

***DYNAMICS AND KINETICS STUDIED BY CHIRPED
PULSE MICROWAVE SPECTROSCOPY IN COLD
UNIFORM SUPERSONIC FLOW***

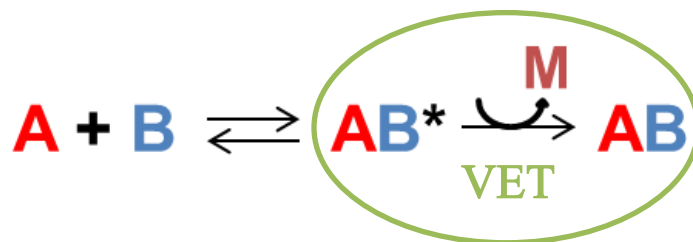
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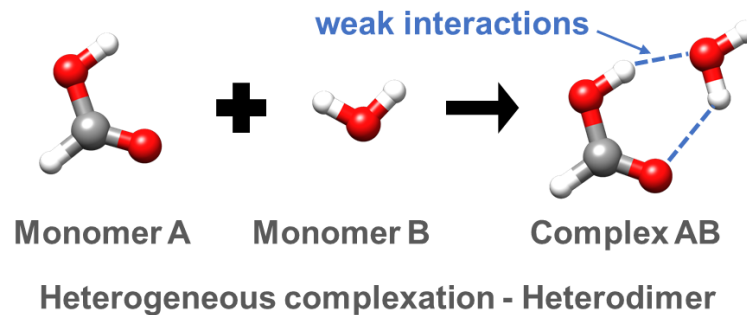
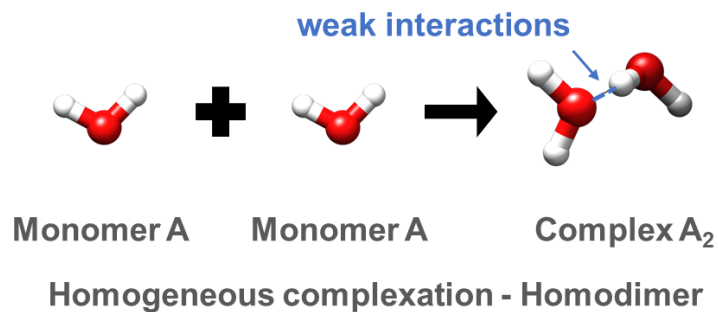
INTRODUCTION

☞ Vibrational Energy Transfer (VET) → Termolecular association



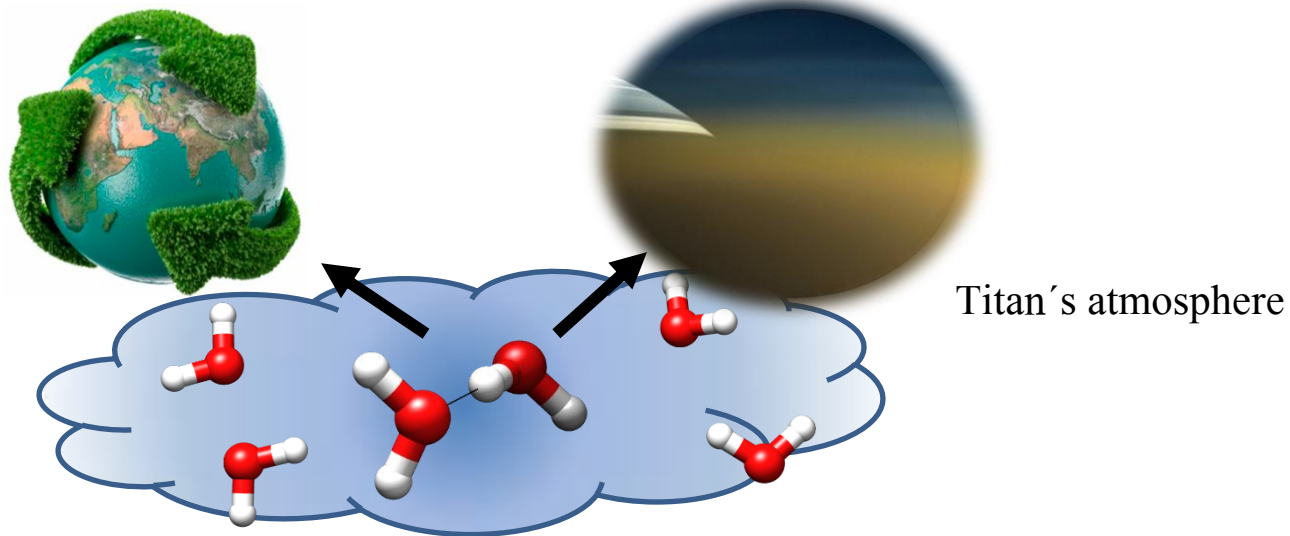
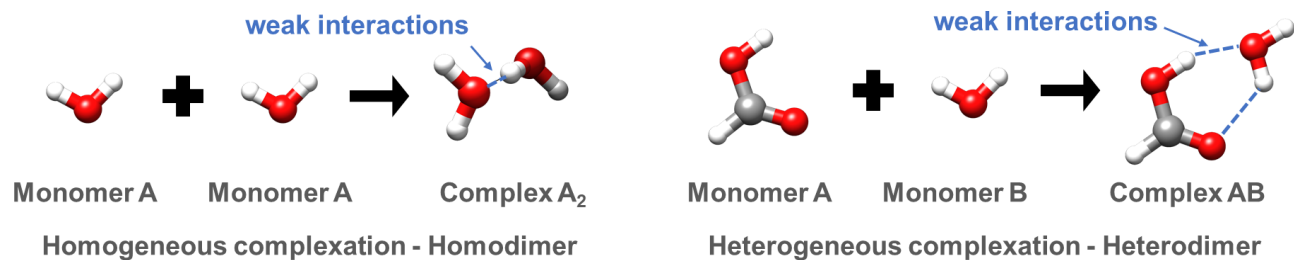
Lindemann mechanism

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



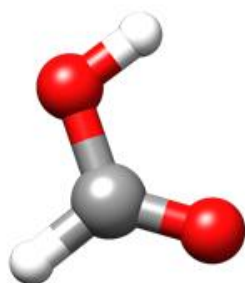
INTRODUCTION

Nucleation

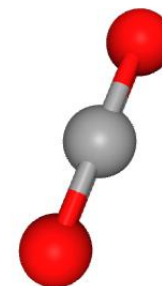


INTRODUCTION

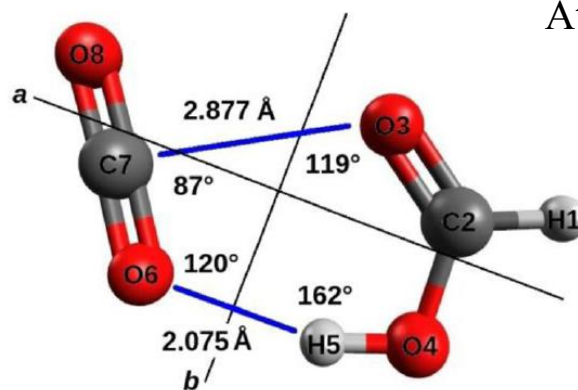
☞ Formic acid – CO₂ complex



Atmospheric importance
Cloud formation
CCU technologies



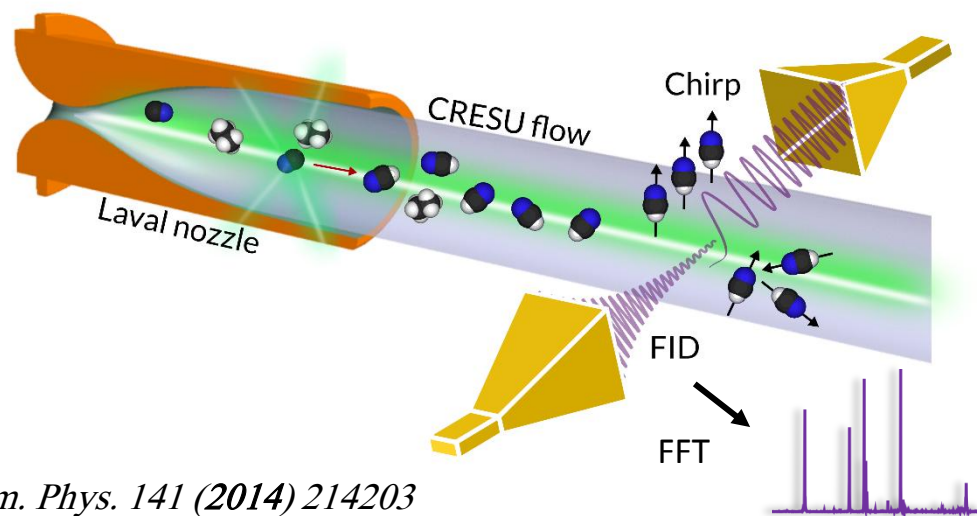
Atmospheric importance
Greenhouse effect



Atmospheric aerosol growth, cloud evolution and environmental impact

EXPERIMENTAL METHOD

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

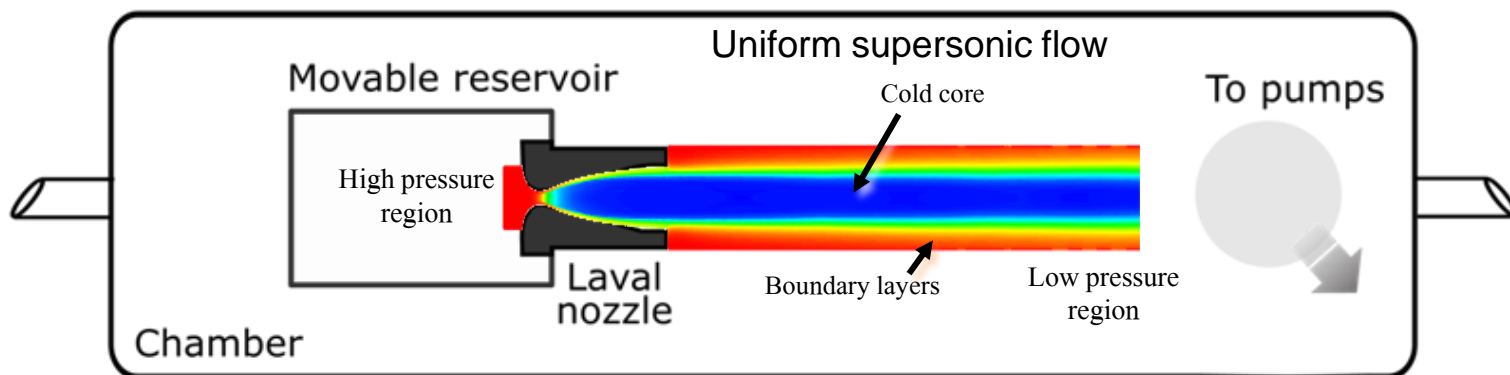


C. Abeysekera *et al.* *J. Chem. Phys.* 141 (2014) 214203

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

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

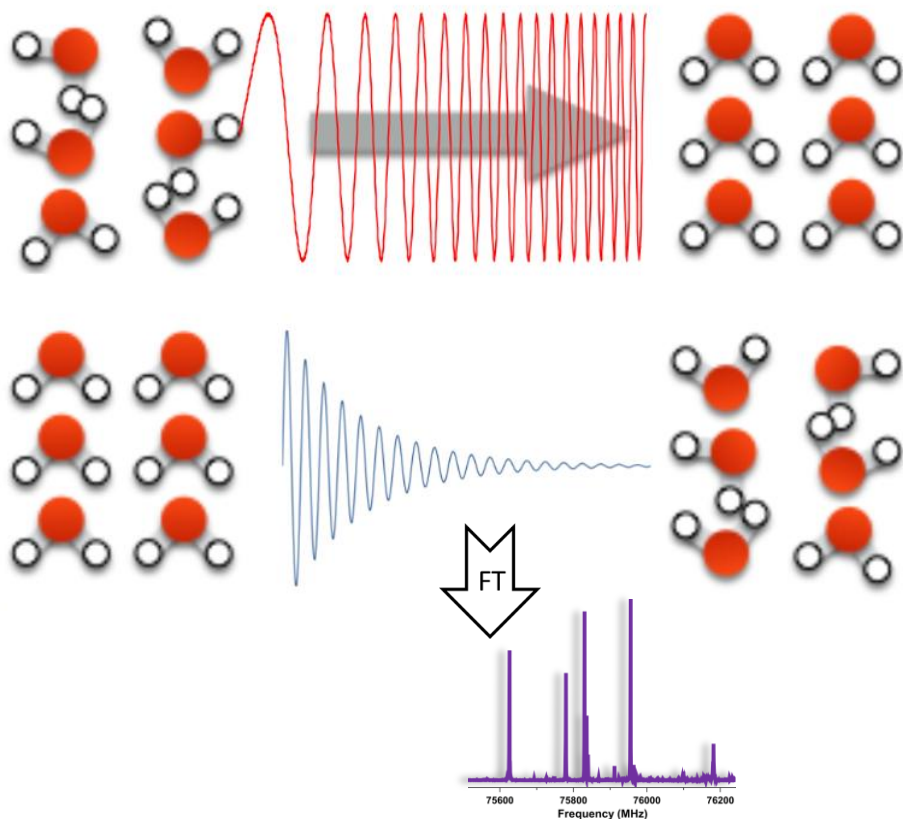
Wall-less cooling reactor

Uniform supersonic flow

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

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

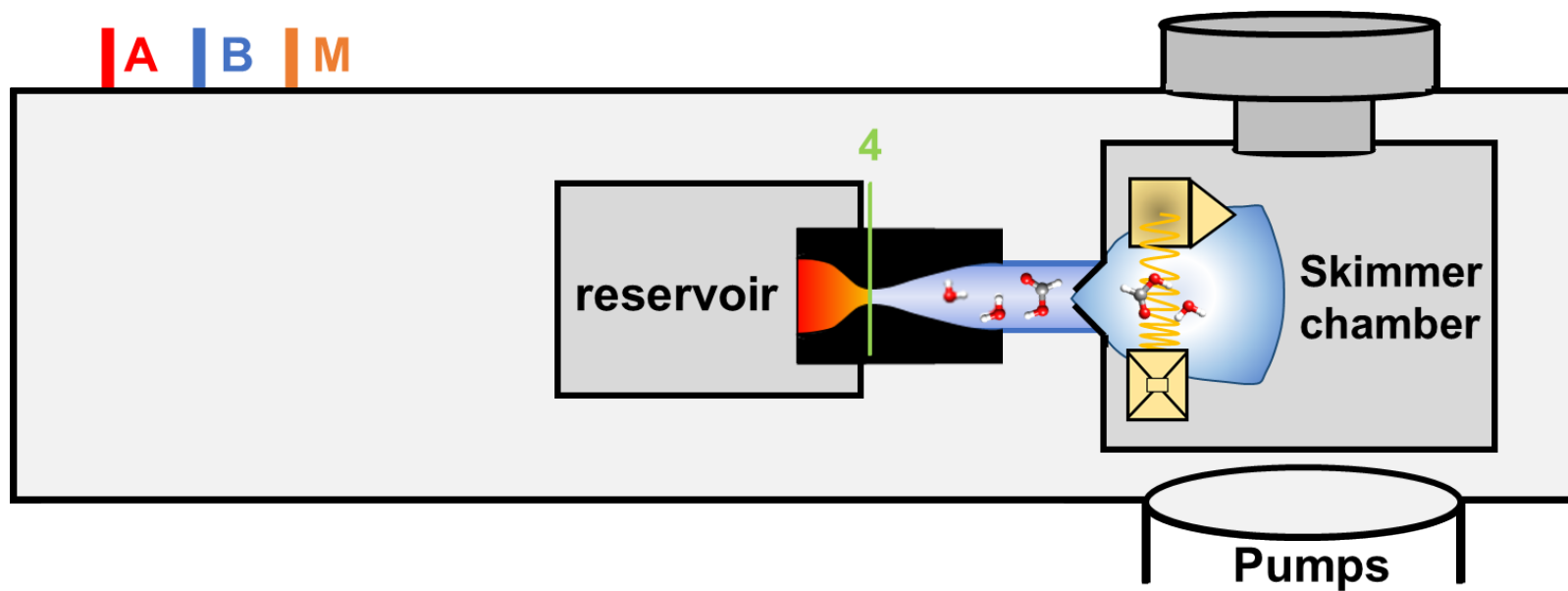
T. S. Hearne *et al. J. Chem Phys.* 153 (2020) 084201

E Band Spectrometer 60-90 GHz

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

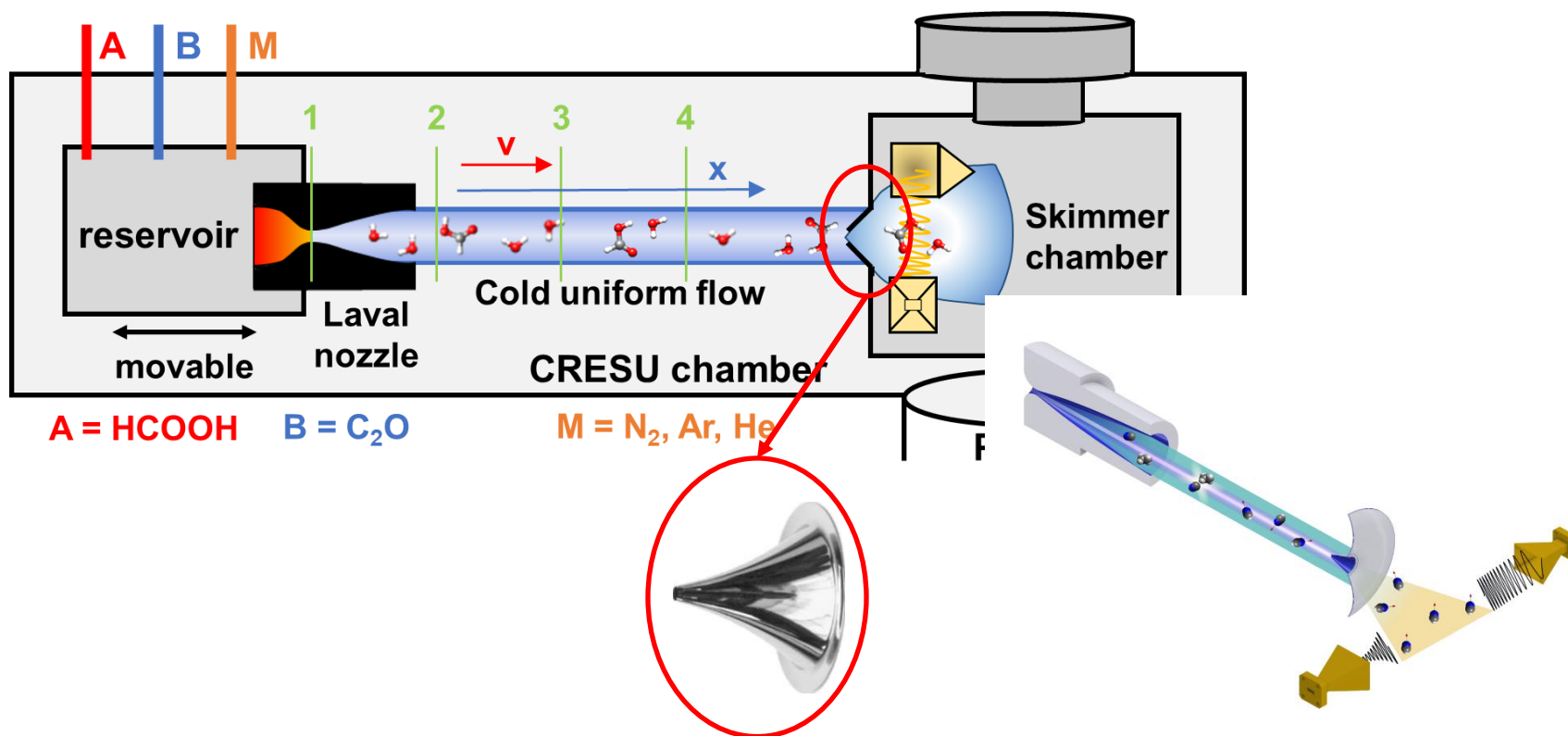
EXPERIMENTAL METHOD

↻ Acquisition procedure → Time dependence

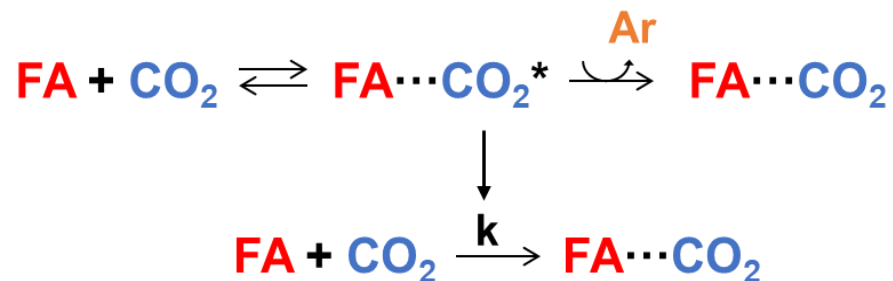


EXPERIMENTAL METHOD

Acquisition procedure → Importance of the skimmer chamber

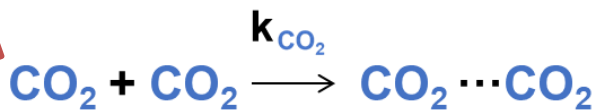


REACTION KINETICS



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

Avoid

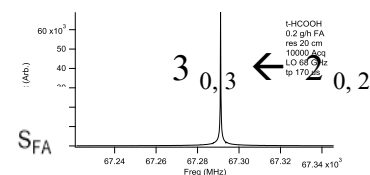
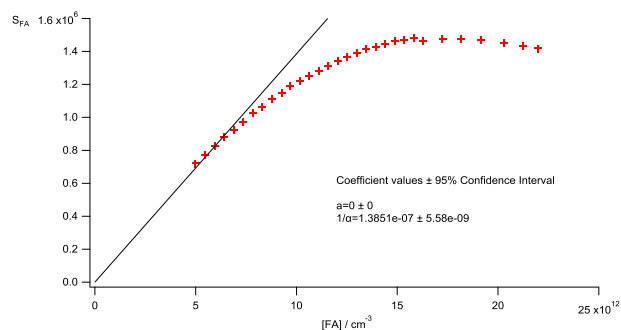
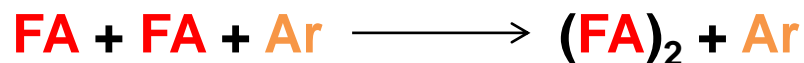


$$k \gg k_{\text{CO}_2}$$

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

PRELIMINARY RESULTS

☞ Formic acid homodimer formation → Termolecular reaction



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

PRELIMINARY RESULTS

Formic acid + CO₂ formation → Heterodimer formation reaction

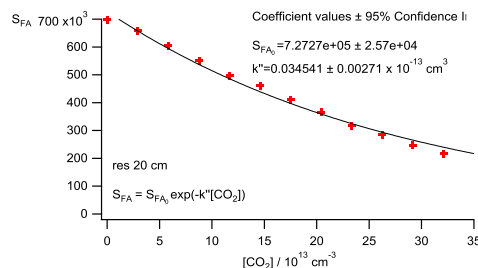


$$-\frac{d[\text{FA}]}{dt} = k'[\text{FA}][\text{CO}_2] \longrightarrow [\text{FA}]_t = [\text{FA}]_{t_0} \exp(-k't [\text{CO}_2])$$

$$k'' = k' t$$

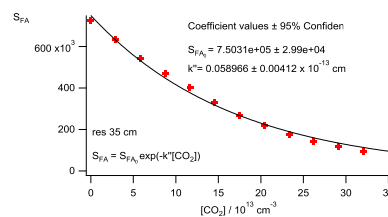
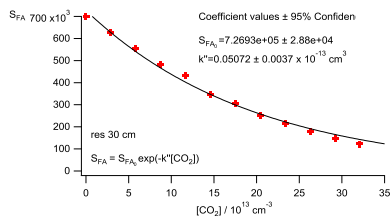
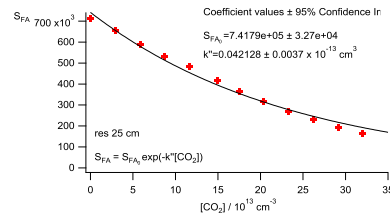
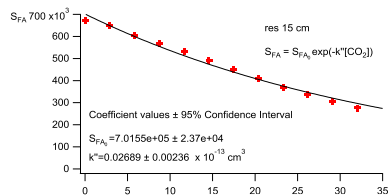
$$[\text{FA}]_t = [\text{FA}]_{t_0} \exp(-k'' [\text{CO}_2])$$

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



PRELIMINARY RESULTS

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

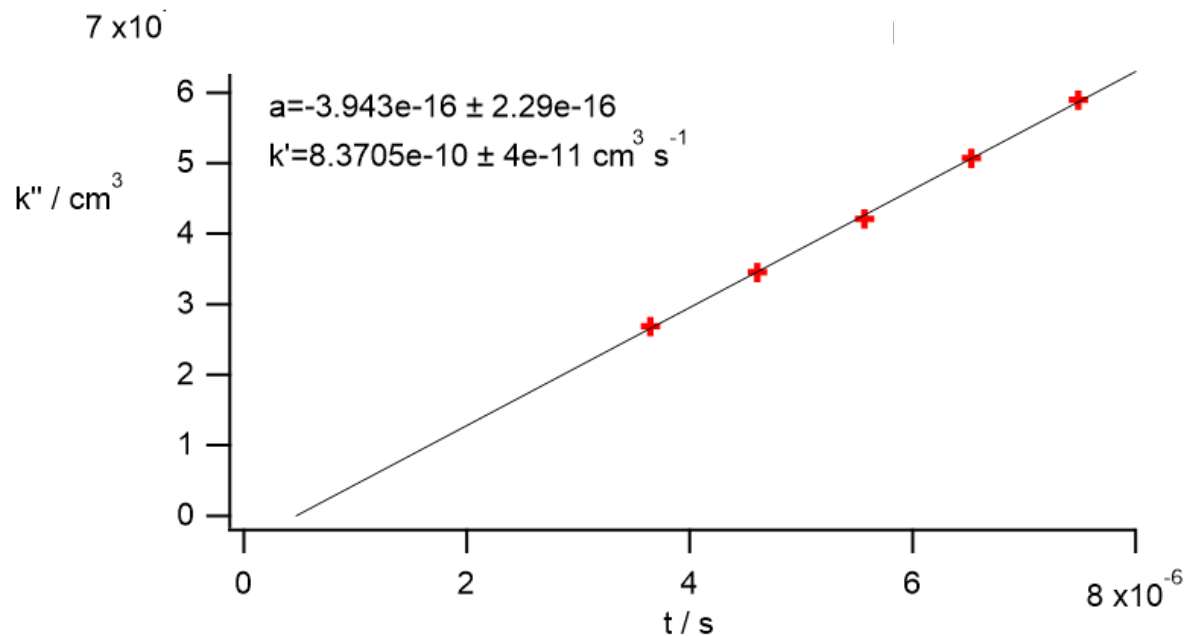


PRELIMINARY RESULTS

☞ Formic acid + CO₂ formation → Heterodimer formation reaction

$$k'' = k' t$$

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

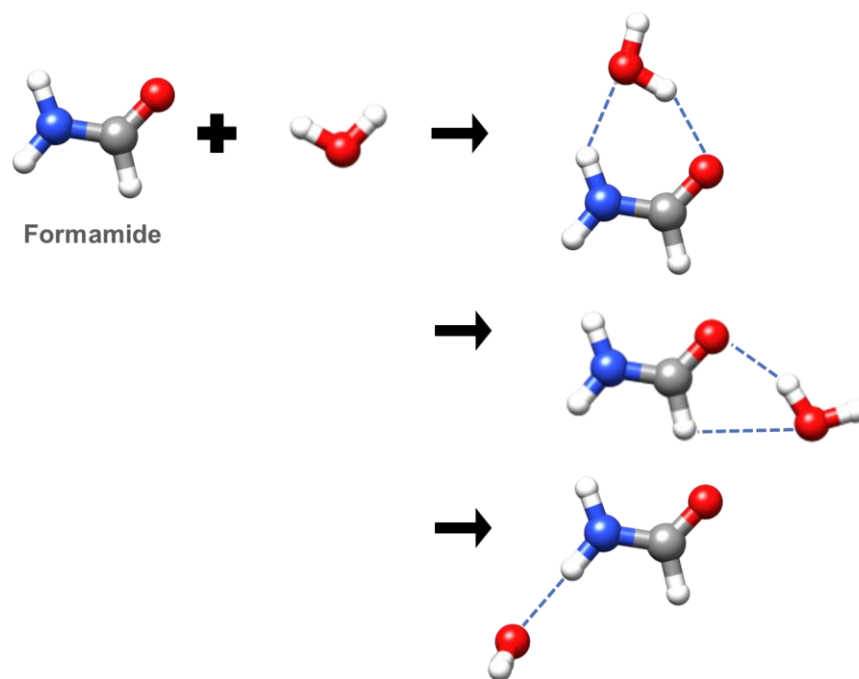
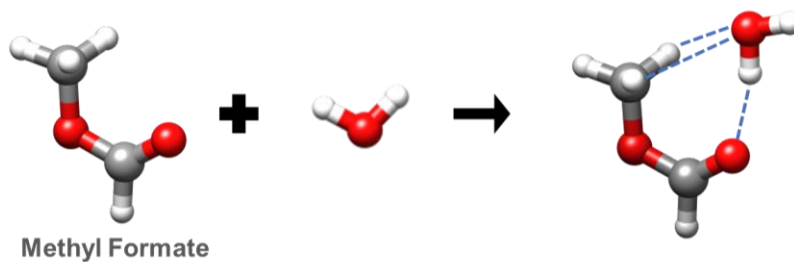
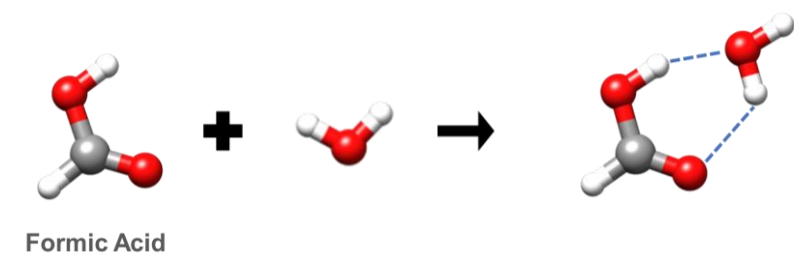


☞ First direct determination of a weakly bound heterodimer formation rate constant

CONCLUSIONS AND NEXT STEPS

- ↪ More measurements
- ↪ Change the temperature of the flow
- ↪ Change the buffer gas

PERSPECTIVES



ACKNOWLEDGEMENTS

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