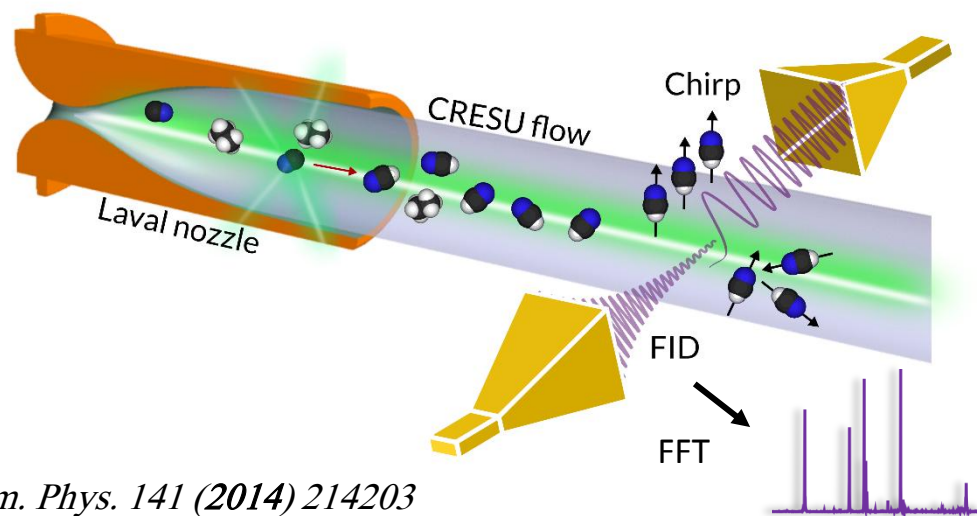
Atmospheric importance  
Greenhouse effect



Atmospheric aerosol growth, cloud evolution and environmental impact

# *EXPERIMENTAL METHOD*

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

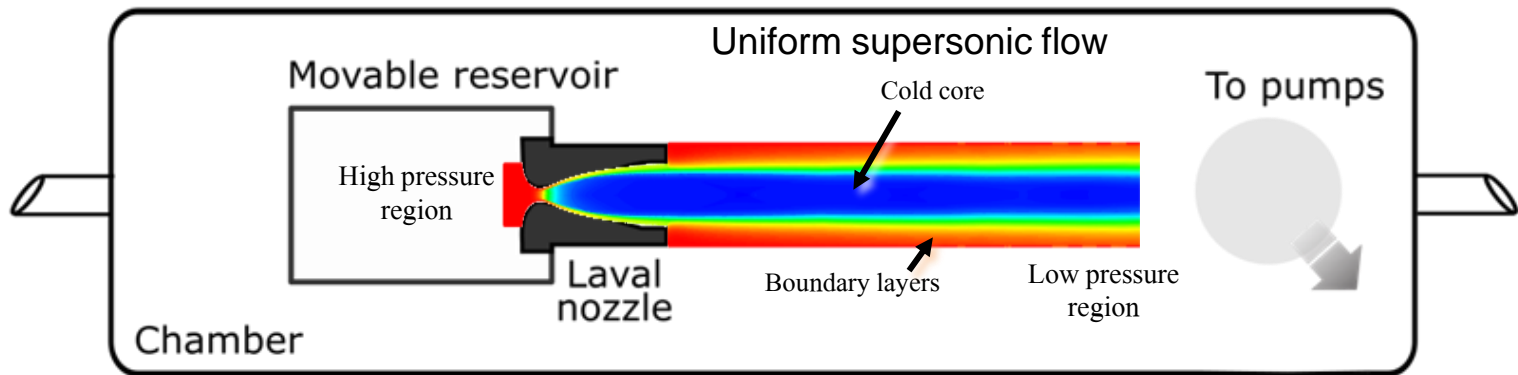


C. Abeysekera *et al.* *J. Chem. Phys.* 141 (2014) 214203

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

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

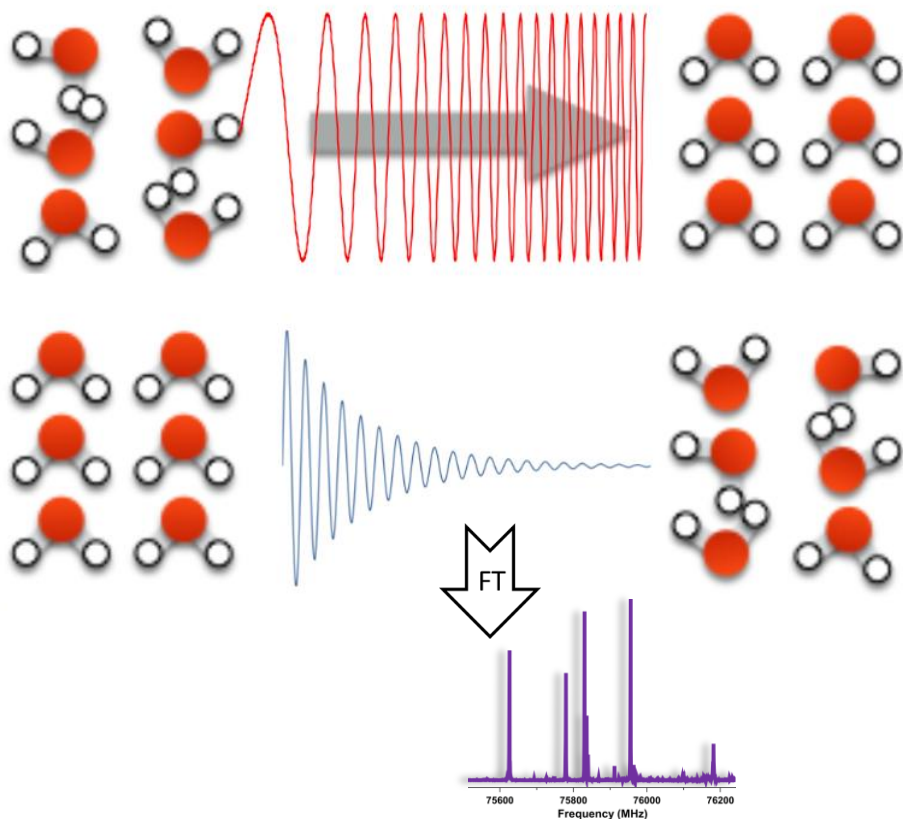
Wall-less cooling reactor

Uniform supersonic flow

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

# *EXPERIMENTAL METHOD*

## Chirped-Pulse microwave spectroscopy



**High specificity**

Distinguish **simultaneously** between different species

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

# *EXPERIMENTAL METHOD*



Ka Band Spectrometer 26.5-40 GHz

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

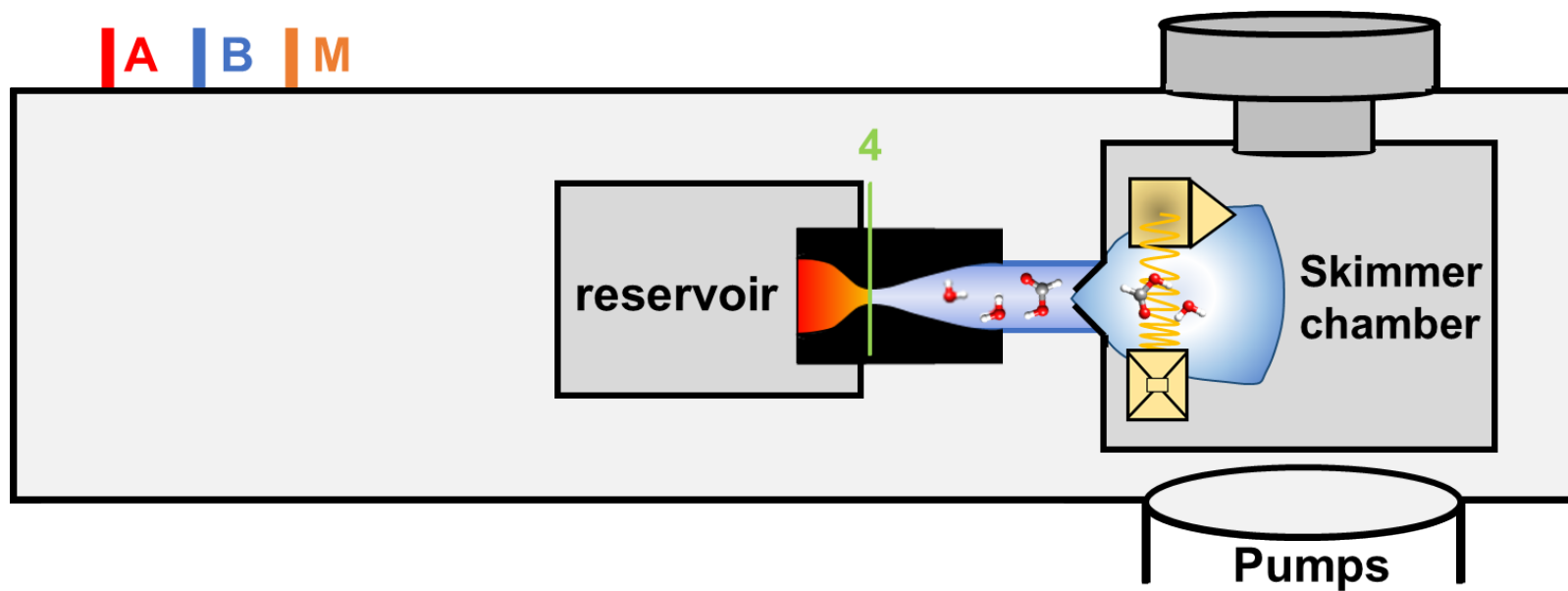
E Band Spectrometer 60-90 GHz

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



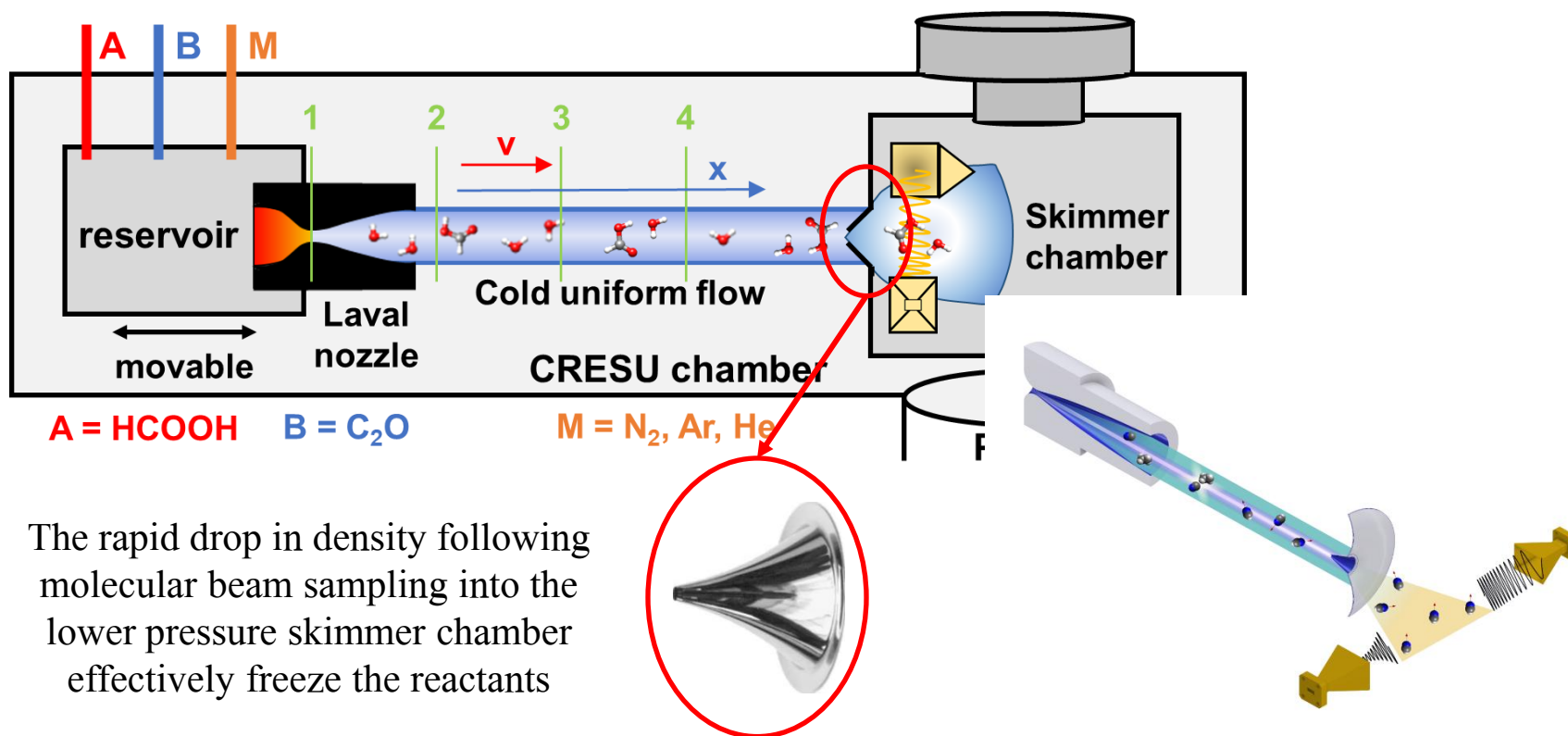
# *EXPERIMENTAL METHOD*

↻ Acquisition procedure → Time dependence

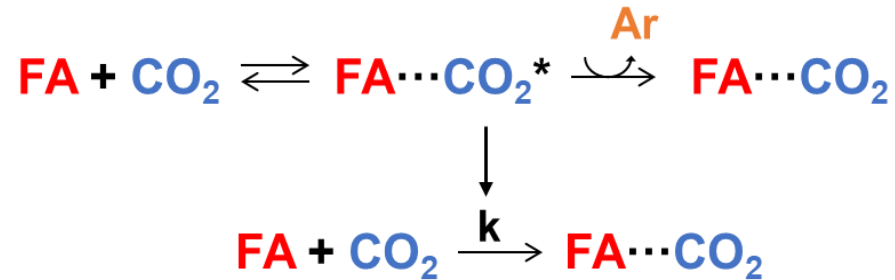


# EXPERIMENTAL METHOD

Acquisition procedure → Importance of the skimmer chamber

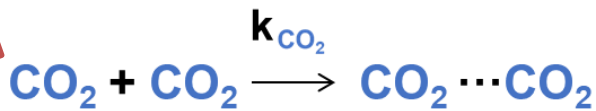


# REACTION KINETICS



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

**Avoid**

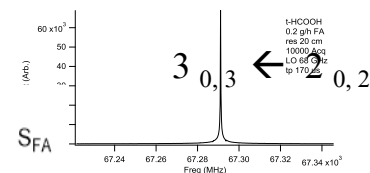
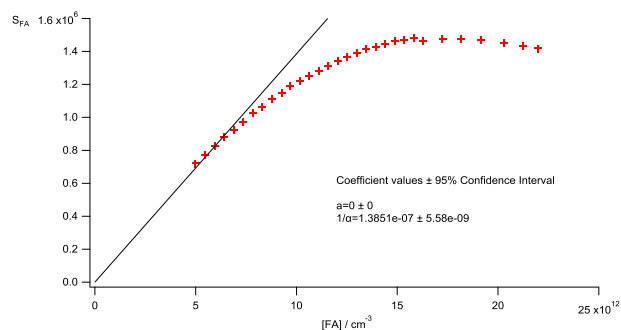
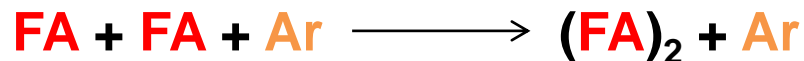


$$k \gg k_{\text{CO}_2}$$

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

# PRELIMINARY RESULTS

☞ Formic acid homodimer formation → Termolecular reaction



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

# PRELIMINARY RESULTS

Formic acid...CO<sub>2</sub> formation → Heterodimer formation reaction

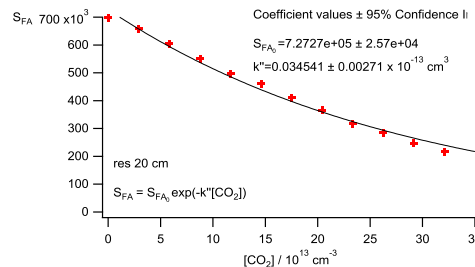


$$-\frac{d[\text{FA}]}{dt} = k'[\text{FA}][\text{CO}_2] \longrightarrow [\text{FA}]_t = [\text{FA}]_{t_0} \exp(-k't [\text{CO}_2])$$

$$k'' = k' t$$

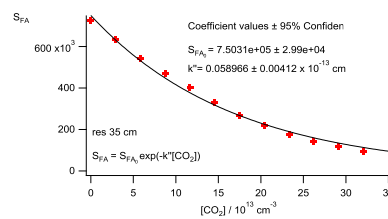
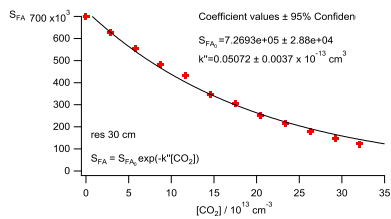
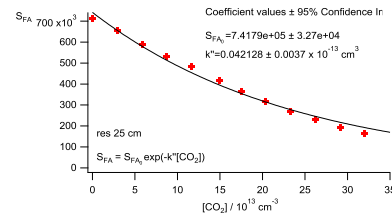
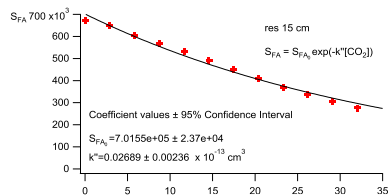
$$[\text{FA}]_t = [\text{FA}]_{t_0} \exp(-k'' [\text{CO}_2])$$

$$S_{\text{FA}} = S_{\text{FA}0} \exp(-k'' [\text{CO}_2])$$



# PRELIMINARY RESULTS

☞ Formic acid  $\bullet\bullet\bullet$  CO<sub>2</sub> formation  $\rightarrow$  Heterodimer formation reaction

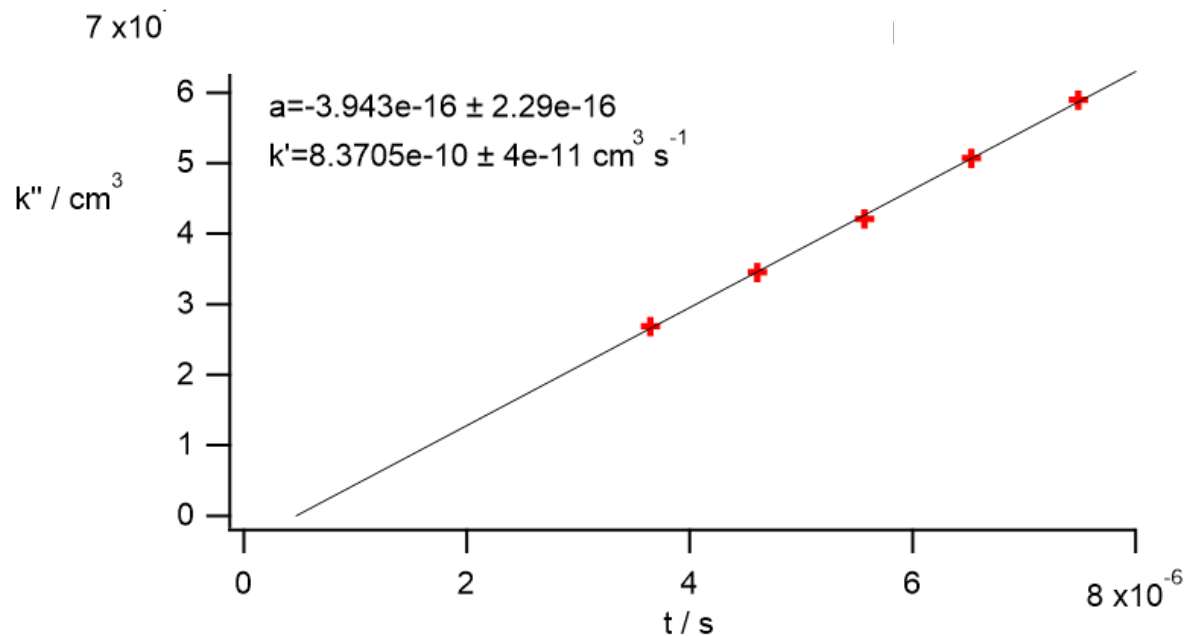


# PRELIMINARY RESULTS

☞ Formic acid ••• CO<sub>2</sub> formation → Heterodimer formation reaction

$$k'' = k' t$$

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



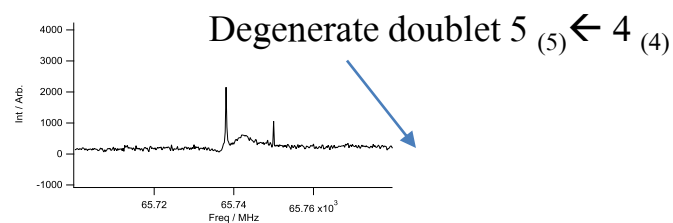
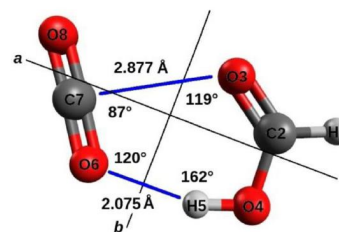
☞ First direct determination of a weakly bound heterodimer formation rate constant

# CONCLUSIONS AND NEXT STEPS

☞ More measurements

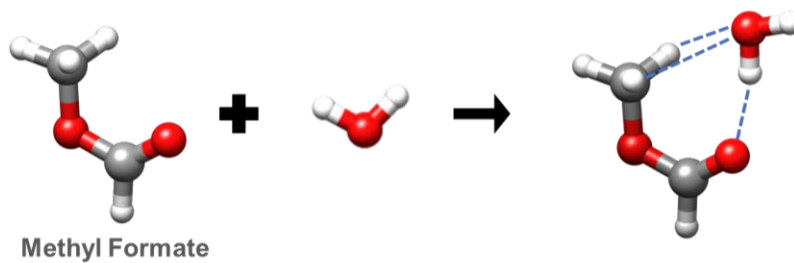
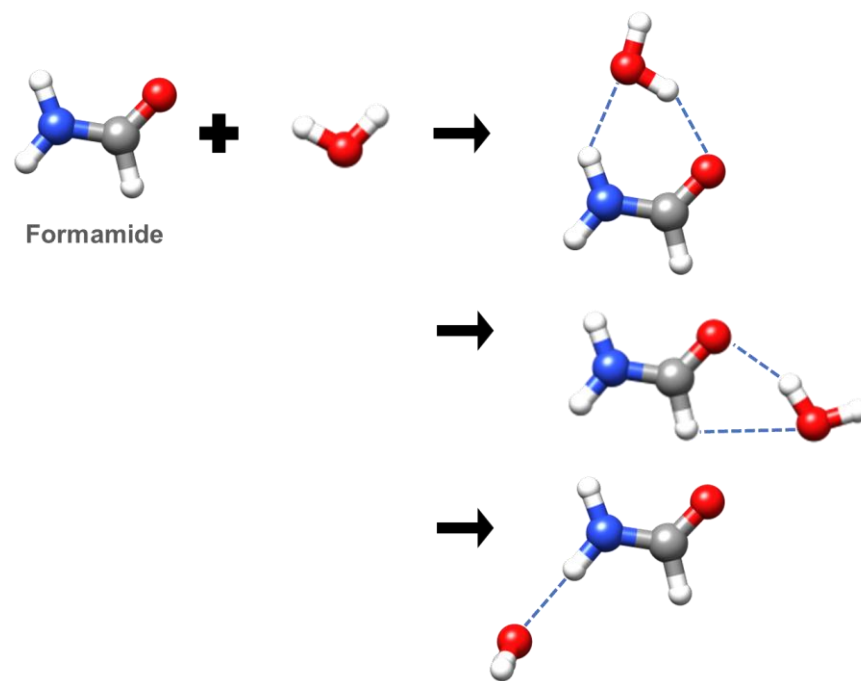
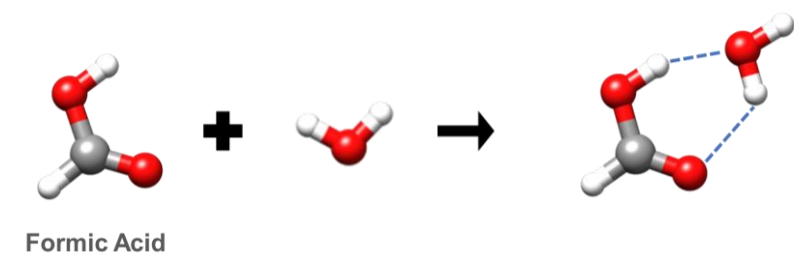
☞ Change the temperature of the flow

☞ Change the buffer gas





# *PERSPECTIVES*



# ACKNOWLEDGEMENTS

🌀 Ian Sims

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



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