CRIEGEE INTERMEDIATES REACTIONS WITH FORMIC ACID PROBED BY FTMW SPECTROSCOPY

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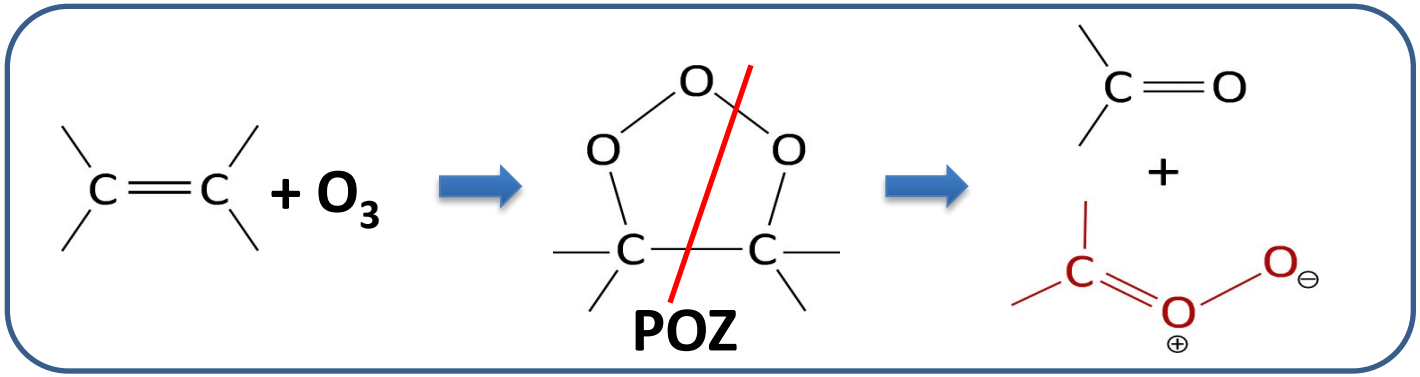
Criegee Intermediates

Ozonolysis process of alkenes was first proposed by Rudolf Criegee in 1949



Stabilized Criegee Intermediates (SCIs)

Bimolecular reactions with H_2O, NO_2, SO_2, themselves…

Unimolecular Dissociation, OH radical

Products with large molecular weights and low vapor pressures than the reactants

Secondary organic aerosols (SOA) formation

Criegee Intermediates and Carboxylic Acids

Reactions with organic acids have not been considered to be an important loss process for SCIs

Kinetic measurements. Rate coefficients for reactions of CH_2OO and CH_3CHOO with formic and acetic acids, Welz *et al.*

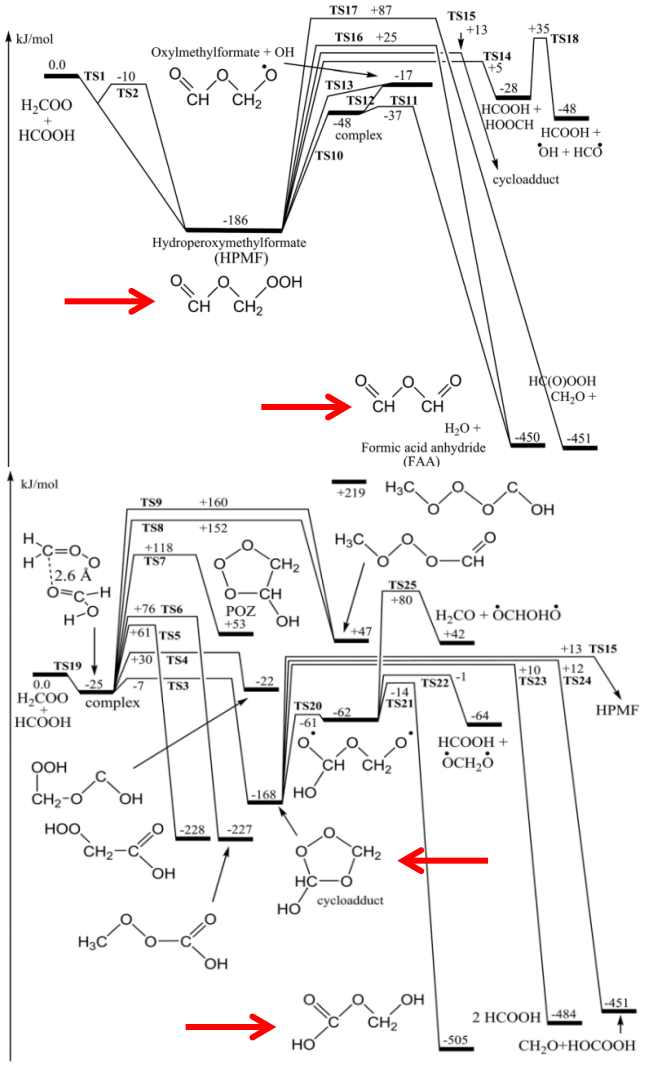
Suggest that reaction of carboxylic acids with SCIs can compete with unimolecular decay and reaction with water as key loss processes for SCIs removal

Previous studies

- **Theoretical calculations.** Reaction mechanisms for reactions of CH_2OO with several carboxylic acids. Aplincourt *et al.*, Long *et al.*, Vereecken *et al.*

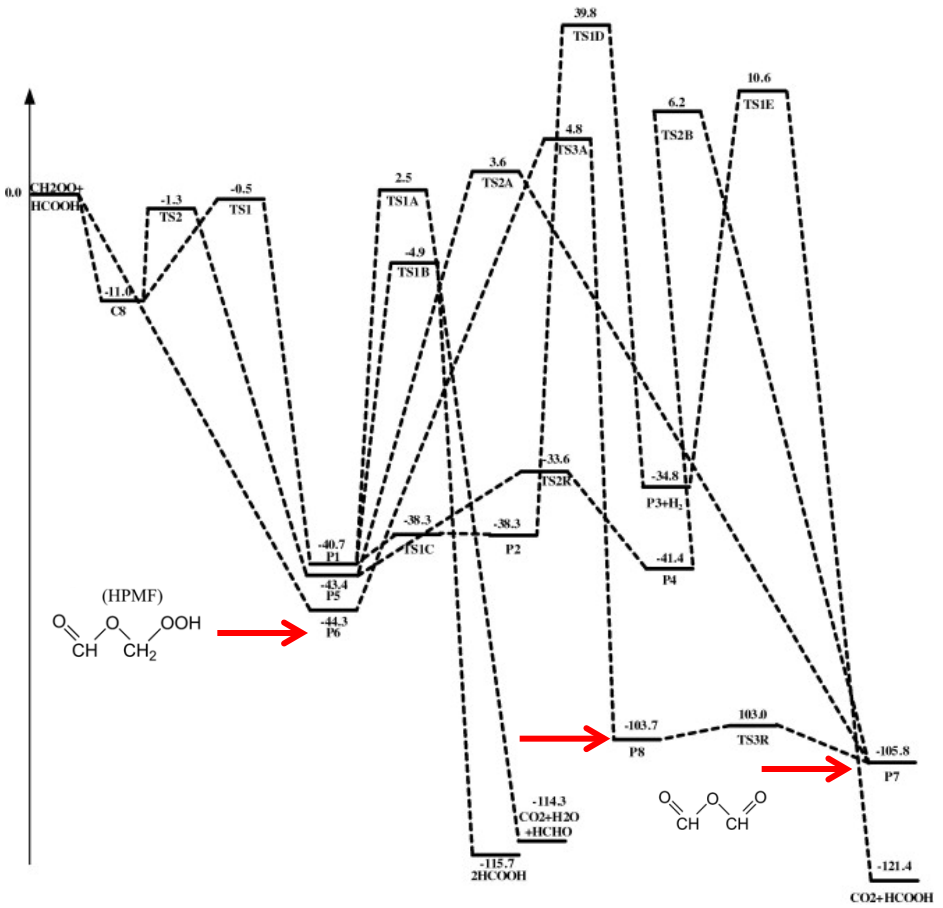
Welz *et al*. *Angew. Chem. Int. Ed.* **2014**, *53*, 4547−4550.
Aplincourt *et al*. *J. Phys. Chem. A* **2000**, *104*, 380–388.
Long *et al*. *THEOCHEM* **2009**, *916*, 159–167.
Vereecken *Phys. Chem. Chem. Phys.* **2017**, *19*, 28630–28640.

Theoretical Studies



CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ

Vereecken *Phys. Chem. Chem. Phys.* **2017**, *19*, 28630–28640



CCSD(T)/ 6-311++G(d,p)//B3LYP/ 6-311++G(d,p)

Long *et al*. *THEOCHEM* **2009**, *916*, 159–167

Criegee Intermediates Reaction with Carboxylic Acids

Reactions with organic acids have not been considered to be an important loss process for SCIs

Kinetic measurements. Rate coefficients for reactions of CH_2OO and CH_3CHOO with formic and acetic acids, Welz *et al.*

Suggest that reaction of carboxylic acids with SCIs can compete with unimolecular decay and reaction with water as key loss processes for SCIs removal

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- **Theoretical calculations.** Reaction mechanisms for reactions of CH_2OO with several carboxylic acids. Aplincourt *et al.*, Long *et al.*, Vereecken *et al.*
- **FTIR spectroscopy.** Ozonolysis of ethene and identification of the reaction products, **HPMF**. Neeb *et al.*

Welz *et al. Angew. Chem. Int. Ed.* **2014**, *53*, 4547−4550.
Aplincourt *et al. J. Phys. Chem. A* **2000**, *104*, 380–388.
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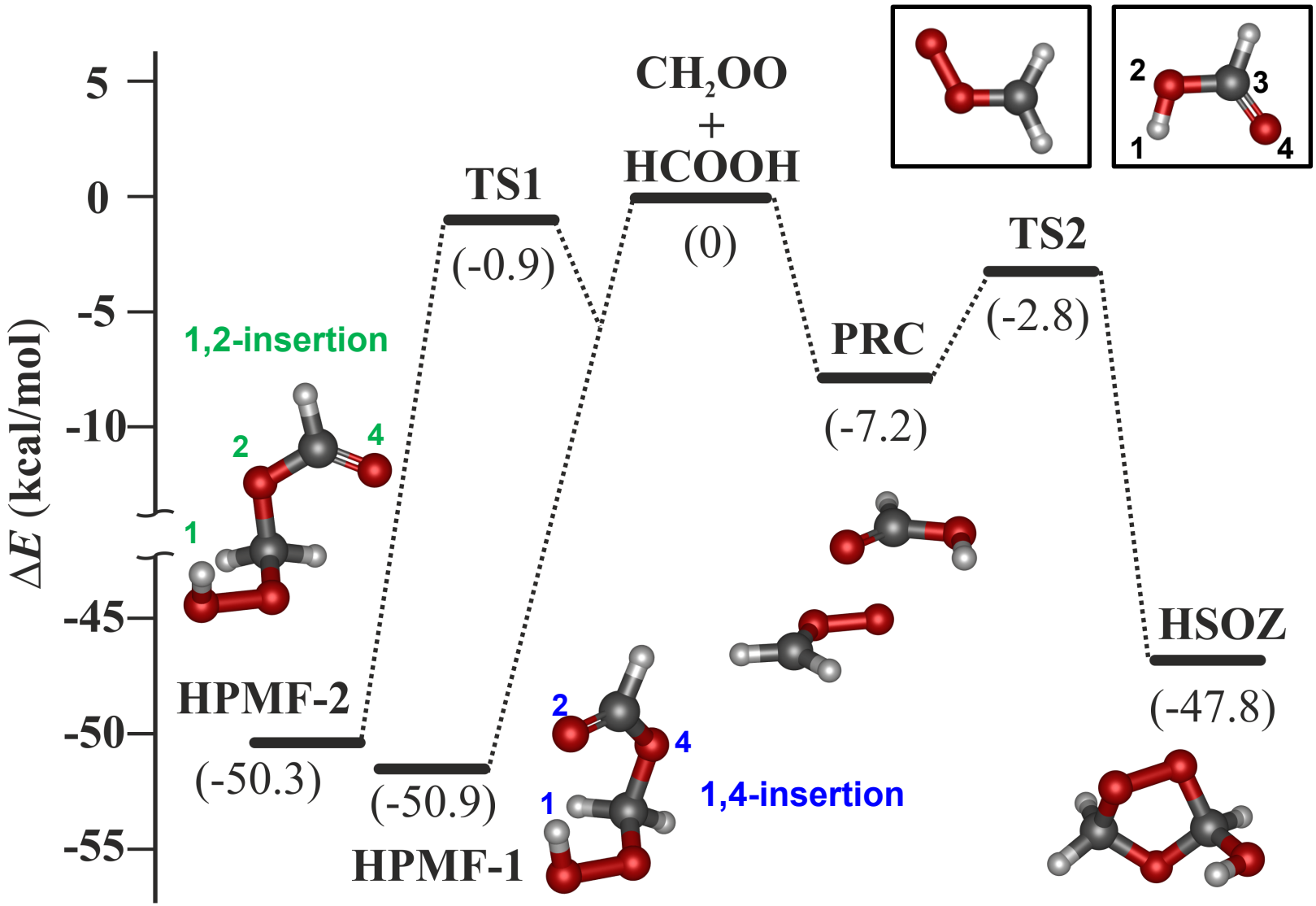
Vereecken *Phys. Chem. Chem. Phys.* **2017**, *19*, 28630–28640.
Neeb *et al.*, *Chem. Phys. Lett.* **1995**, *246*, 150–156 & *Int. J. Chem. Kinet.* **1996**, *28*, 721–730.

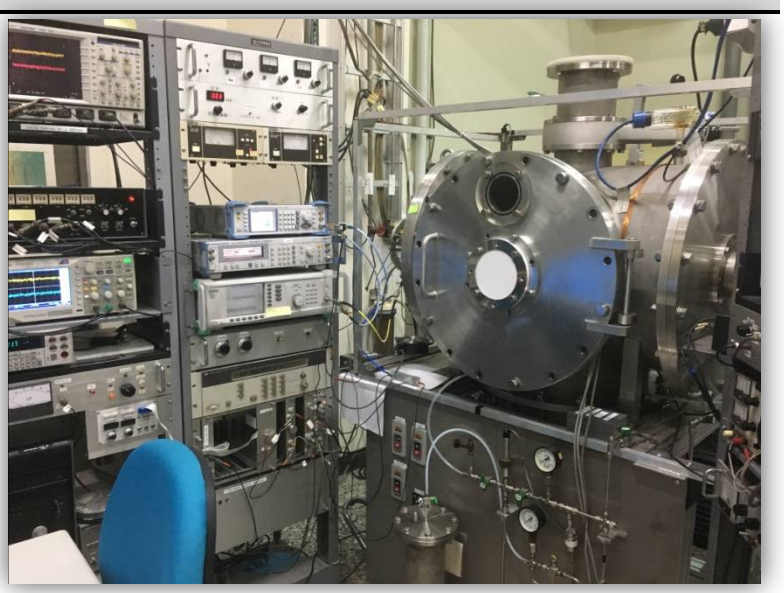
CH_2OO + HCOOH reaction



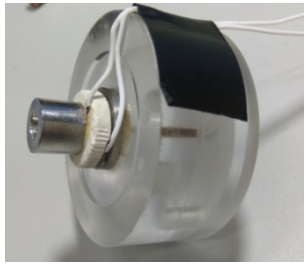
CCSD/aug-cc-pVTZ

Experimental

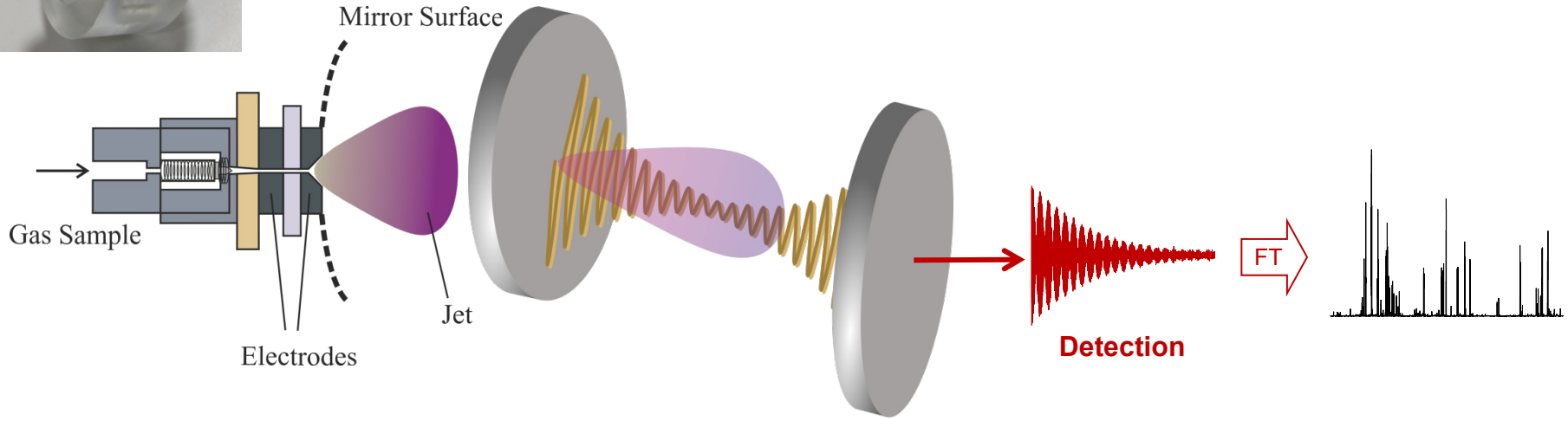
- 2% O_2 and 0.3% HCOOH diluted in Ar
- CH_2I_2 in a sample holder



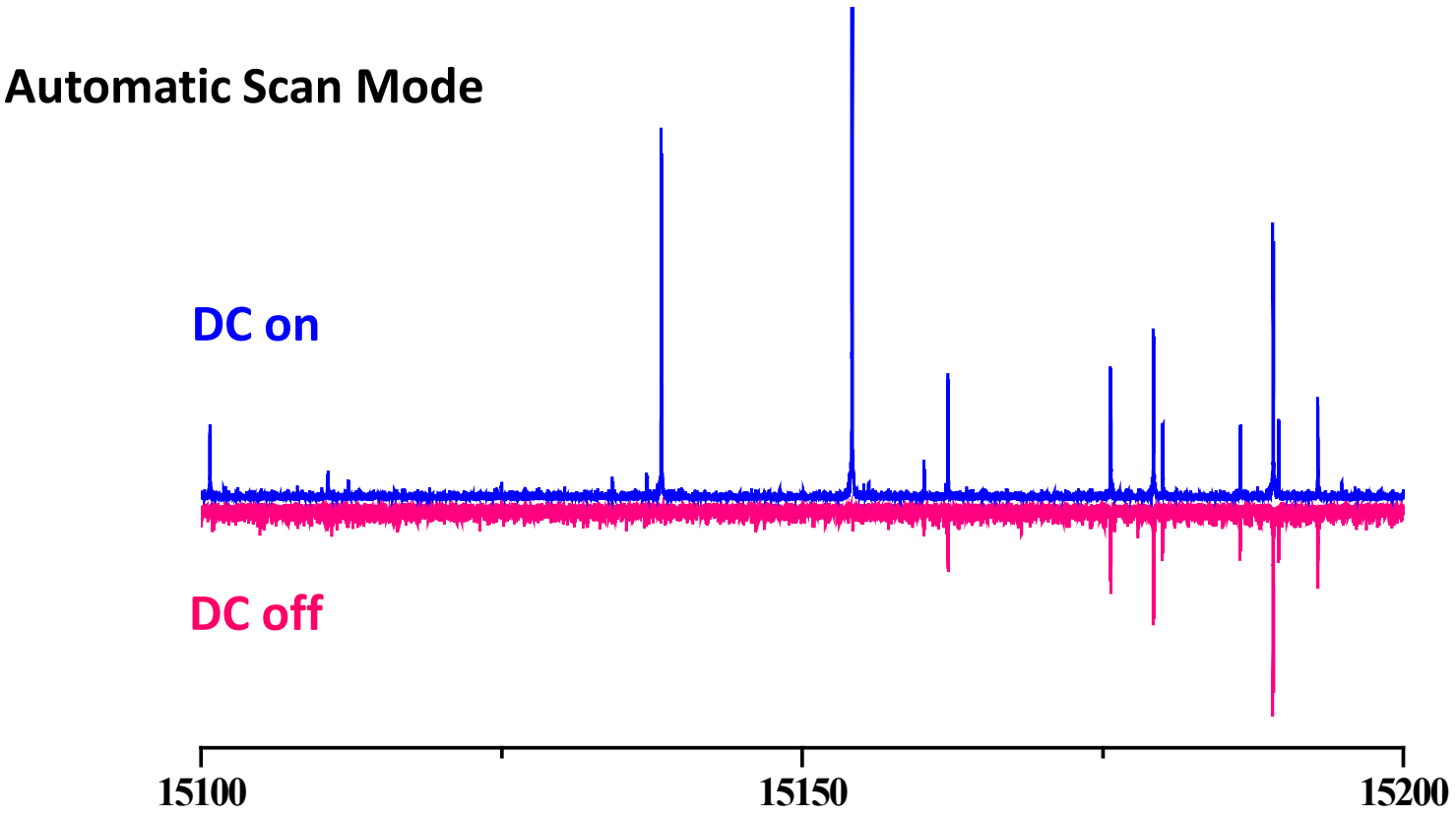
FTMW spectrometer 4 – 40 GHz



Pulsed discharge nozzle



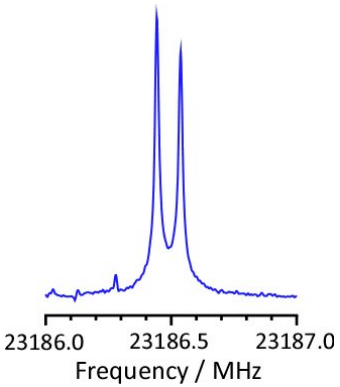
Experimental



- Frequency steps of 0.8-1 MHz
- Scan of 100 accumulation pulses; 1GHz ≈ 2h 45 min

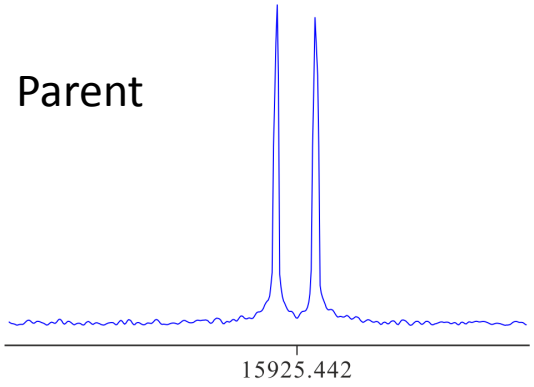
Rotational Spectrum

Strong signal of the 1_{01}–0_{00} pure rotational transition of CH_2OO was observed at 23186.49 MHz during the experiment, confirming an efficient production of CH_2OO



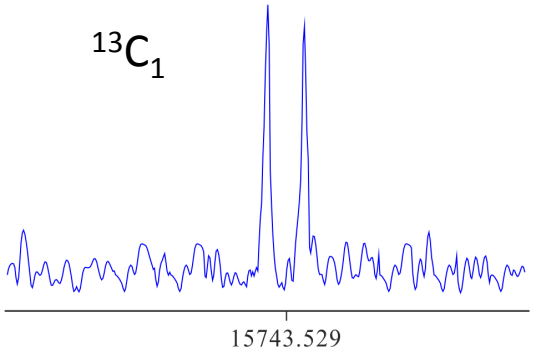
3_{03}-2_{02}

Parent



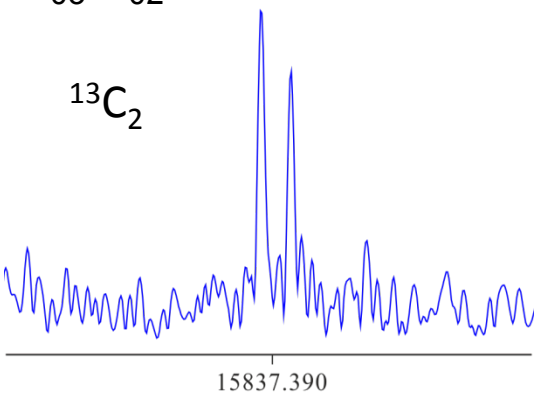
3_{03}-2_{02}

$^{13}C_1$



3_{03}-2_{02}

$^{13}C_2$

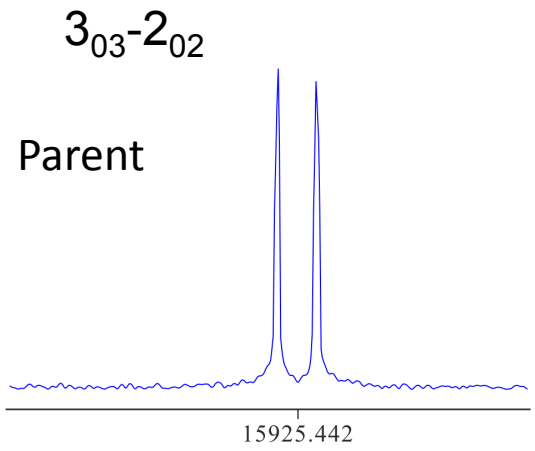


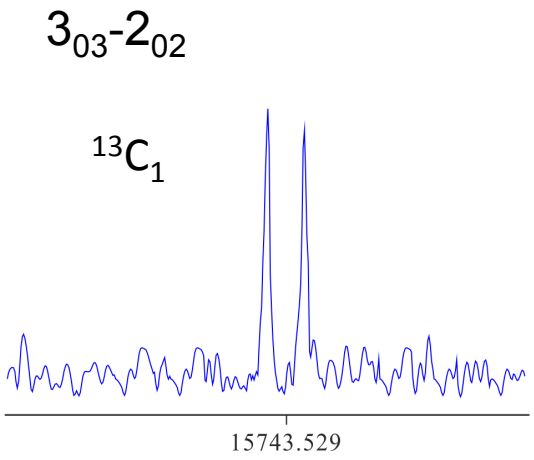
Rotational Spectrum

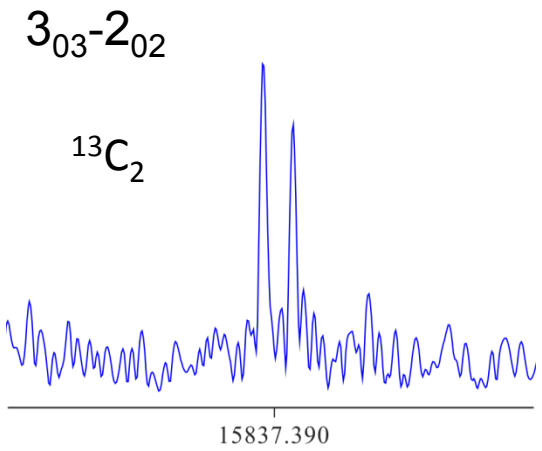
	HPMF-1	$^{13}C_1$-HPMF-1	$^{13}C_2$-HPMF-1
A /MHz	5927.30314 (34)	5924.3394 (15)	5842.1576 (15)
B /MHz	3333.24609 (17)	3280.04624 (38)	3325.84947 (34)
C /MHz	2288.75075 (14)	2263.49713 (22)	2275.95818 (22)
Δ_J /kHz	1.2903 (44)	1.2903[fix]	1.2903[fix]
Δ_{JK} /kHz	1.389 (27)	1.389[fix]	1.389[fix]
Δ_K /kHz	0.153 (69)	0.153[fix]	0.153[fix]
δ_J /kHz	0.4336 (18)	0.433[fix]	0.433[fix]
δ_K /kHz	2.727 (50)	2.727[fix]	2.727[fix]
N	31	6	7
σ /kHz	0.6	1.4	1.5

CCSD/aug-cc-pVTZ

	HPMF-1	HPMF-2
A /MHz	5996	9068
B /MHz	3364	2170
C /MHz	2314	2048
$\lvert\mu_a\rvert$/D	2.29	0.27
$\lvert\mu_b\rvert$/D	1.71	2.24
$\lvert\mu_c\rvert$/D	0.86	0.17





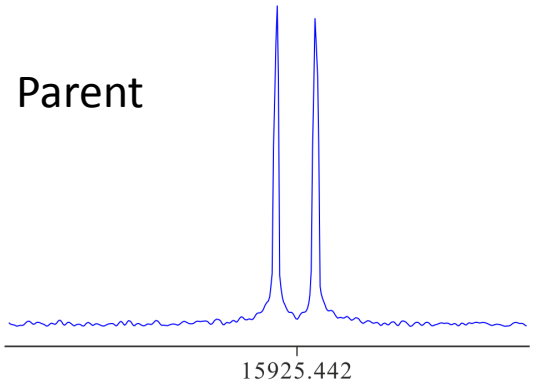


Rotational Spectrum

HPMF-1

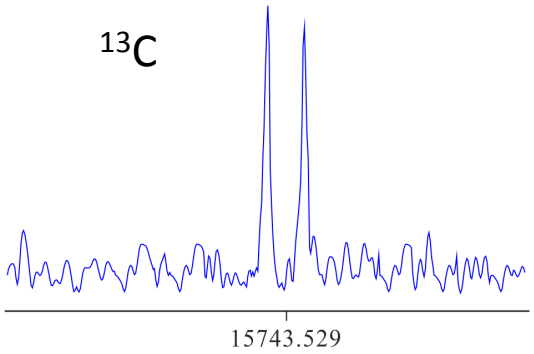
3_{03}-2_{02}

Parent



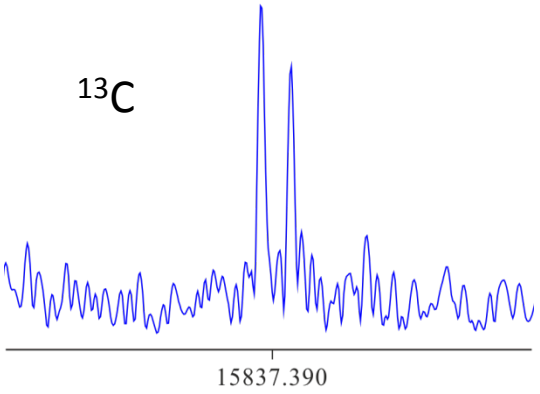
3_{03}-2_{02}

^{13}C



3_{03}-2_{02}

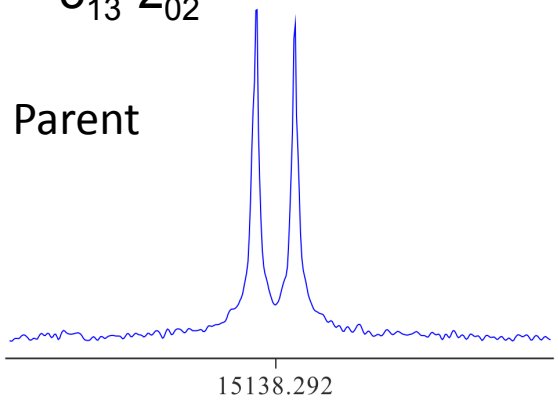
^{13}C



HPMF-2

3_{13}-2_{02}

Parent



- **HPMF-1/HPMF-2= 2.9/1**
- **For HPMF-2 no ^{13}C species were observed**

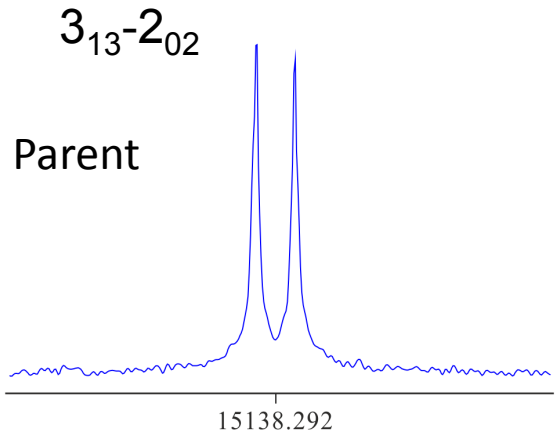
Rotational Spectrum

	HPMF-1	HPMF-2
A /MHz	5927.30314 (34)	9071.46988 (34)
B /MHz	3333.24609 (17)	2142.16573 (17)
C /MHz	2288.75075 (14)	2022.31566 (14)
Δ_J /kHz	1.2903 (44)	3.0491 (14)
Δ_{JK} /kHz	1.389 (27)	-43.680 (11)
Δ_K /kHz	0.153 (69)	204.381 (89)
δ_J /kHz	0.4336 (18)	-13.95 (35)
δ_K /kHz	2.727 (50)	-0.0181 (13)
N	31	29
σ /kHz	0.6	0.8

CCSD/aug-cc-pVTZ

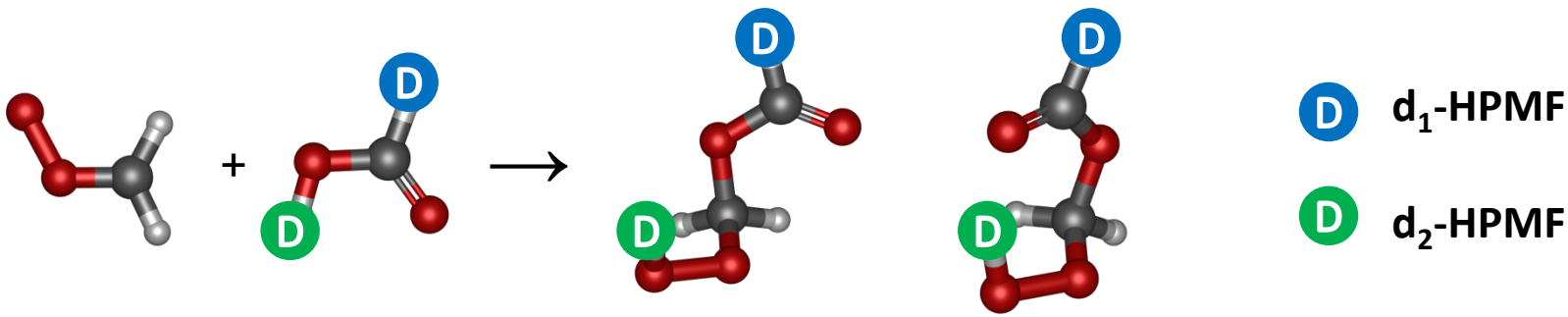
	HPMF-1	HPMF-2
A /MHz	5996	9068
B /MHz	3364	2170
C /MHz	2314	2048
$\lvert\mu_a\rvert$/D	2.29	0.27
$\lvert\mu_b\rvert$/D	1.71	2.24
$\lvert\mu_c\rvert$/D	0.86	0.17

HPMF-2



- **HPMF-1/HPMF-2= 2.9/1**
  In agreement with our calculations
- **For HPMF-2 no ^{13}C species were observed**

Isotopic Substitution



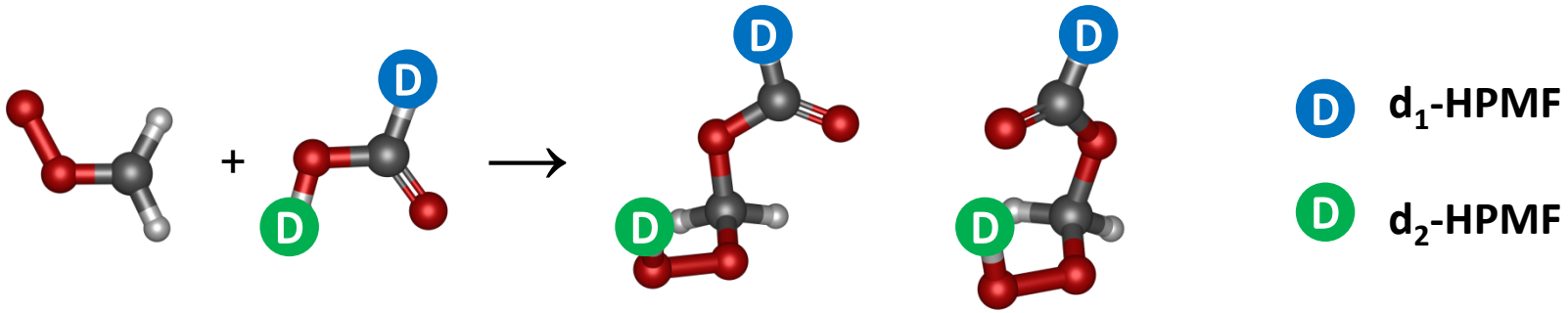
Experimental results confirm HPMF as the nascent product of the CH_2OO + HCOOH reaction:

• HPMF rotational transitions disappear in absence of electric discharge

• The lines disappear when any of the reactants (CH_2I_2, O_2 or HCOOH) is removed from the gas mixture

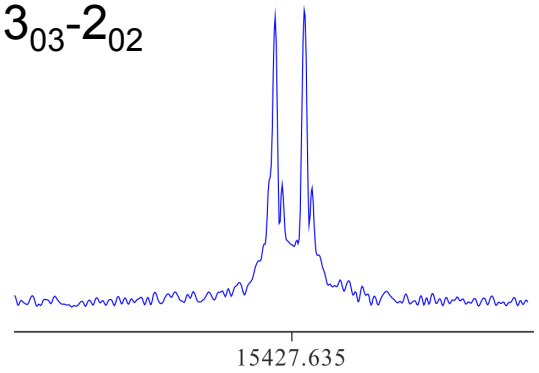
•Isotopic substitution experiments

Isotopic Substitution



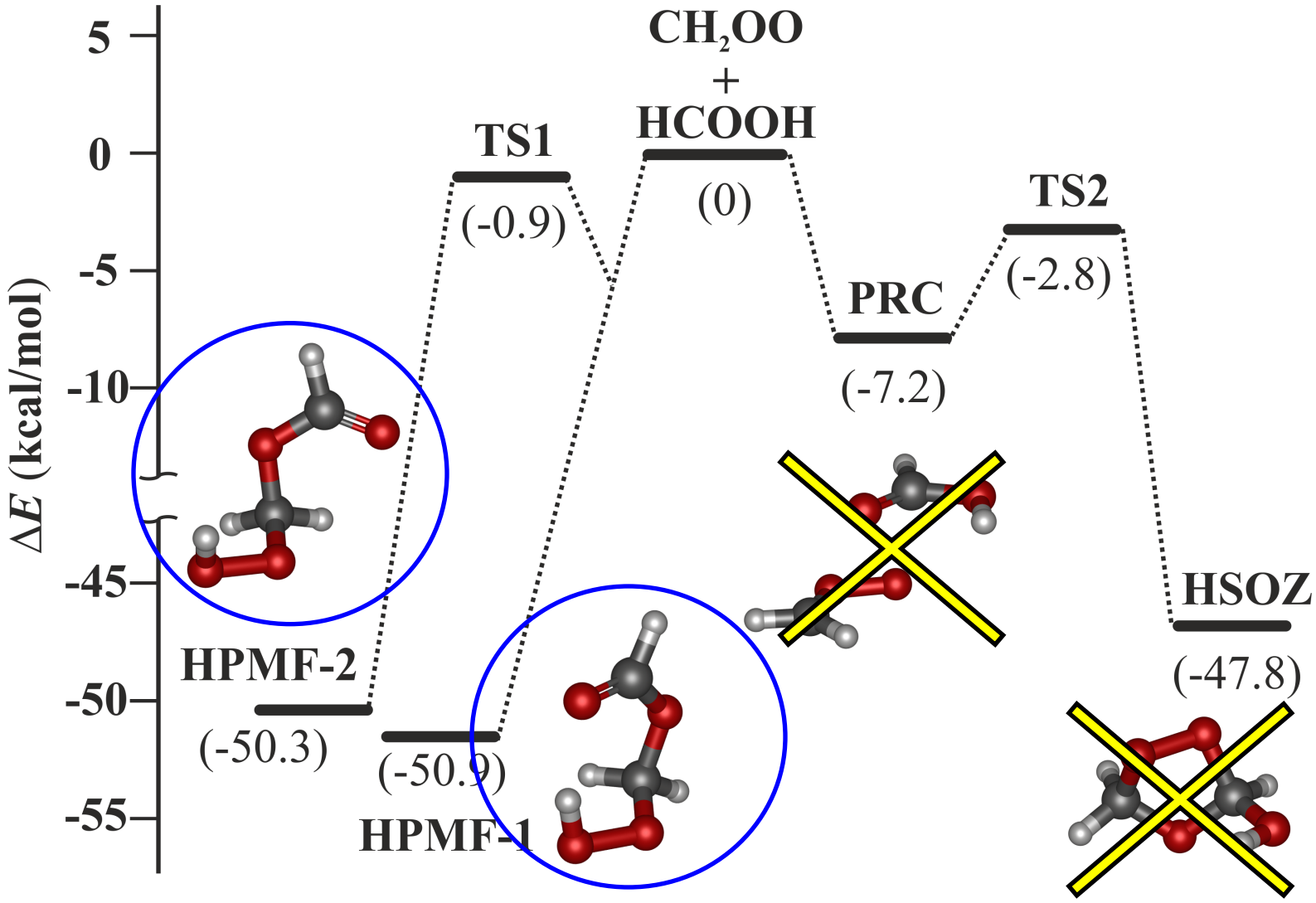
d_1-HPMF-1

3_{03}-2_{02}

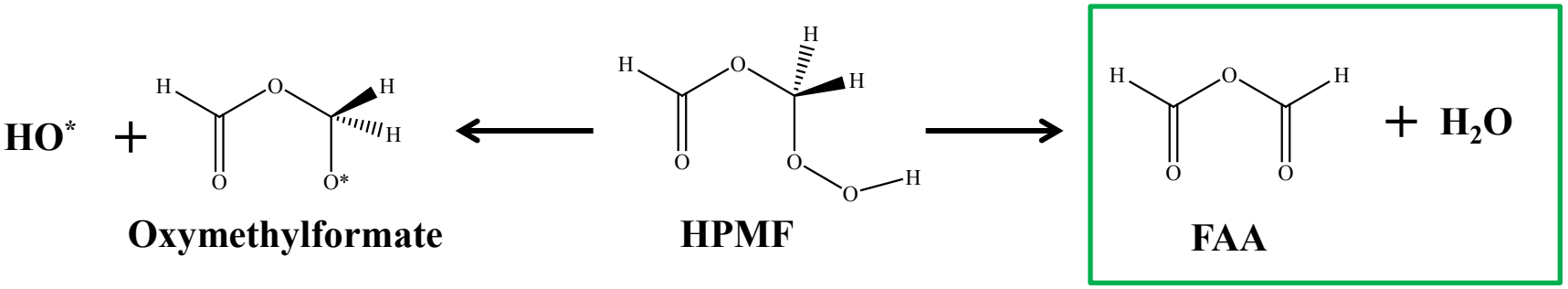


	d_1-HPMF-1	d_2-HPMF-1	d_1-HPMF-2	d_2-HPMF-2
A /MHz	5912.6540 (15)	5800.6058 (18)	8740.6441 (17)	8799.3473 (44)
B /MHz	3187.40460 (42)	3323.20478 (42)	2094.99127 (44)	2093.9678 (12)
C /MHz	2220.90246 (55)	2264.70487 (48)	1972.77876 (53)	1989.3366 (21)
Δ_J /kHz	1.182 (18)	1.278 (14)	2.754 (11)	3.402 (58)
Δ_{JK} /kHz	1.389[fix]	1.389[fix]	-37.55 (20)	-43.680[fix]
Δ_K /kHz	0.153[fix]	0.153[fix]	204.381[fix]	204.381[fix]
δ_J /kHz	0.433[fix]	0.433[fix]	-13.95[fix]	-13.95[fix]
δ_K /kHz	2.727[fix]	2.727[fix]	-0.0181[fix]	-0.0181[fix]
χ_{aa} /MHz	0.1409 (52)	0.1197 (40)	-0.0133 (20)	-0.221 (15)
χ_{bb} /MHz	-0.0598 (72)	-0.0133 (51)	0.0723 (73)	-0.0548 (59)
N	37	29	21	21
σ /kHz	4.3	3.0	2.9	3.8

CH_2OO + HCOOH reaction

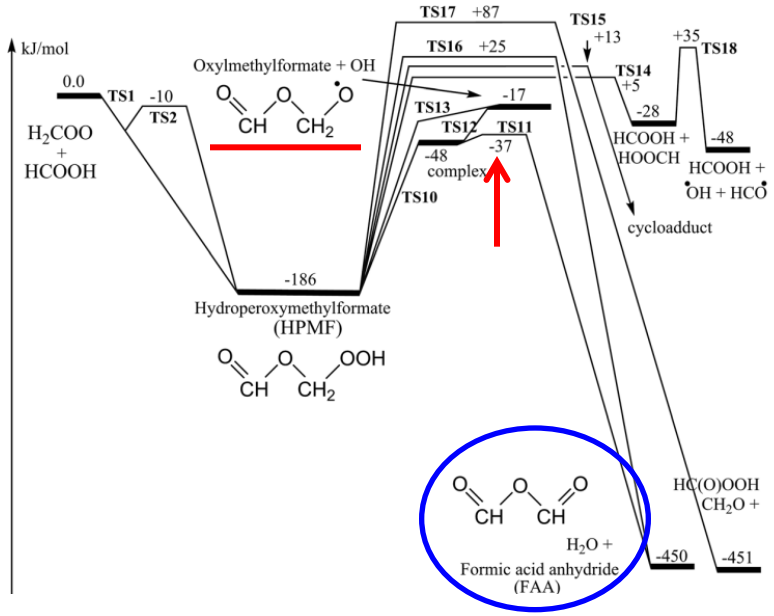


Stability of HPMF



HPMF undergoes dehydration to yield formic acid anhydride (FAA)

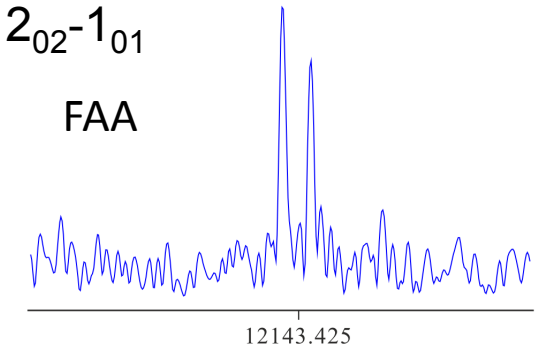
- **FTIR spectroscopy reported by Neeb *et al.*** (Chem. Phys. Lett. 1995, 246, 150)
- **Theoretical calculations**

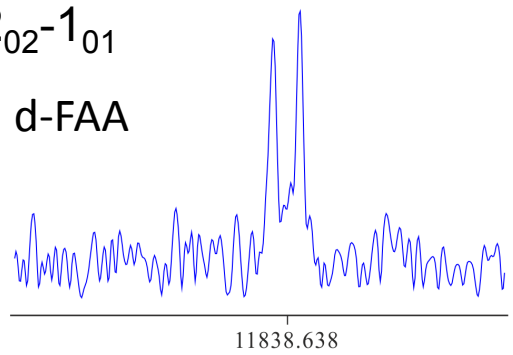


FAA is formed through a TS submerged below the reactants by 37 kJ/mol

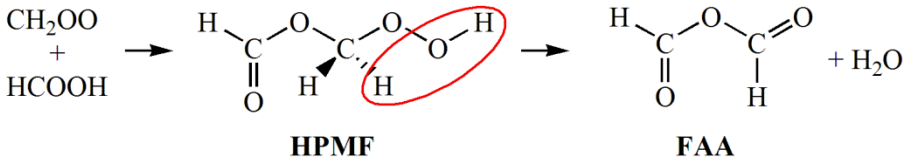
Vereecken *Phys. Chem. Chem. Phys.* **2017**, *19*, 28630–28640

Stability of HPMF

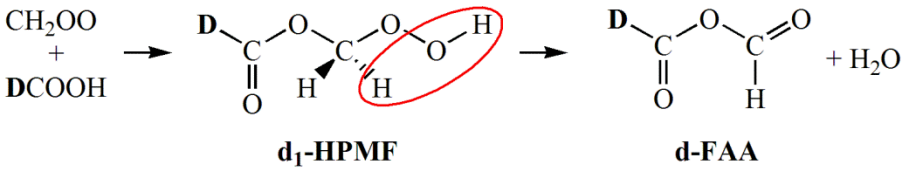




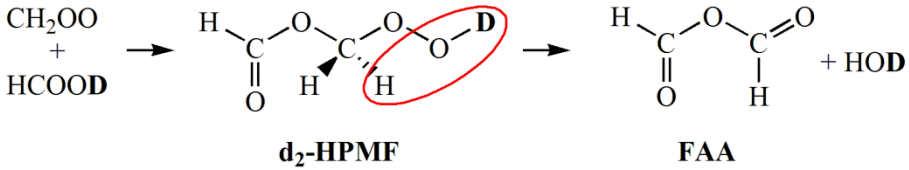
HPMF/FAA= 15/1 → HPMF seems to be very stable



FAA observed



Only d-FAA observed



Only FAA observed

Summary

• High resolution rotational spectroscopy has been used to study the reaction between formic acid and the simplest Criegee intermediate.

• The nascent product has been identified as hydroperoxymethyl formate, HPMF, for which two different conformers have been identified.

• The isotopic substitution experiments indicate that HPMF seems to be a stable product, but a small portion dehydrates to form formic anhydride, FAA

Thanks for listening