Detection and Reactivity of Short-lived Species in the Atmosphere— Criegee Intermediate as an Example

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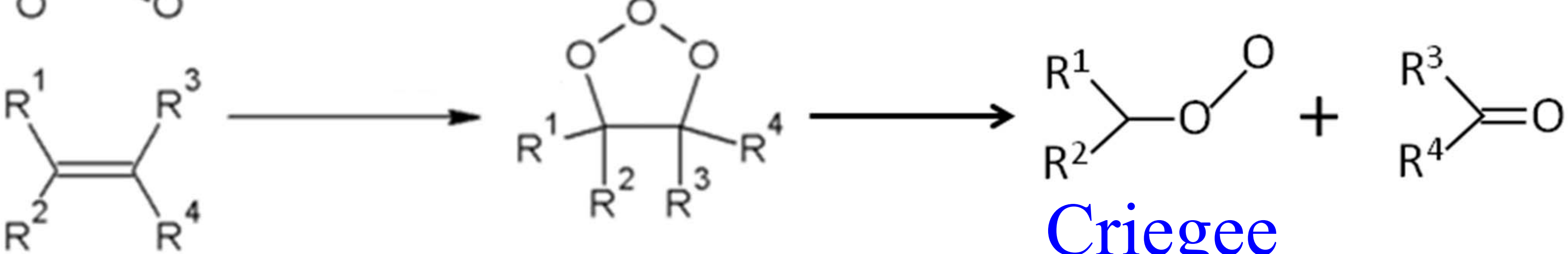
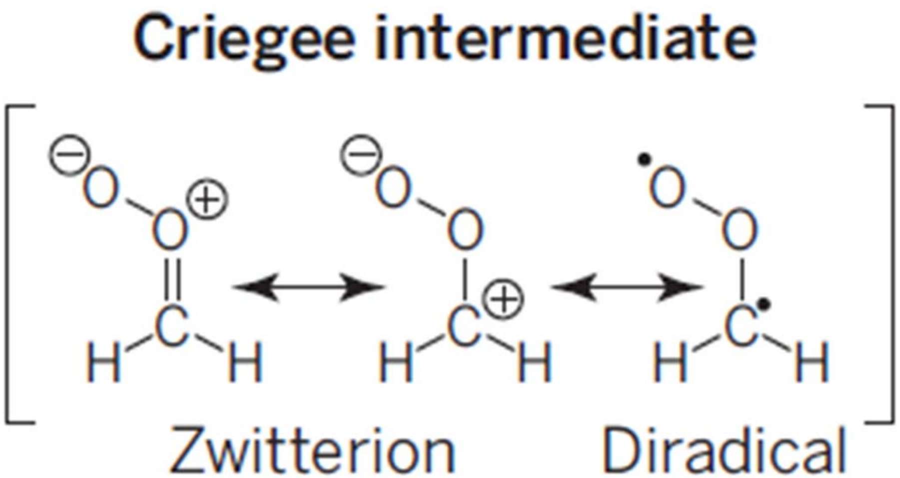
What are Criegee Intermediates?

Rudolf Criegee
1902 – 1975

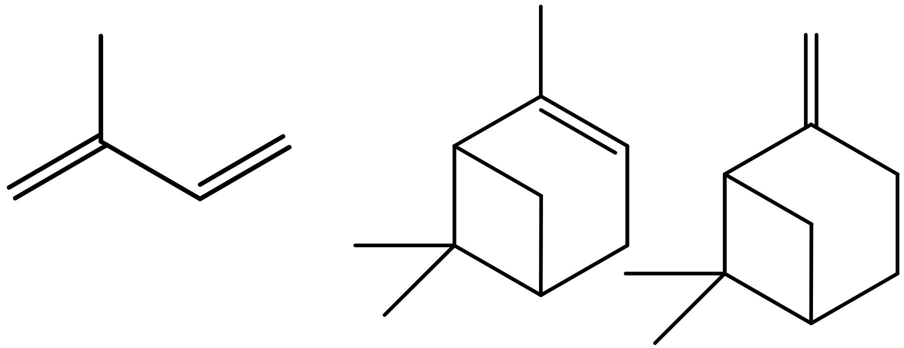


Criegee
Intermediate
(CI)



ethene, propene,

isoprene, limonene, ***pinene***, ···

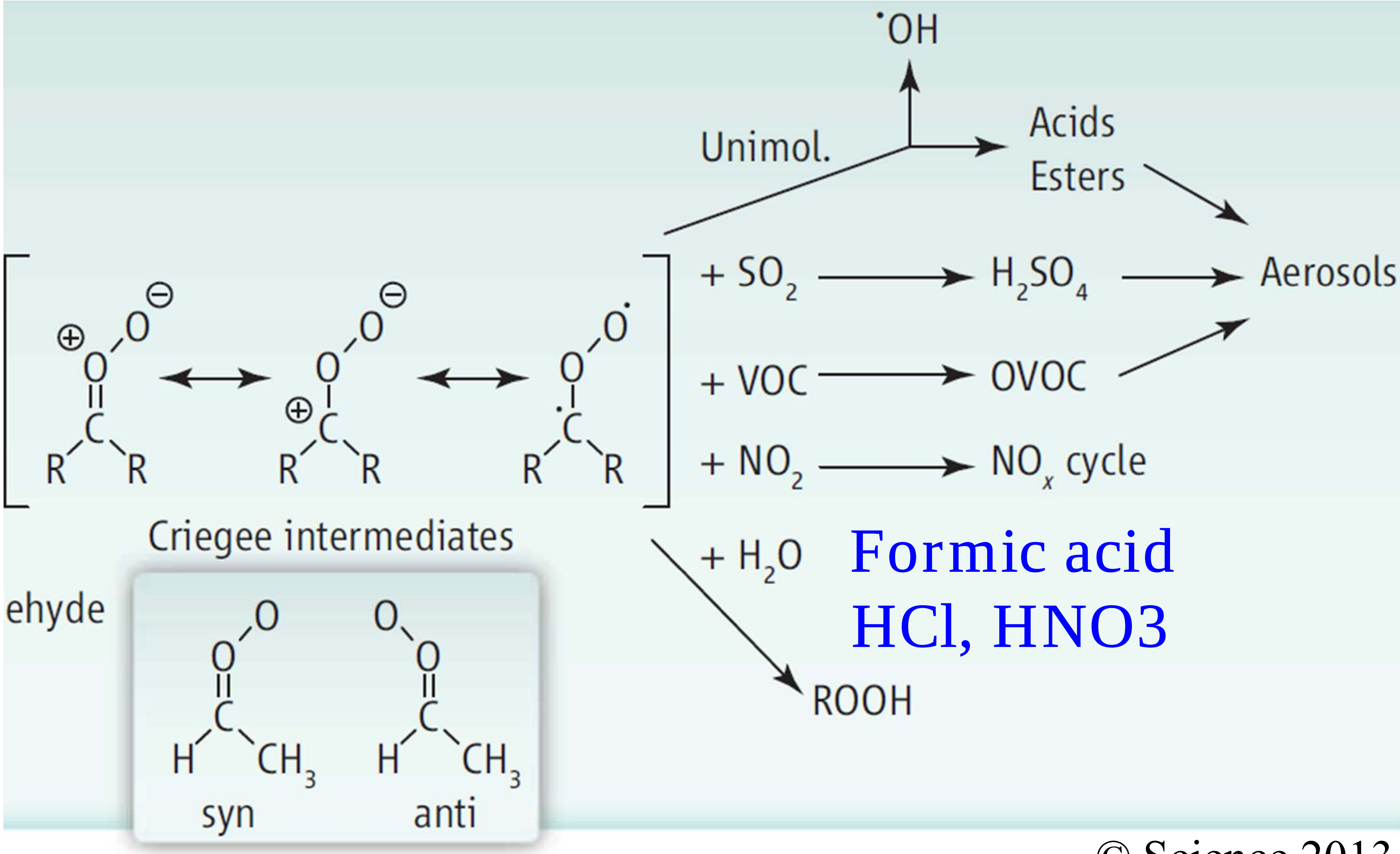


O_3 + Alkenes

↓

Criegee Intermediates

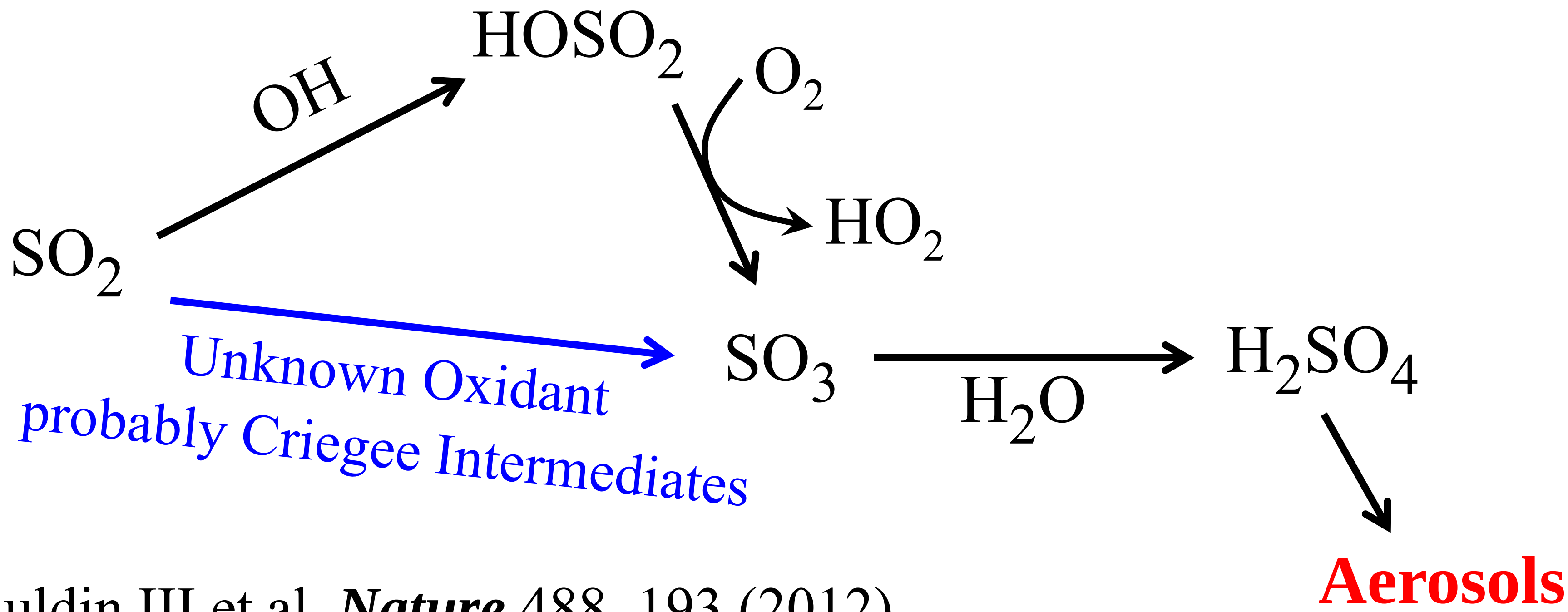
Criegee Intermediates are important.



Formic acid

HCl, HNO3

Criegee Intermediates are important.



Mauldin III et al. ***Nature*** 488, 193 (2012)

$[H_2SO_4]_{model} < [H_2SO_4]_{observed}$

The Simplest Criegee Intermediate CH_2OO

Direct Kinetic Measurements of Criegee Intermediate (CH_2OO) Formed by Reaction of CH_2I with O_2
Oliver Welz *et al.*
Science **335**, 204 (2012);

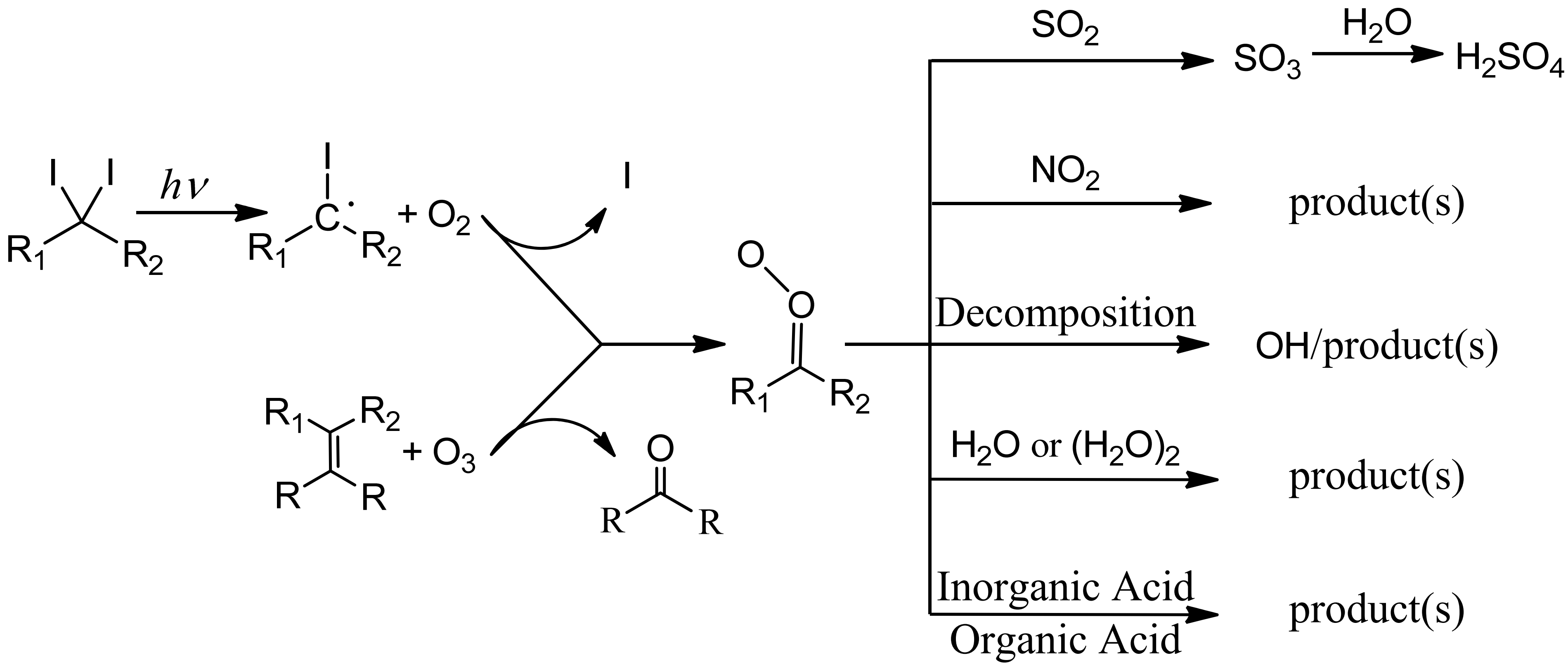
Science AAAS

$$CH_2I_2 + h\nu \rightarrow CH_2I + I$$

Taatjes group
Time-resolved
PI-MS

$$CH_2I + O_2 \rightarrow CH_2OO + I$$

$$\left.\begin{array}{l} CH_2OO + SO_2 \rightarrow \text{Prod.} \\ CH_2OO + NO_2 \rightarrow \text{Prod.} \end{array}\right\} \text{faster than previously thought}$$



I
I
hν
R1
R2
C
+ O2
I
O
O
R1
R2
R1
R2
R
R
+ O3
O
R
R
SO2
SO3
H2O
H2SO4
NO2
product(s)
Decomposition
OH/product(s)
H2O or (H2O)2
product(s)
Inorganic Acid
Organic Acid
product(s)

Steady-state approximation for

$$O_3 + \text{Alkene} \rightarrow \text{CI} + \text{Carbonyl}$$

$$\frac{d[\text{CI}]}{dt} = k_{\text{ozo}}\phi_{\text{CI}}[\text{O}_3][\text{alkene}] - k_{\text{decay}}[\text{CI}] \cong 0$$

$$[\text{CI}]_{\text{ss}} = \frac{k_{\text{ozo}}\phi_{\text{CI}}[\text{O}_3][\text{alkene}]}{k_{\text{decay}}}$$

(small)

(large)

$$k_{\text{decay}} \cong k_{\text{th}} + k_{\text{O3}}[\text{O}_3] + k_{\text{ene}}[alkene] + 2k_{\text{self}}[\text{CI}] + \cdots$$

$CH_2I_2 + h\nu \rightarrow CH_2I + I$ (10 ns)

$CH_2I + O_2 \rightarrow CH_2OO + I$ (1~10 us)

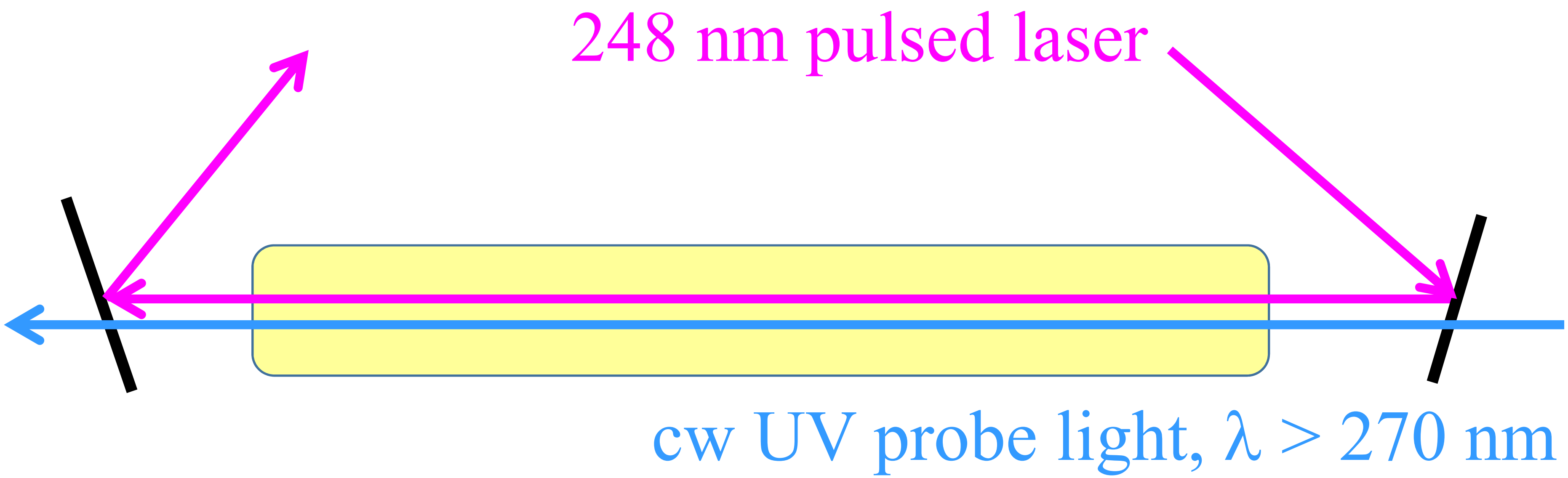
$CH_2I+O_2+M \rightarrow ICH_2OO+M$ (high pressure)

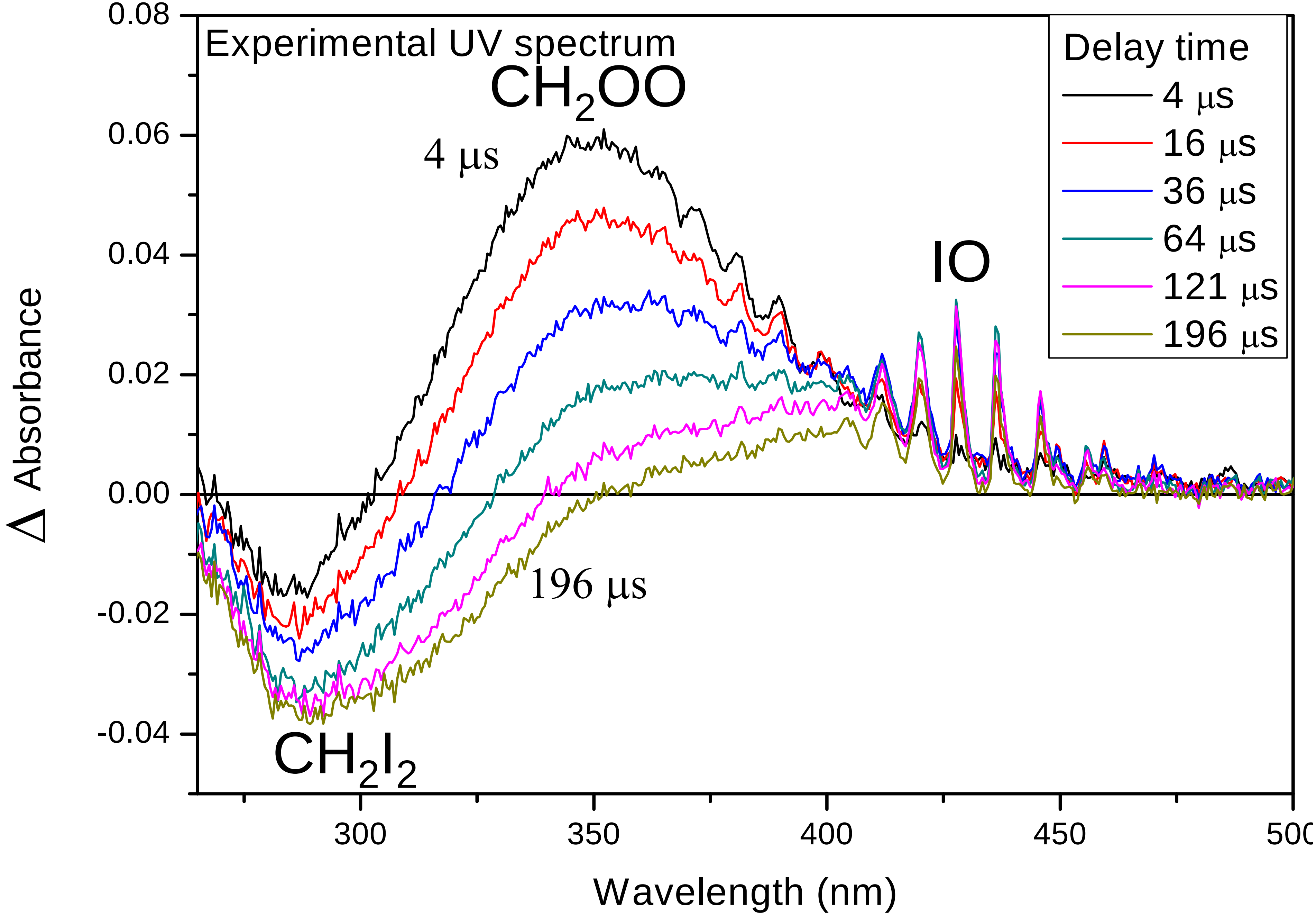
$CH_2OO + I \rightarrow H_2CO + IO$ (>100 us, depends)

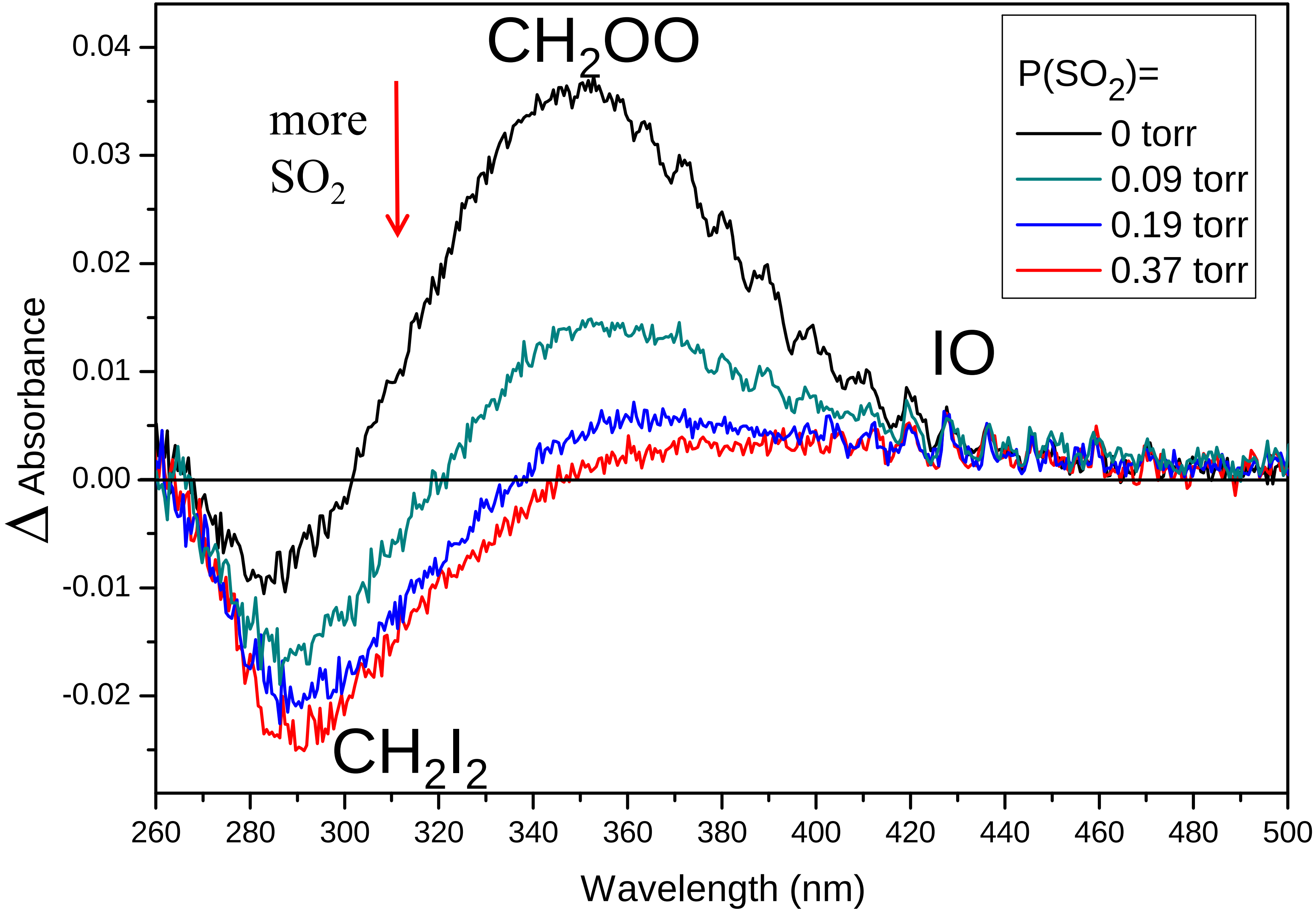
$2CH_2OO \rightarrow O_2 + 2H_2CO$ (>100 us, depends)

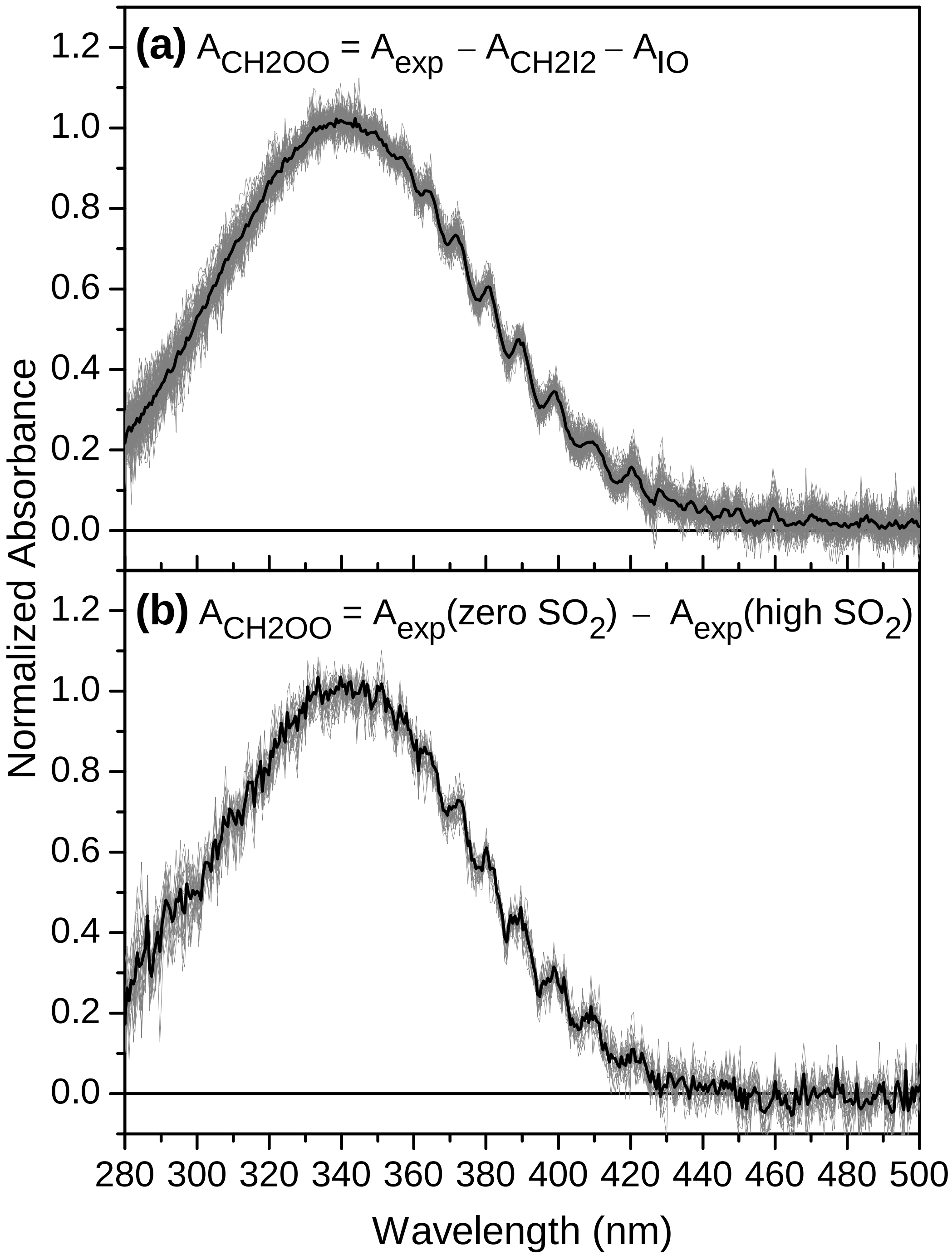
Ting, YP Lee, Lin, & coworkers, JCP, 141, 104308 (2014).

IAMS group, Time-resolved UV-Abs




Experimental UV spectrum
CH2OO
4 μs
IO
196 μs
CH2I2
Delay time
4 μs
16 μs
36 μs
64 μs
121 μs
196 μs
Δ Absorbance
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
300
350
400
450
500
Wavelength (nm)

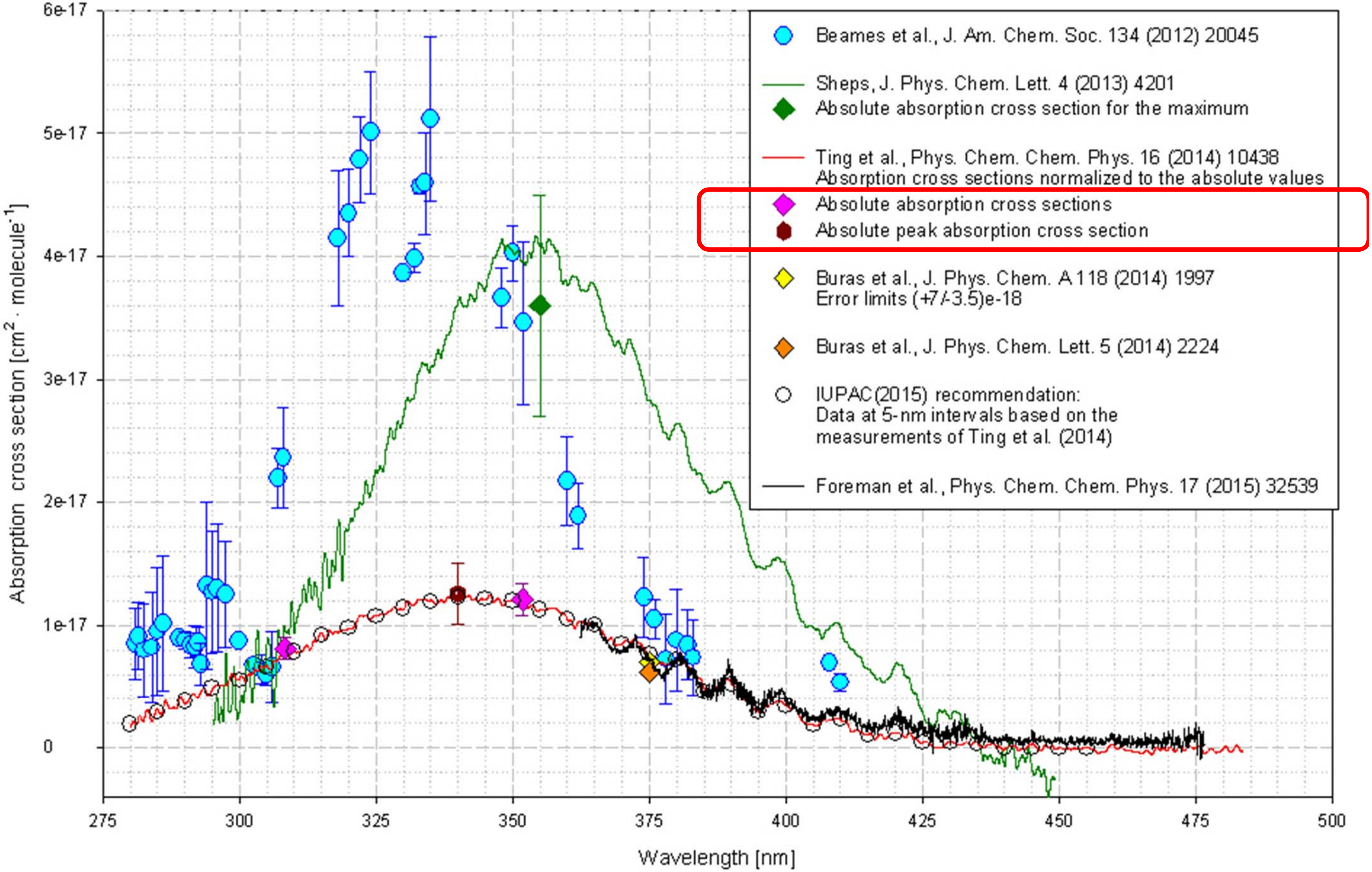

CH2OO
more SO2
P(SO2)=
0 torr
0.09 torr
0.19 torr
0.37 torr
IO
CH2I2
Δ Absorbance
Wavelength (nm)
0.04
0.03
0.02
0.01
0.00
-0.01
-0.02
260
280
300
320
340
360
380
400
420
440
460
480
500



99 curves

24 curves

MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest



Absorption cross sections of the Criegee biradical intermediate CH_2OO (formaldehyde oxide) at room temperature

How to measure the <u>absorption cross section σ</u> without knowing the <u>number density n</u>?

$$Abs = \ln\frac{I_0}{I} = \sigma\, n\, L \cong \frac{-\Delta I}{I_0}$$

Beer-Lambert Law, assuming # of Molecules >> # of Photons

- σ: in cm^2
- n: in $molecule/cm^3$
- L: in cm

Measure: I/I_0

How to know L? by a ruler

How to know n? by using $PV = n\,k\,T$

What if you don't know *P*

What if # of Photons >> # of Molecules N, and if absorption leads to dissociation

$$Dep = \ln\frac{N_0}{N} = \sigma F \cong \frac{-\Delta N}{N_0}$$

σ: in cm^2

F: in $photon/cm^2$ (Pulsed Laser)

# of Molecules >> # of Photons

$$\sigma n L \cong \frac{-\Delta I}{I_0}$$

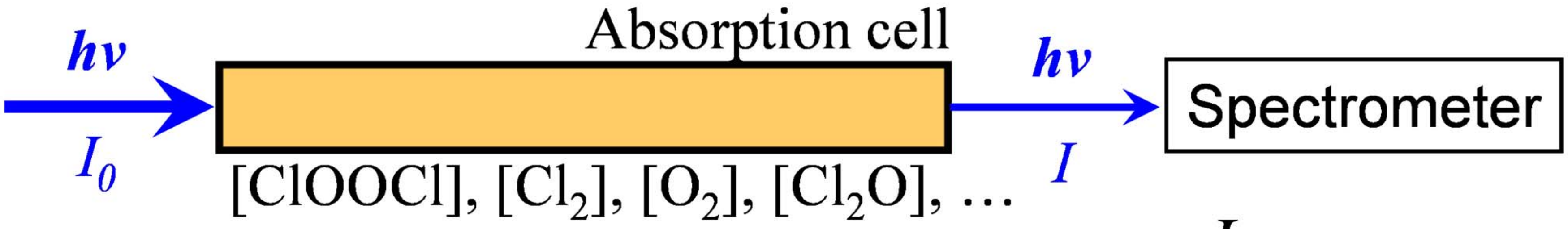
σ: in cm^2

n: in $molecule/cm^3$

L: in cm

Conventional Method

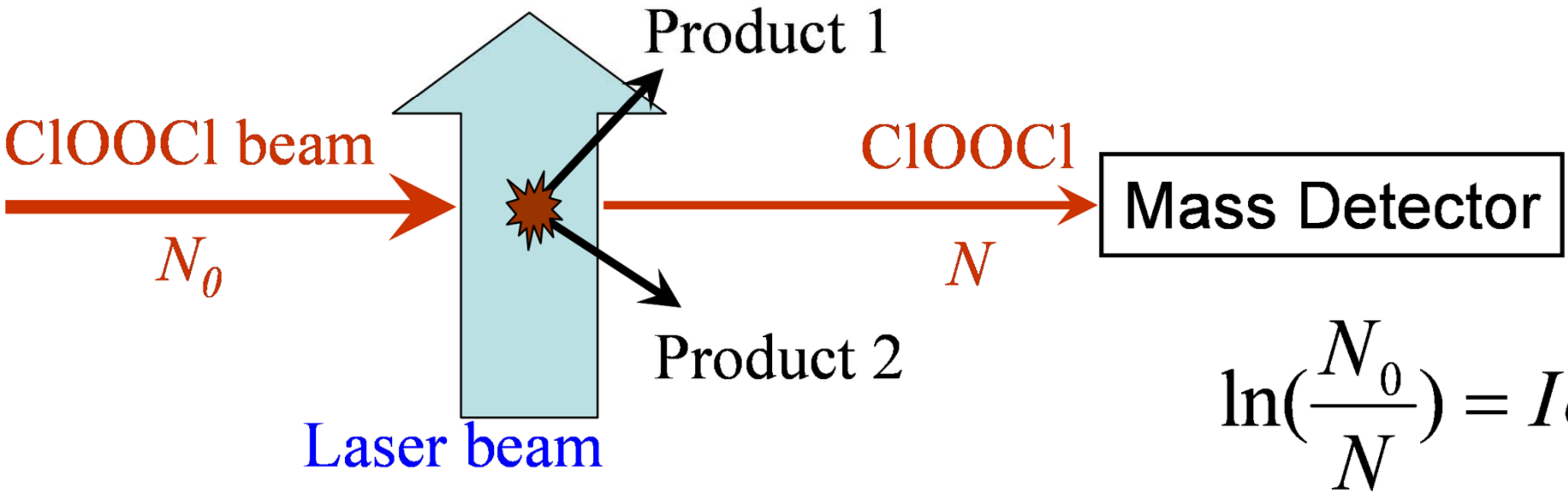
\# of molecules >> # of photons



$$\ln\left(\frac{I_0}{I}\right) = \sigma n l$$

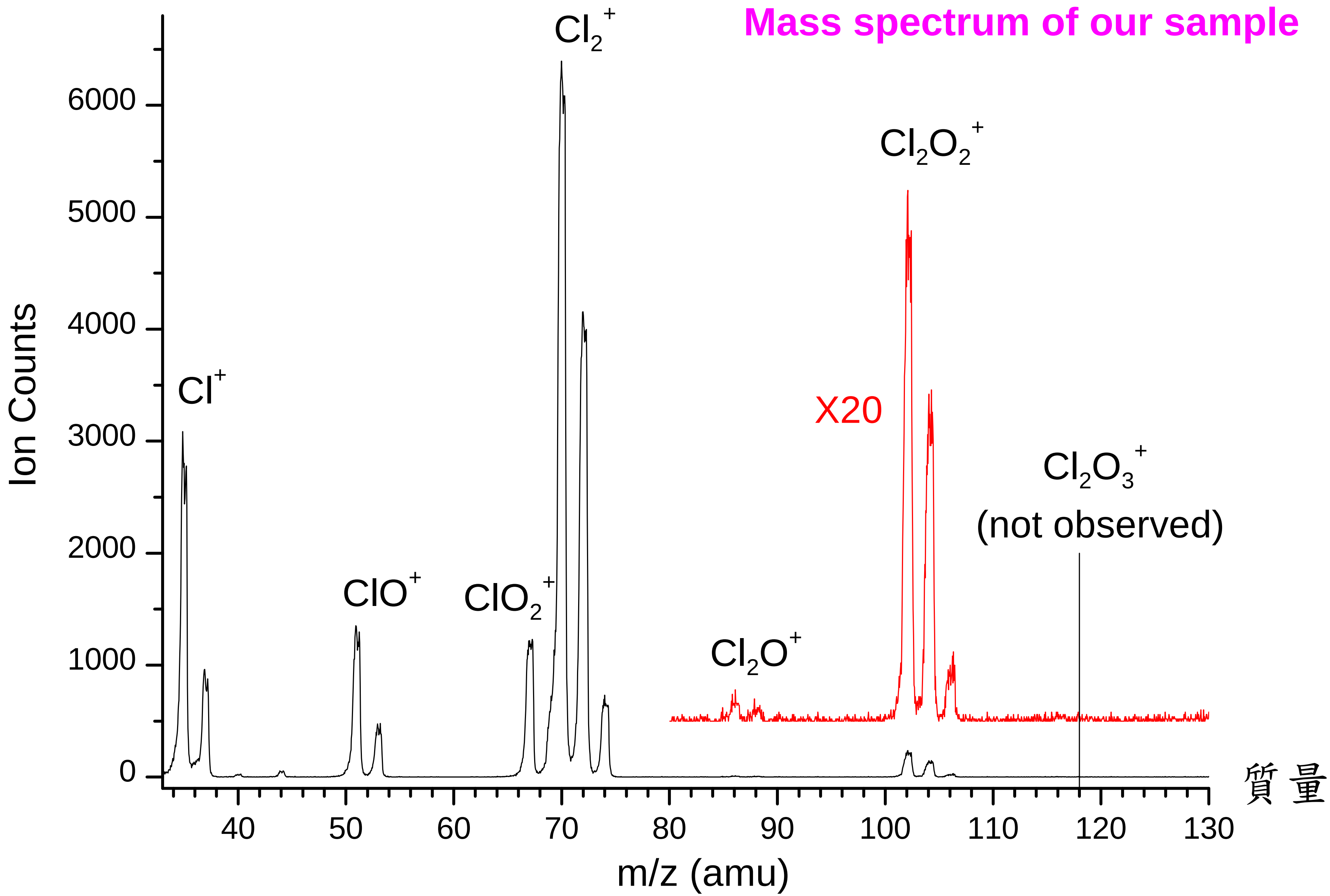
Our Method

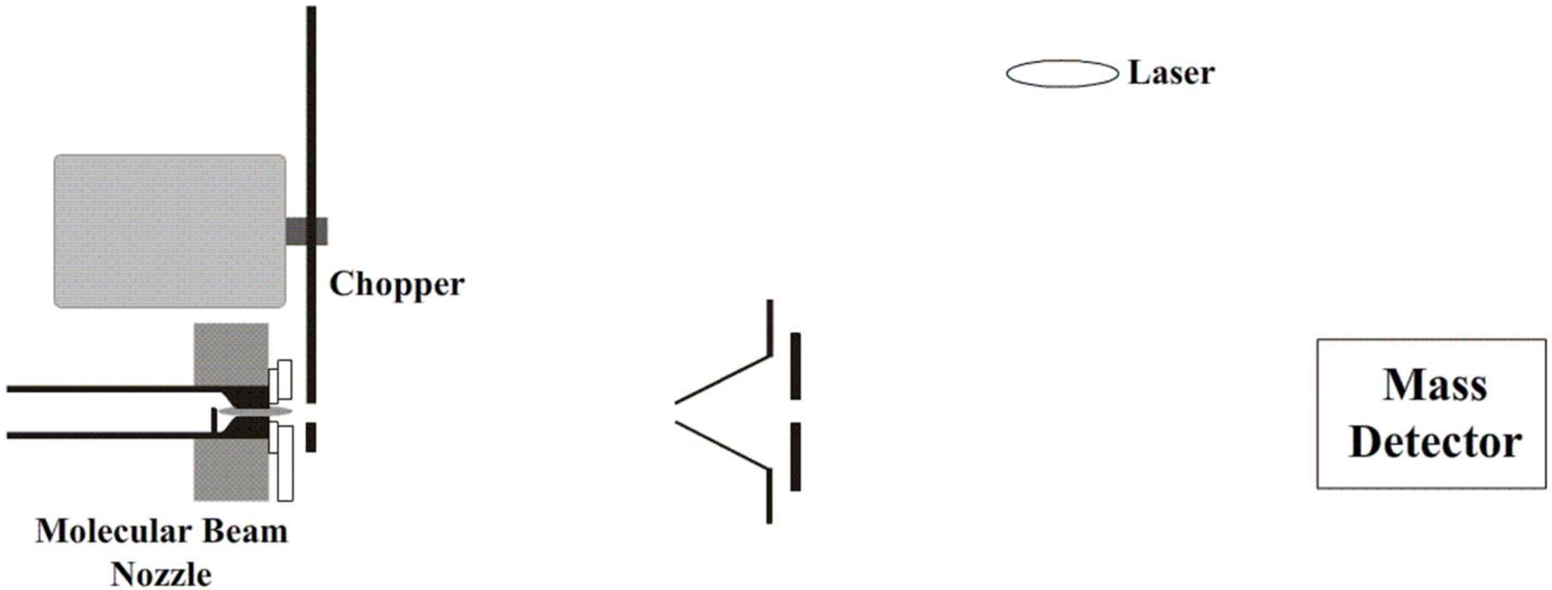
\# of photons >> # of molecules



$$\ln\left(\frac{N_0}{N}\right) = I\sigma\phi_{dis}$$

Pure ClOOCl sample is not available.




Laser
Chopper
Mass
Detector
Molecular Beam
Nozzle

If # of Molecules >> # of Photons, and if absorption leads to disappearance of the photon,

$$Abs = \ln\frac{I_0}{I} = \sigma n L \cong \frac{-\Delta I}{I_0}$$

Beer-Lambert Law

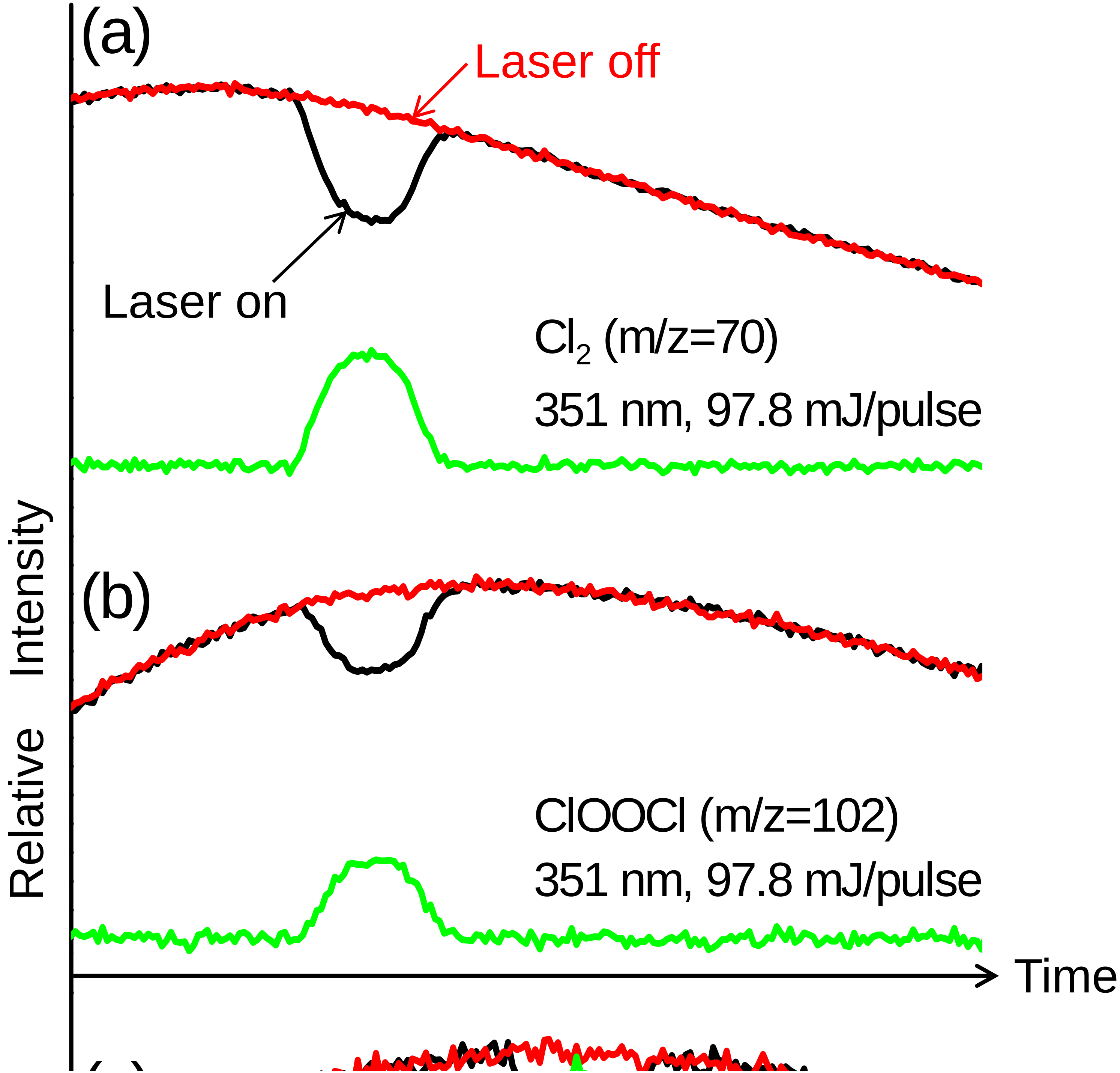
# of Molecules >> # of Photons

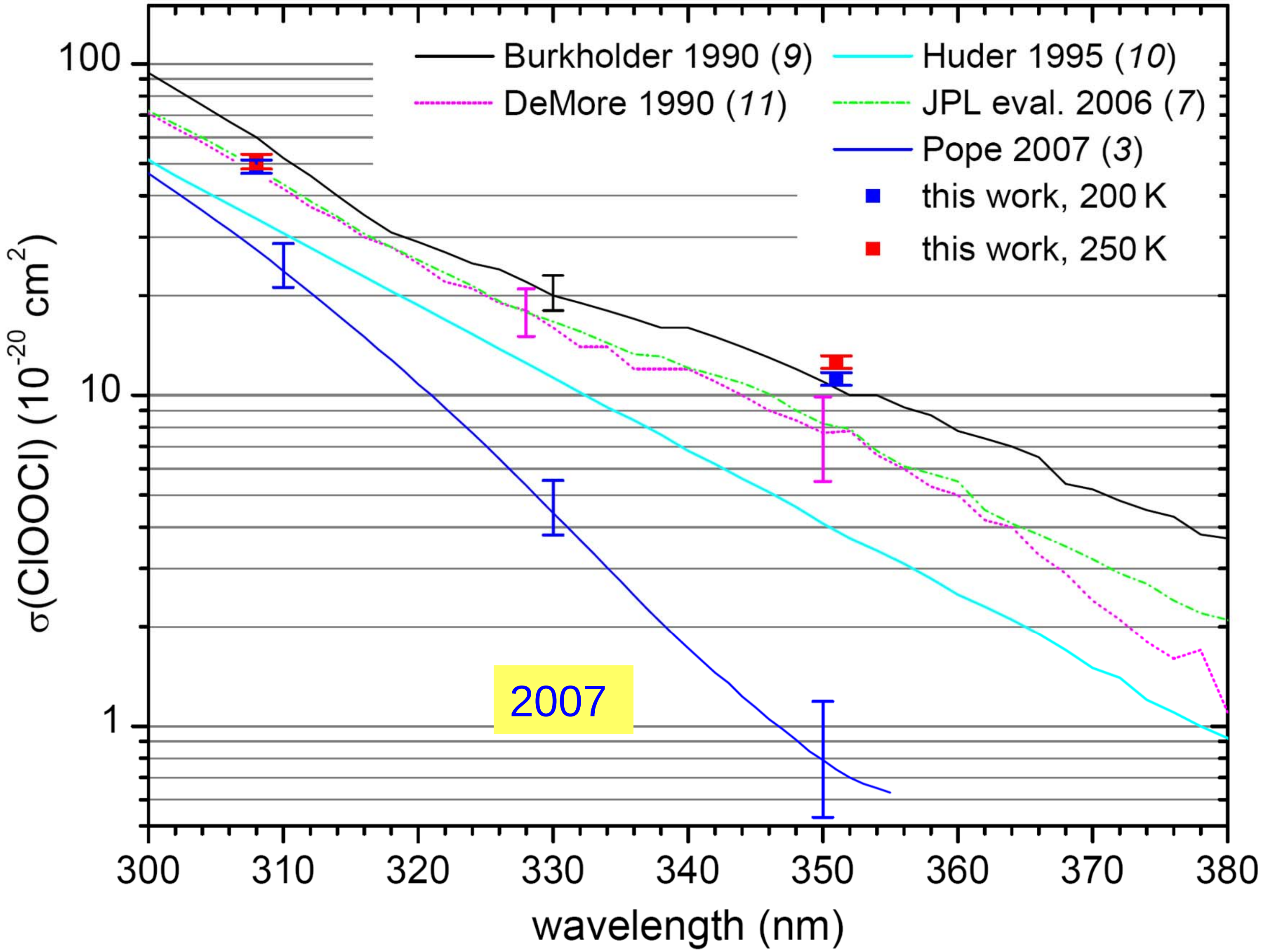
If # of Photons >> # of Molecules, and if absorption leads to dissociation

$$Dep = \ln\frac{N_0}{N} = \sigma F \cong \frac{-\Delta N}{N_0}$$

σ: in cm^2

F: in photon/cm^2 (Pulsed)


(a)
Laser off
Laser on
Cl_2 (m/z=70)
351 nm, 97.8 mJ/pulse
(b)
ClOOCl (m/z=102)
351 nm, 97.8 mJ/pulse
Relative Intensity
Time



Hsueh-Ying Chen, Chien-Yu Lien, Wei-Yen Lin, Yuan T. Lee, Jim J. Lin,*
Science **324**, 781 (2009)

Question:

Can Criegee intermediates (CI) oxidize atmospheric SO_2?

$CI + SO_2 \rightarrow SO_3$ k_{SO2} is very fast.

$CI + nH_2O \rightarrow$ products $k_{water}[H_2O]^n$

$CI \rightarrow$ products $k_{thermal}$

CI reacts with water or not ?

Controversial results in literature!

depends on preparation!?

Direct Kinetic Measurements of Criegee Intermediate (CH_2OO) Formed by Reaction of CH_2I with O_2
Oliver Welz *et al.*
Science **335**, 204 (2012);
DOI: 10.1126/science.1213229

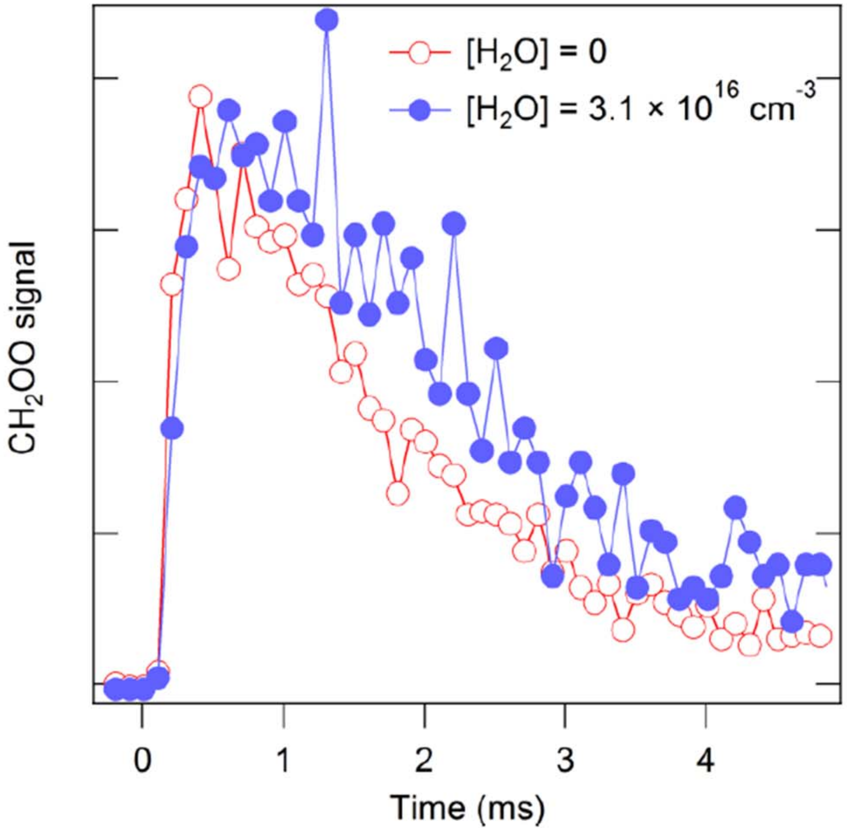


Figure S13. Time profiles of CH_2OO for low and high water concentrations. The decays are essentially identical (see Fig. S12), but the shape of CH_2OO is slightly different at high [H_2O].

CH_2OO reaction with water was **not observed** in other papers.

D. Stone, M. Blitz, L. Daubney, N. U. Howes, P. Seakins, *Kinetics of CH_2OO reactions with SO_2, NO_2, NO, H_2O and CH_3CHO as a function of pressure.* Phys. Chem. Chem. Phys. 16, 1139–1149 (2014). with $P(H_2O) \leq 5$ Torr

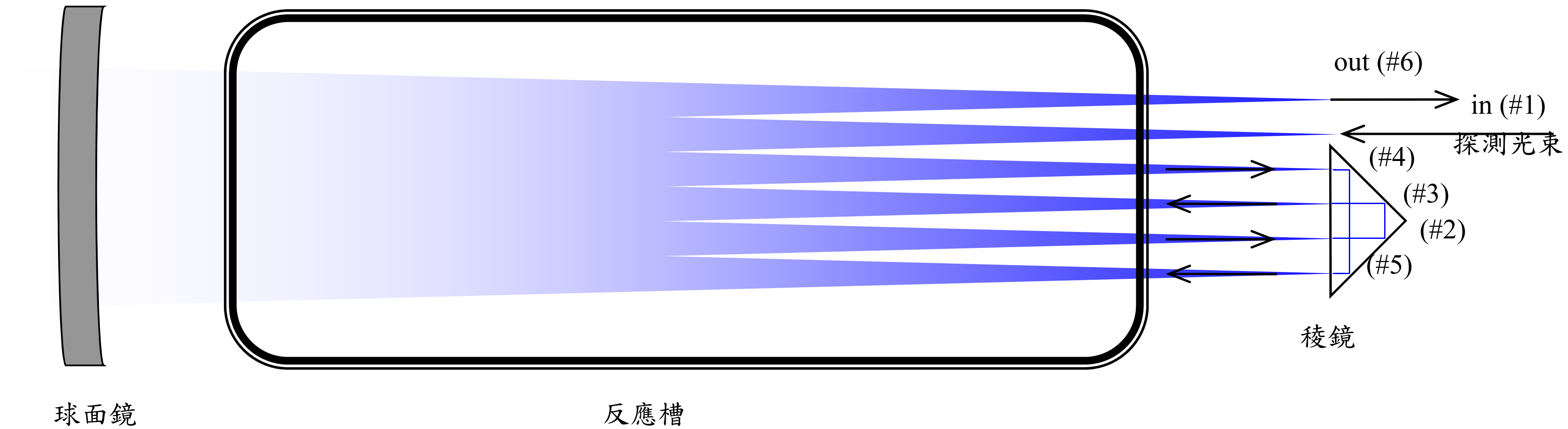
B. Ouyang, M. W. McLeod, R. L. Jones, W. J. Bloss, *NO_3 radical production from the reaction between the Criegee intermediate CH_2OO and NO_2.* Phys. Chem. Chem. Phys. 15, 17070–17075 (2013). with $P(H_2O) \leq 21$ Torr

Lower concentrations

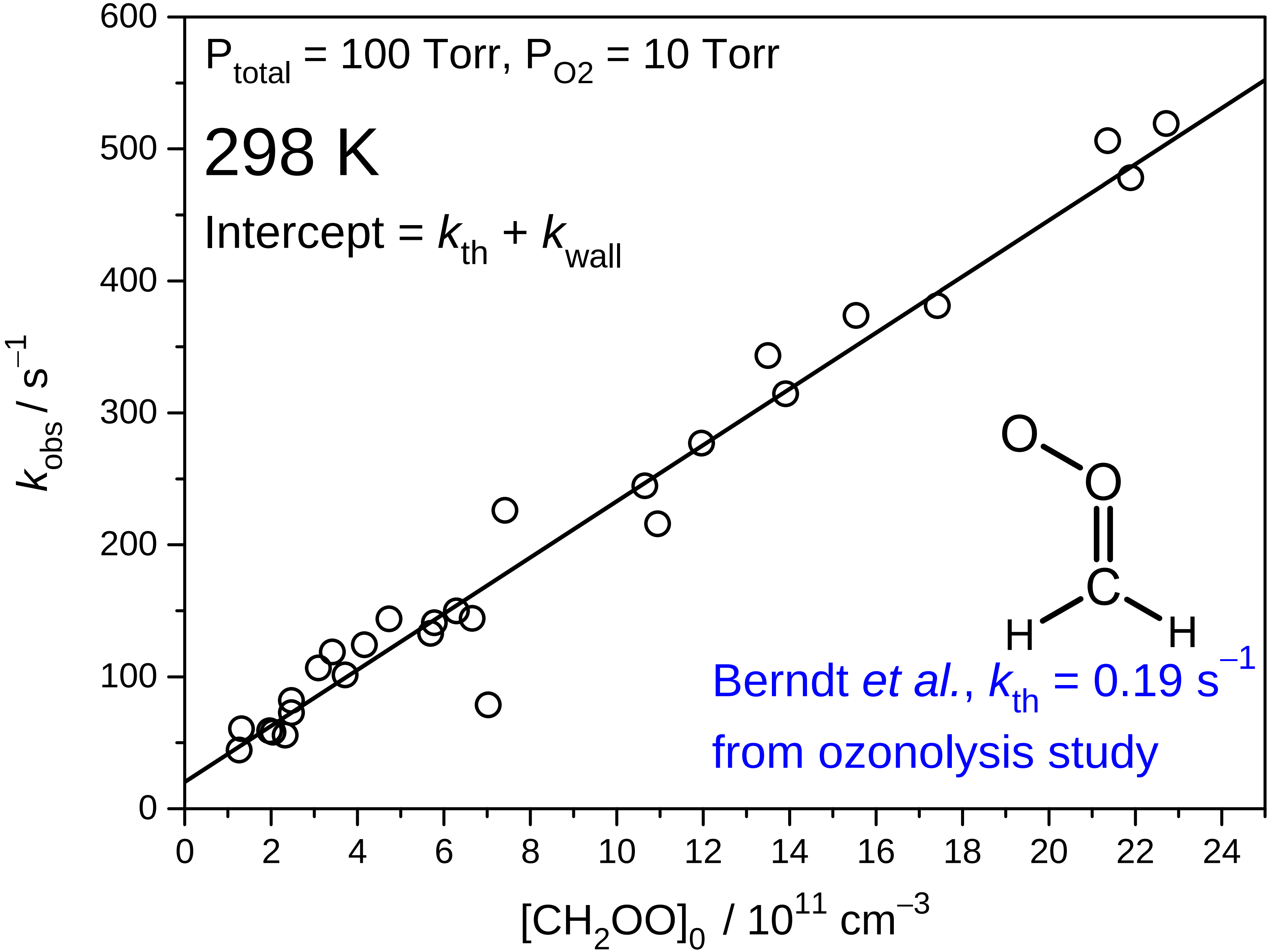
→ Slower reactions between radicals

But also weaker signal*!*

Solution: Use longer absorption path

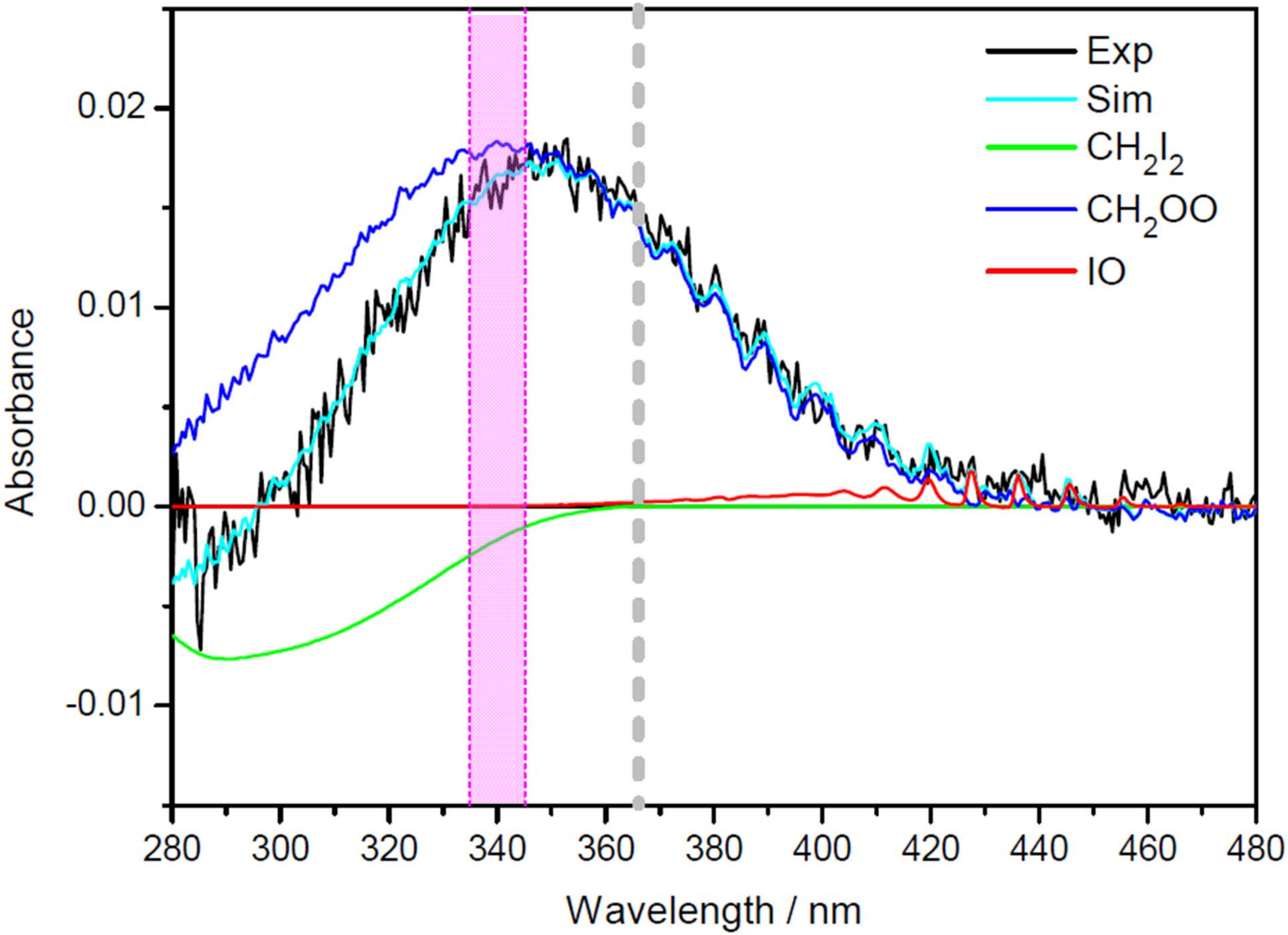


65 cm x 8 = 520 cm



Wen Chao, master thesis, National Taiwan University 2017

Probe CH_2OO with Time-resolved UV Absorption



Probe CH_2OO with Time-resolved UV Absorption

$\sigma(CH_2OO) \sim 1\text{x}10^{-17}$ cm^2

>> σ(non radicals) @ 340–380 nm

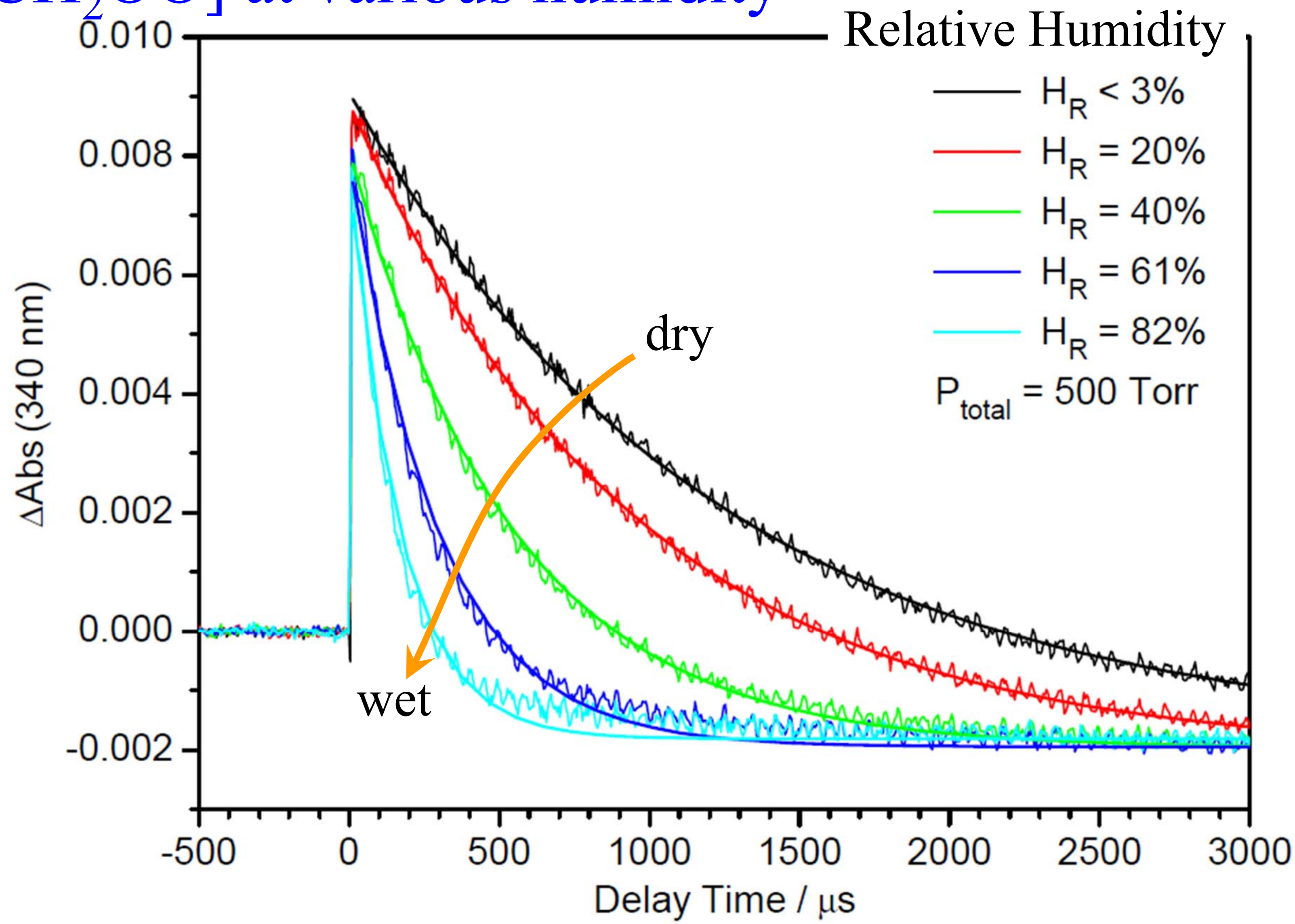
- Sensitivity: $\Delta I/I_0 = \sigma\, \boldsymbol{n}\, L$

$\sim (1\text{x}10^{-17}$ cm^2) **(2x10^{11} cm^{-3})** (500 cm) $\sim 10^{-3}$

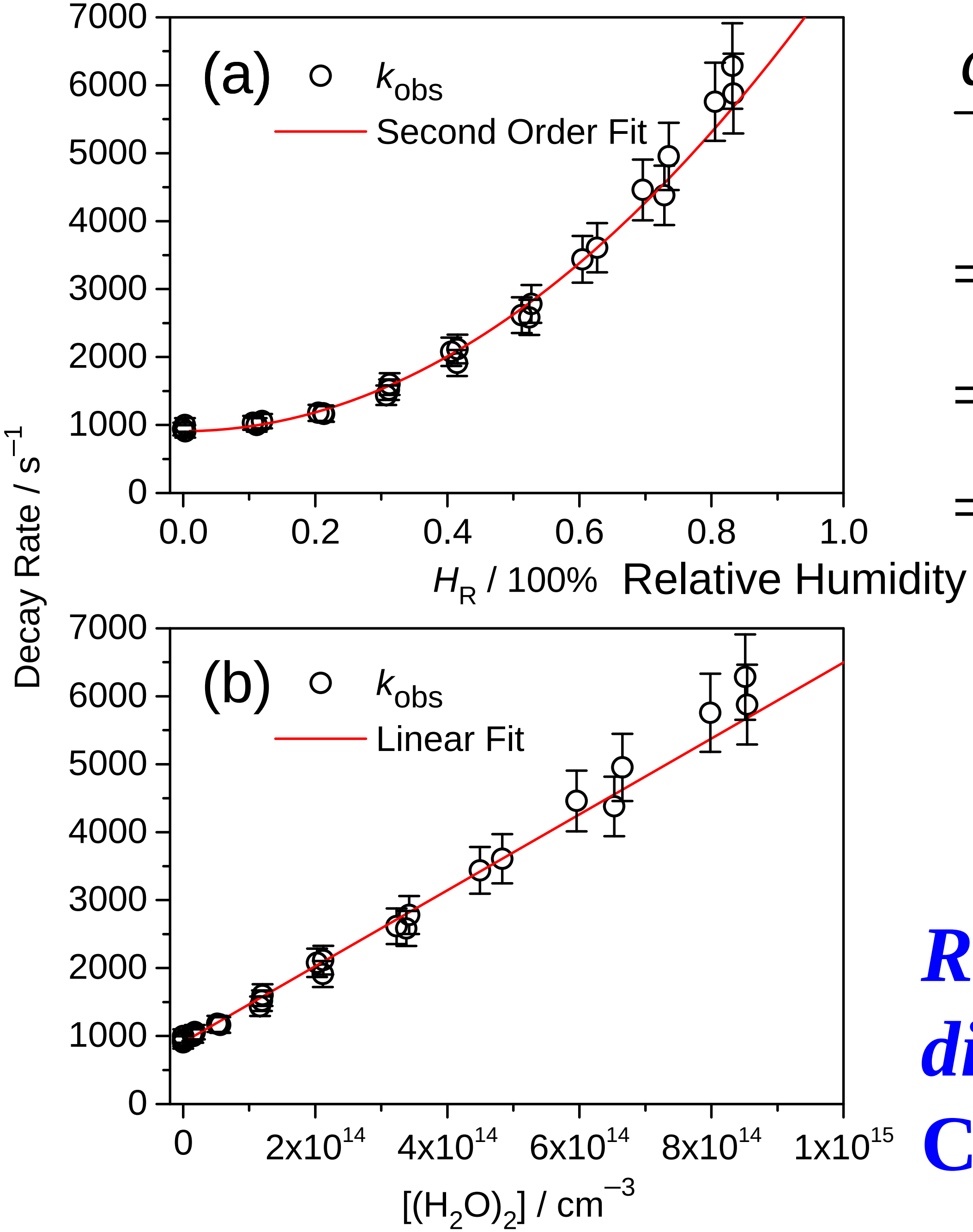
Can be performed ***at Near Atmospheric Conditions***

(Relative Humidity: 0–80%)

[CH_2OO] at various humidity



Science 347, 751 (2015)



$$\frac{d[CH_2OO]}{dt}$$

$$= -k_{ap}[H_2O]^2\ [CH_2OO]$$

$$= -k_{w2}[(H_2O)_2]\ [CH_2OO]$$

$$= -k_{obs}\ [CH_2OO]$$

$$\frac{[(H_2O)_2]}{[H_2O]^2} = K_{eq}$$

Reaction with water dimer predominates for CH_2OO decay!

Science 347, 751 (2015)

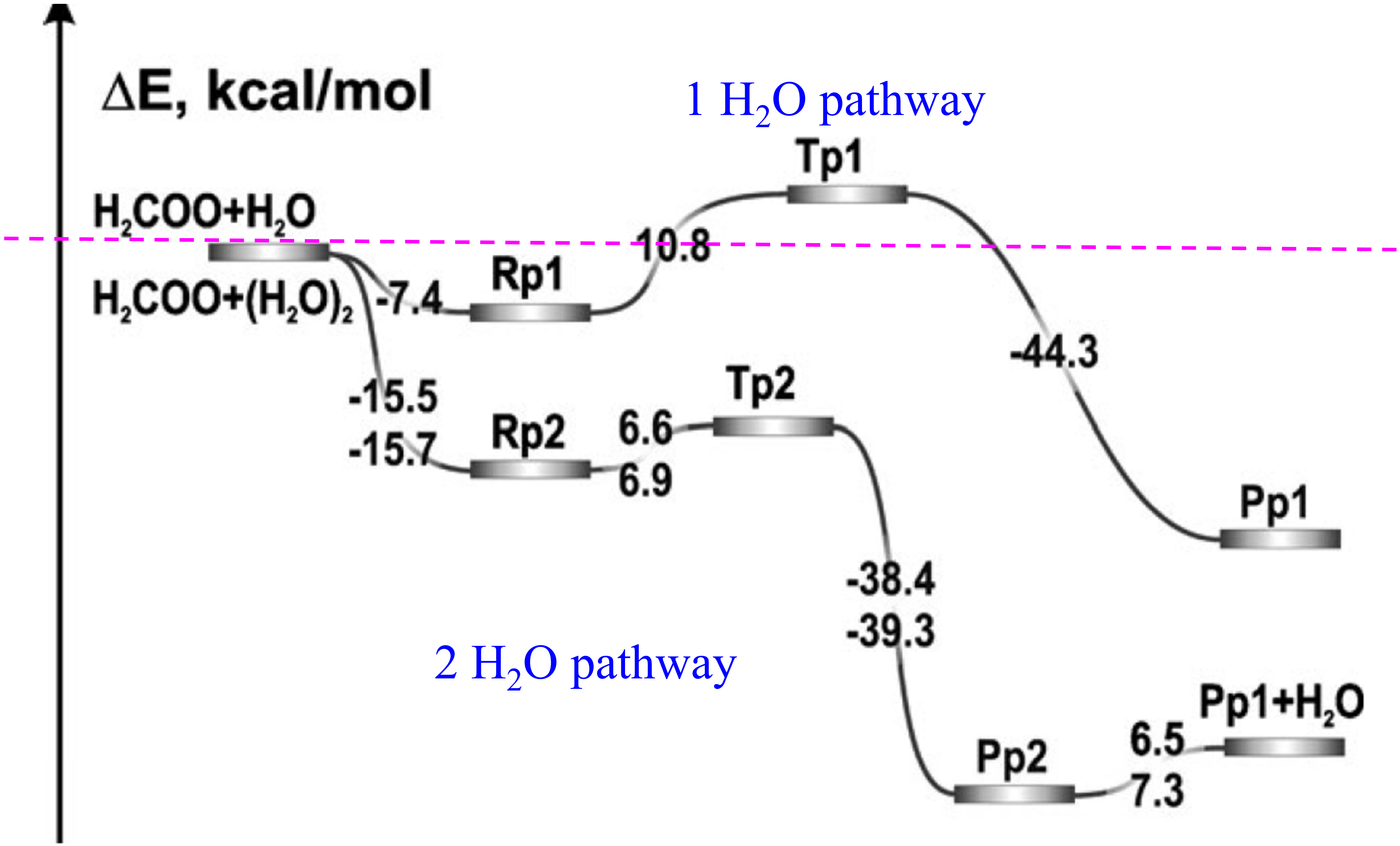
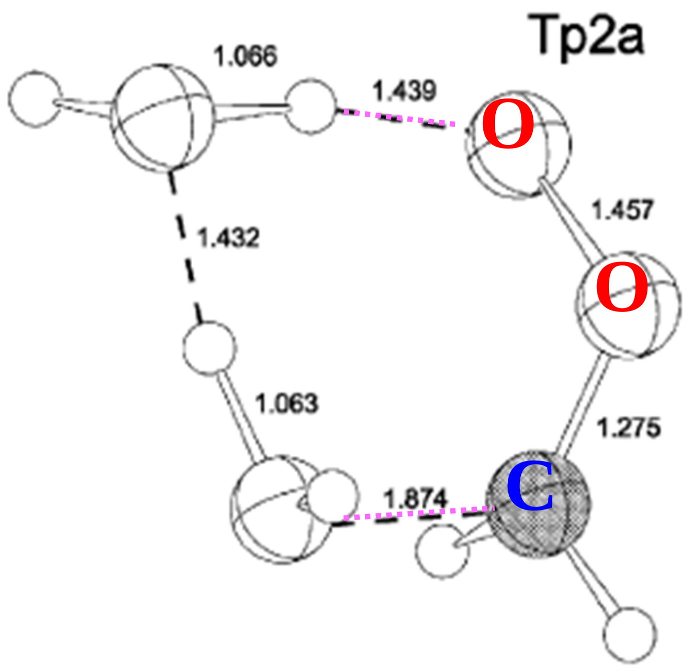
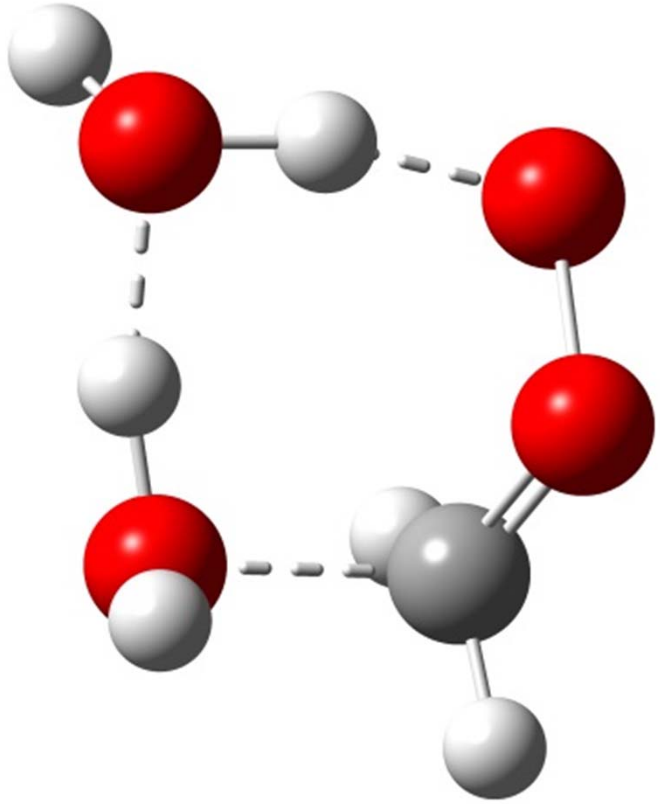


Fig. 4 Energy diagram for the reaction of H_2COO with H_2O and $(H_2O)_2$. Ryzhkov and Ariya, *Phys. Chem. Chem. Phys.* 2004, 6, 5042



Ryzhkov and Ariya
Phys. Chem. Chem. Phys. , 2004, 6, 5042



Liang-Chun Lin & Kaito Takahashi

IAMS group

Direct Kinetic Measurements of Criegee Intermediate (CH_2OO) Formed by Reaction of CH_2I with O_2

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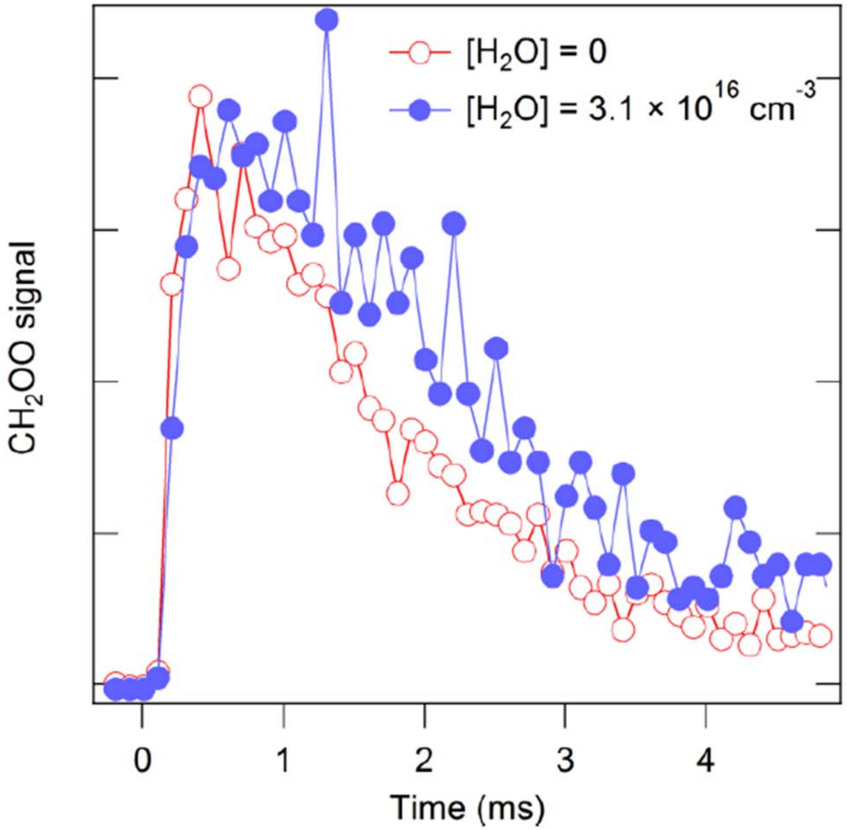
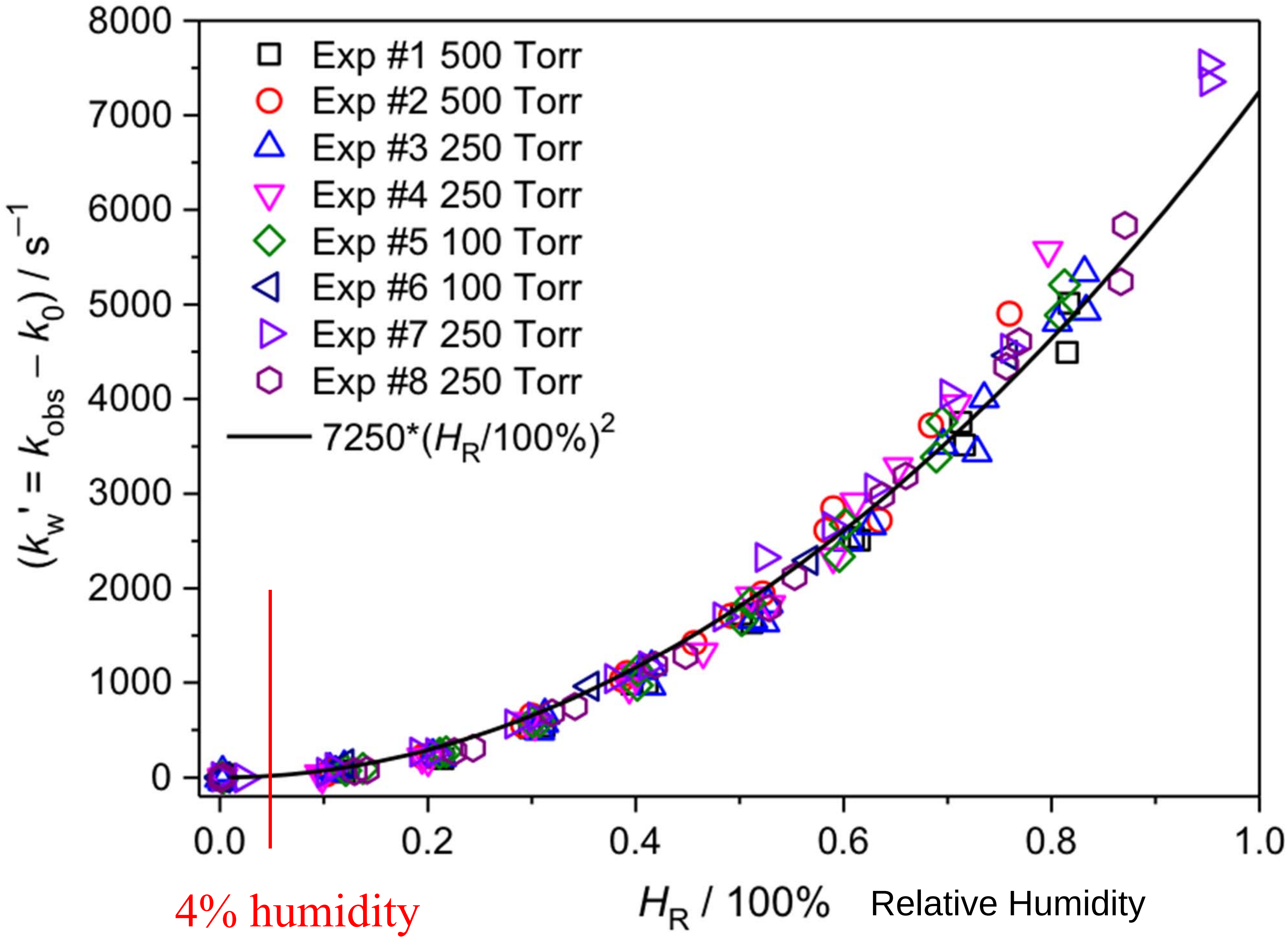


$P(H_2O) \sim 1$ Torr

relative humidity

~ 4%

Figure S13. Time profiles of CH_2OO for low and high water concentrations. The decays are essentially identical (see Fig. S12), but the shape of CH_2OO is slightly different at high $[H_2O]$.



Science 347, 751 (2015)

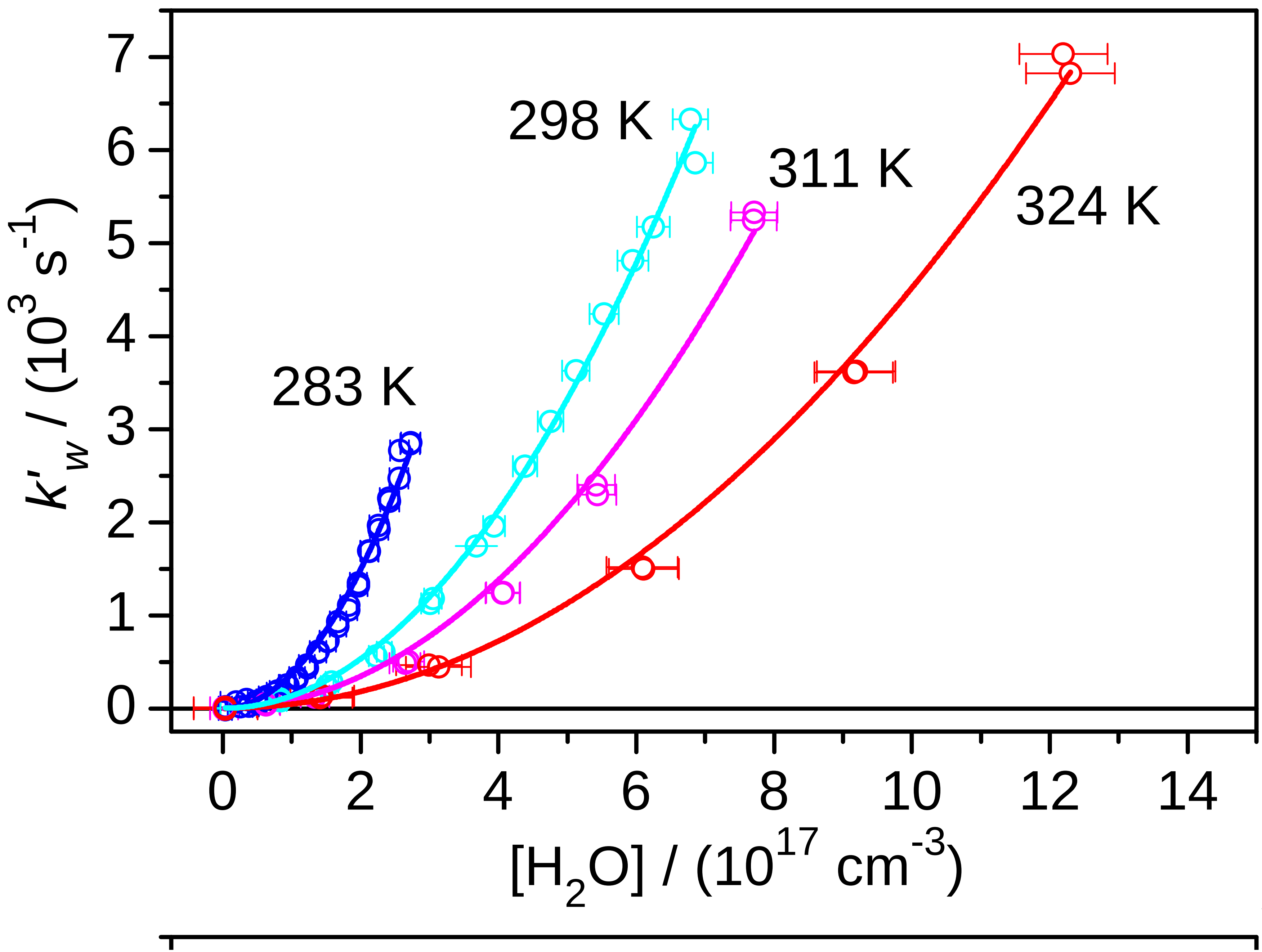
Co-reactant	k_{rxn} ($cm^3\ sec^{-1}$)	Assumed Concentration	Number density[d] (cm^{-3})	k_{eff} (sec^{-1})
$(H_2O)_2$	$(5.9x10^{-12})^a$	$H_R \geq 38\%$	$\geq 1.8x10^{14}$	≥ 1000
SO_2	$(4x10^{-11})^b$	50 ppb	$1.2x10^{12}$	50
NO_2	$(7x10^{-12})^b$	50 ppb	$1.2x10^{12}$	9
carboxylic acids	$(1x10^{-10})^c$	5 ppb	$1.2x10^{11}$	12

[a] This work. [b] O. Welz et al. *Science* **335**, 204–207 (2012).

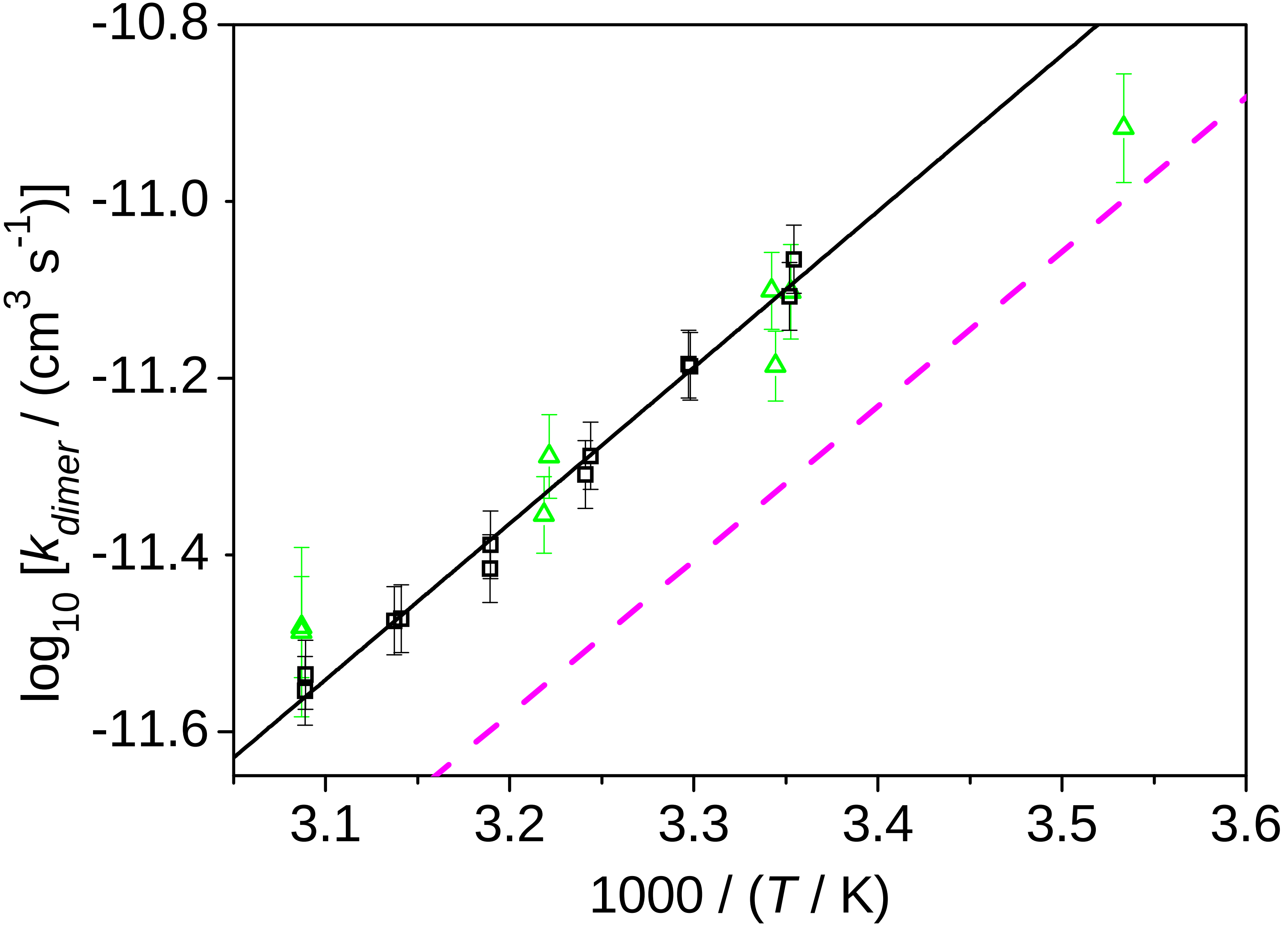
[c] O. Welz et al. *Angew. Chem. Int. Ed.* **53**, 4547-4550 (2014).

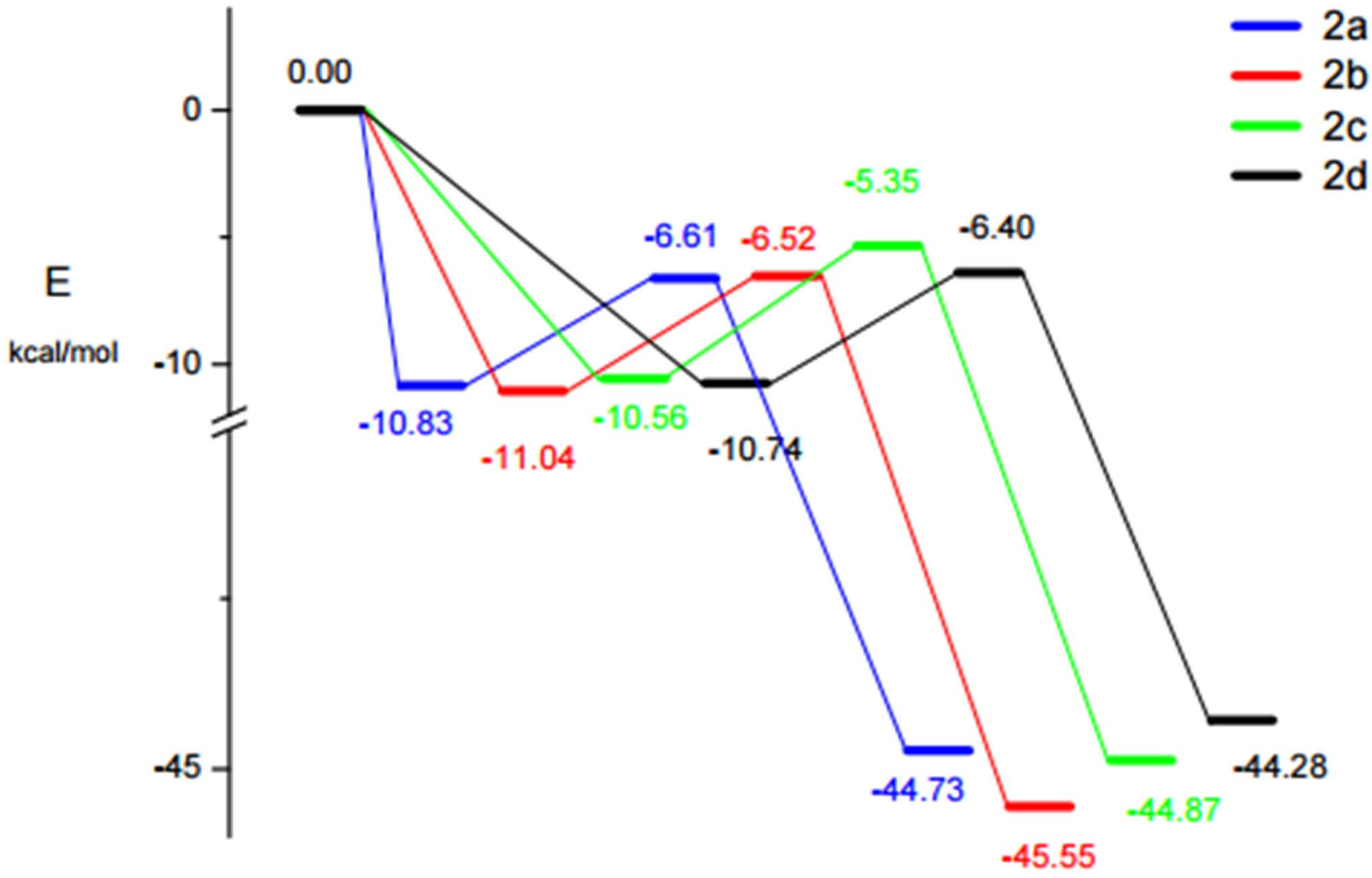
Science 347, 751 (2015)

Faster at lower Temperature!



- Arrhenius activation energy: $E_a = -8.1 \pm 0.6$ kcal mol^{-1}
- $CH_2OO + (H_2O)_2$ reaction rate: $k(298\text{ K}) = (7.4 \pm 0.6) \times 10^{-12}$ cm^3 s^{-1}





Liang-Chun Lin & Kaito Takahashi

$CI + SO_2 \rightarrow SO_3$ k_{SO2} is very fast.

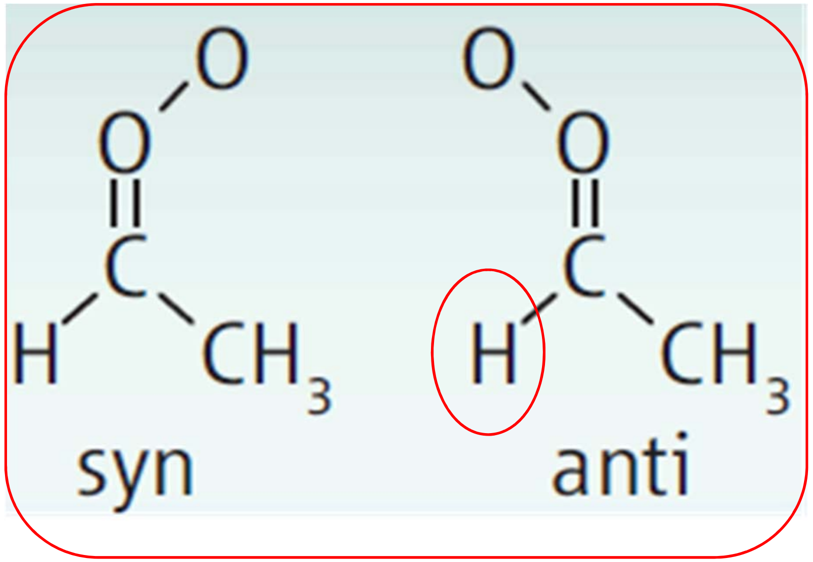
$CI + (H_2O)_2 \rightarrow$ products k_{dimer} is also fast

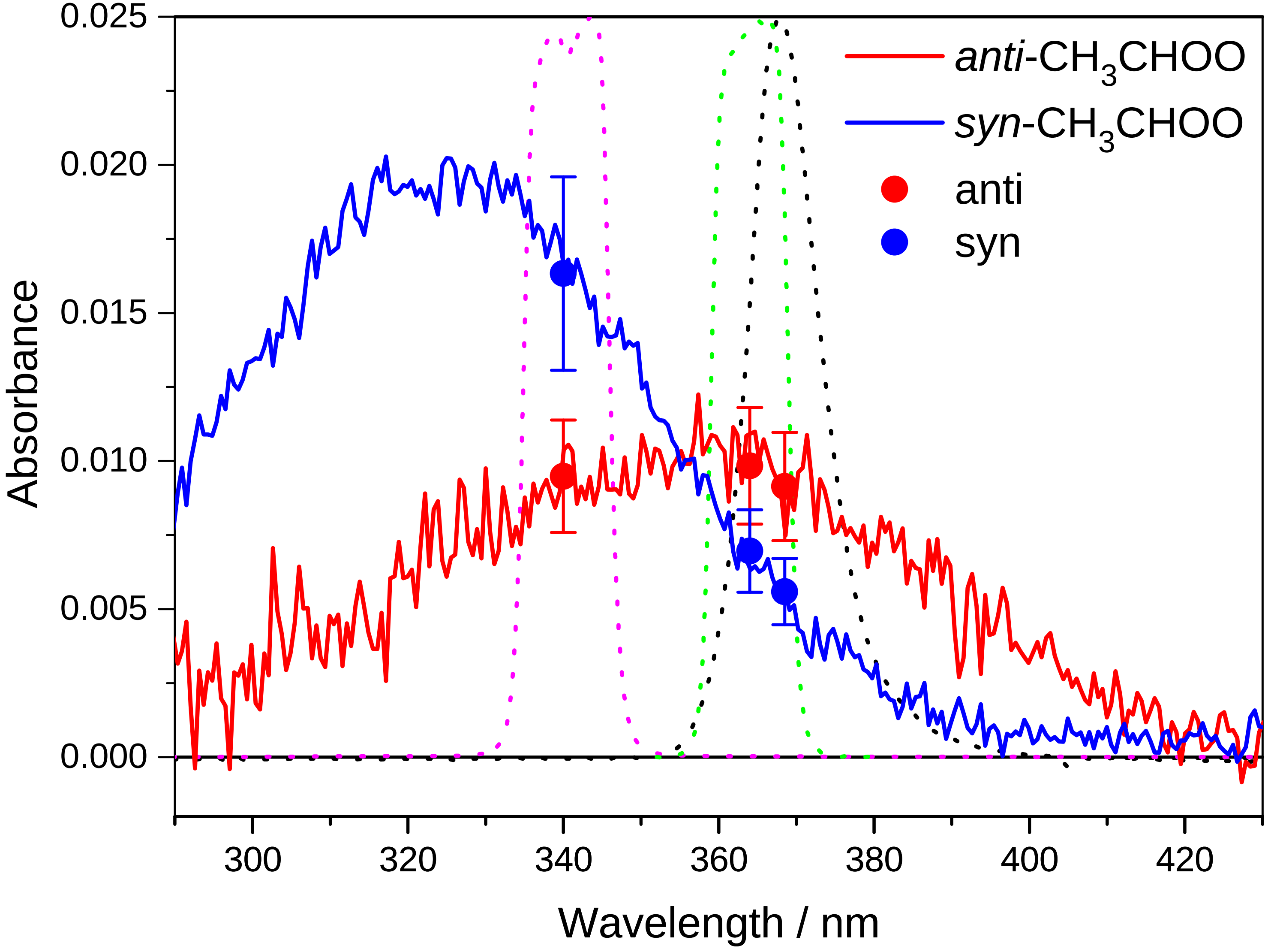
$CI \rightarrow$ products $k_{thermal}$

Direct Measurements of Conformer-Dependent Reactivity of the Criegee Intermediate CH_3CHOO
Craig A. Taatjes *et al.*
Science **340**, 177 (2013);

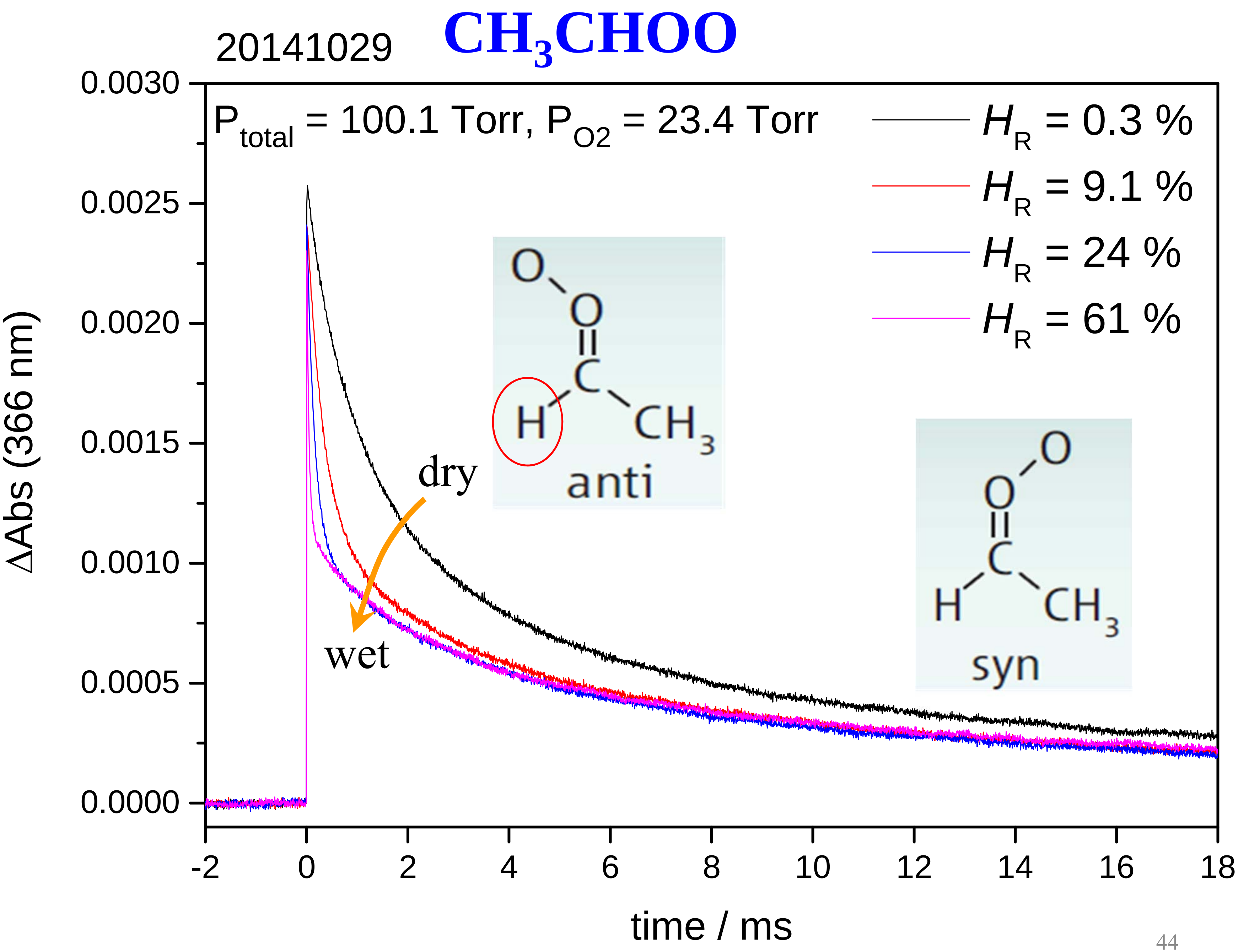
Reaction with water vapor

slow *fast*



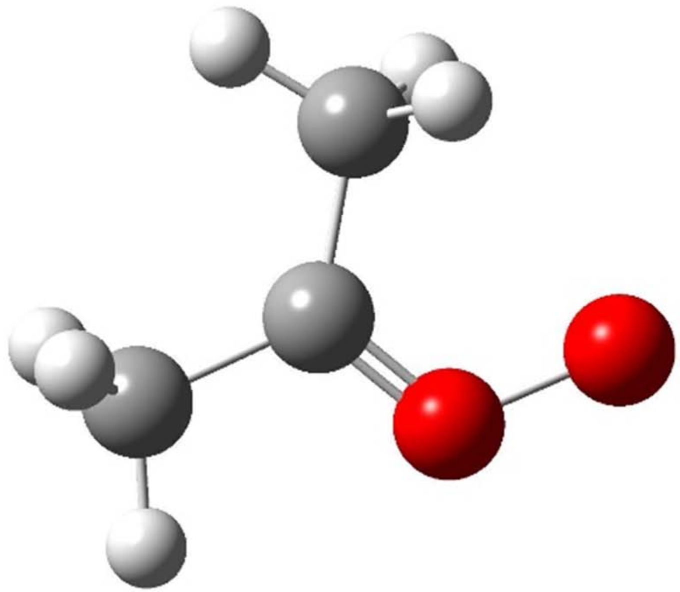


0.025
0.020
0.015
0.010
0.005
0.000
Absorbance
300
320
340
360
380
400
420
Wavelength / nm
anti-CH3CHOO
syn-CH3CHOO
anti
syn



20141029
CH3CHOO
P total = 100.1 Torr, P O2 = 23.4 Torr
H R = 0.3 %
H R = 9.1 %
H R = 24 %
H R = 61 %
O
O
C
H
CH3
anti
O
O
C
H
CH3
syn
dry
wet
ΔAbs (366 nm)
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
-2
0
2
4
6
8
10
12
14
16
18
time / ms

How about acetone oxide, $(CH_3)_2COO$?



$(CH_3)_2CI_2 + h\nu$

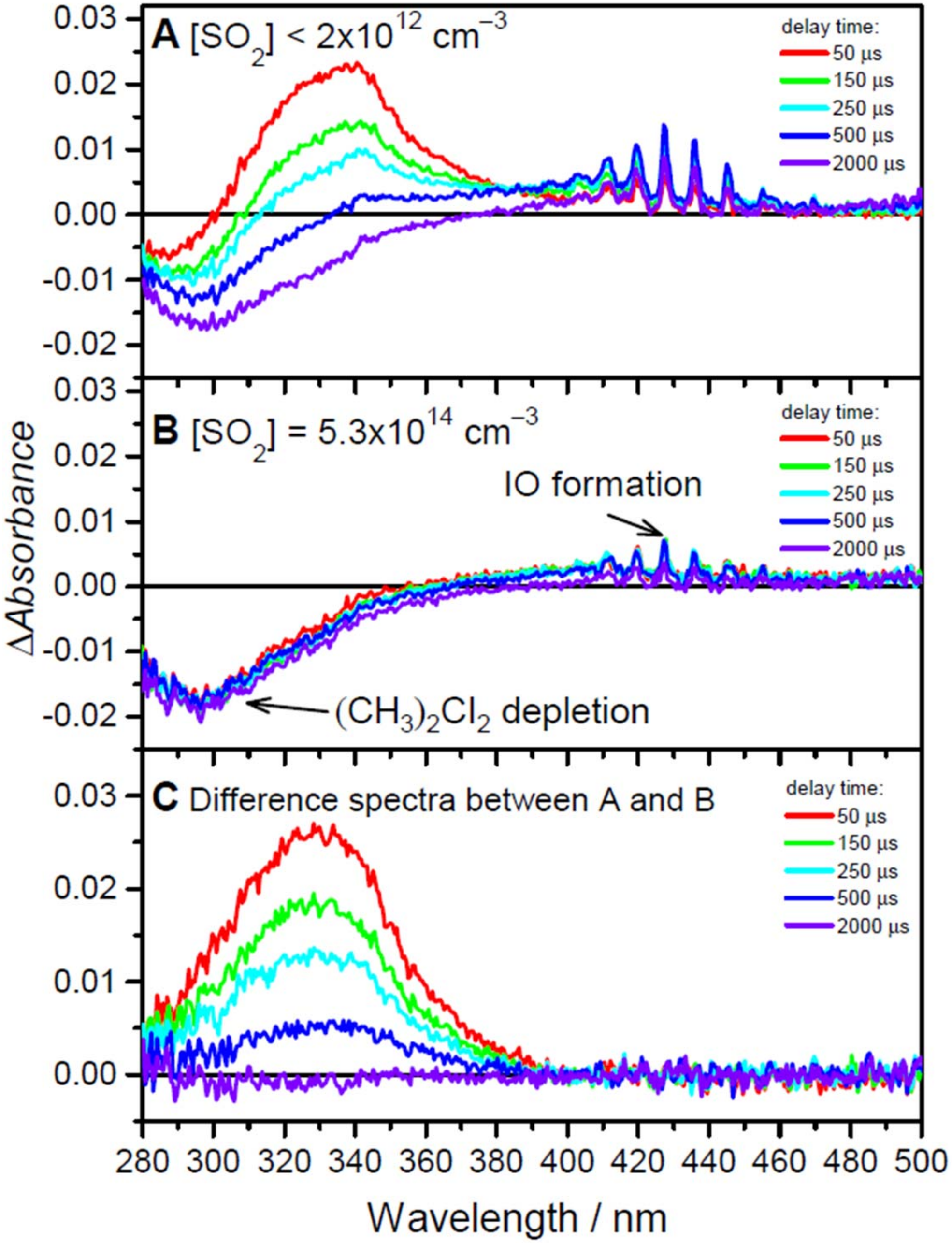
$\rightarrow (CH_3)_2CI + I$

$(CH_3)_2CI + O_2$

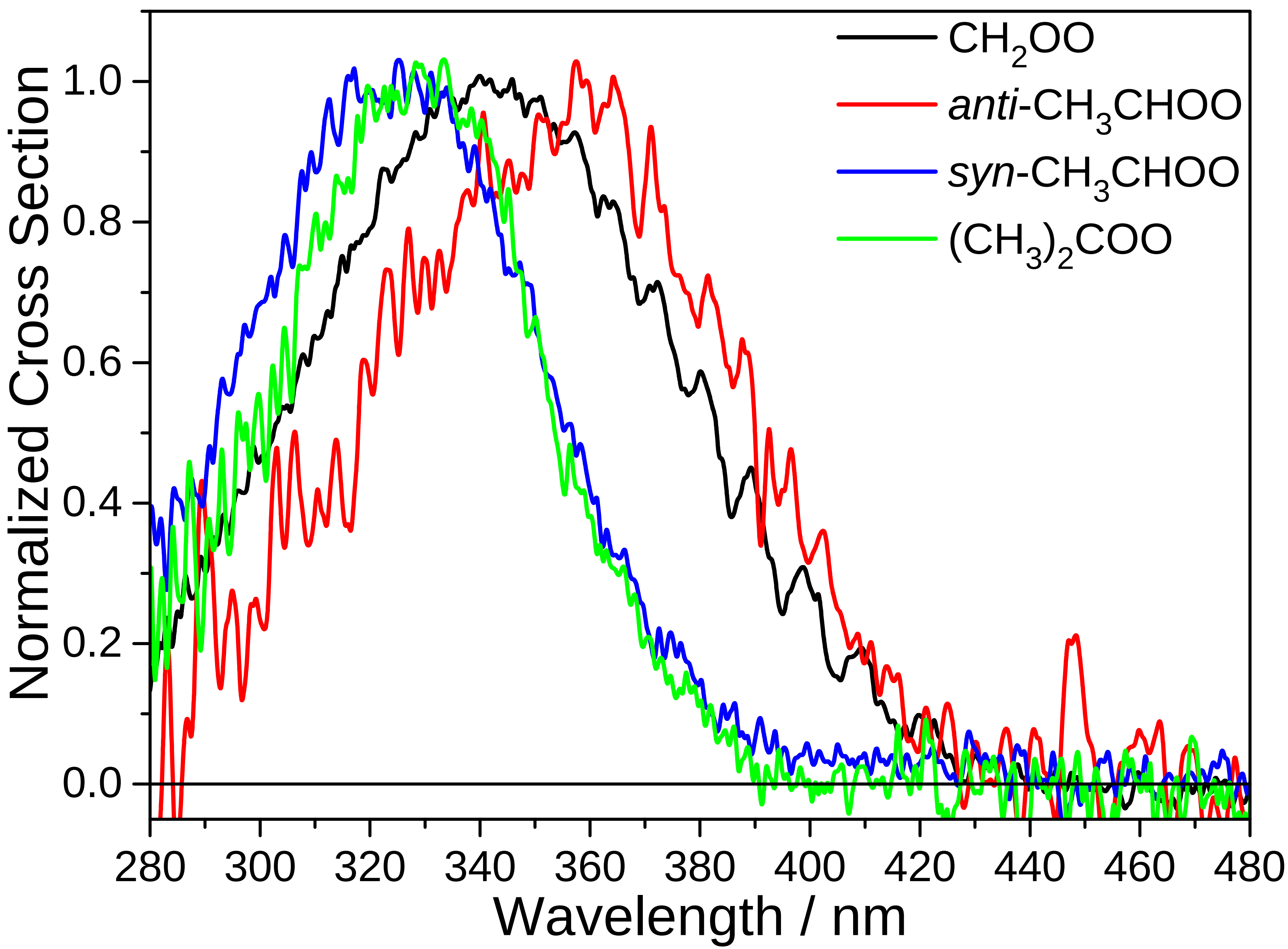
$\rightarrow (CH_3)_2COO + I$

$(CH_3)_2COO + SO_2$

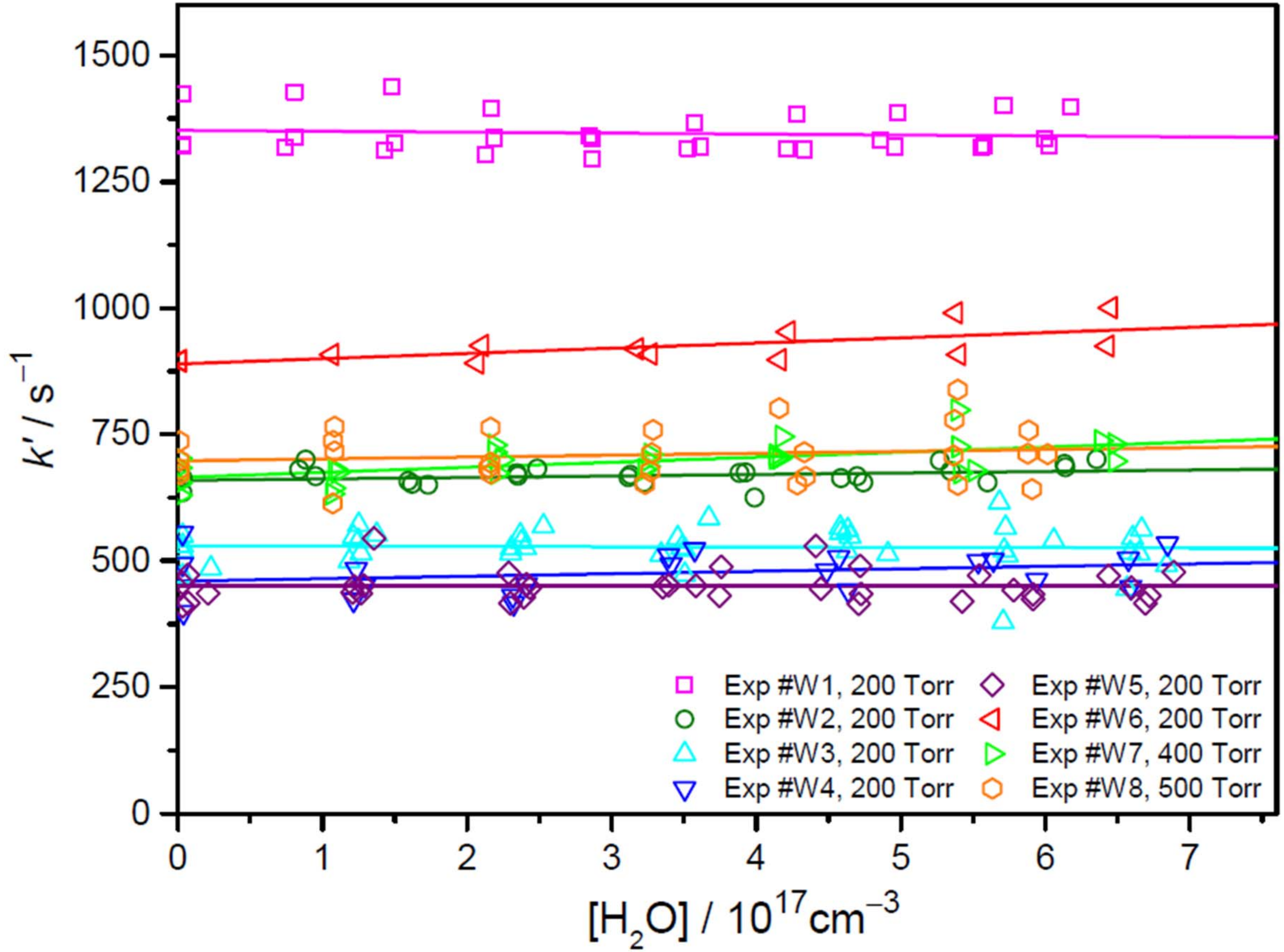
$\rightarrow$ Products



Proc. Natl. Acad. Sci. USA, 112 (35), 10857–10862 (2015).


CH2OO
anti-CH3CHOO
syn-CH3CHOO
(CH3)2COO
Normalized Cross Section
1.0
0.8
0.6
0.4
0.2
0.0
280
300
320
340
360
380
400
420
440
460
480
Wavelength / nm

What happens after adding water?



Proc. Natl. Acad. Sci. USA, 112 (35), 10857–10862 (2015).

Kinetics of a Criegee intermediate that would survive high humidity and may oxidize atmospheric SO_2

Hao-Li Huang (黃皓立)[a], Wen Chao (趙彣)[a,b], and Jim Jr-Min Lin (林志民)[a,b,1]

[a]Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan; and [b]Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

Edited by John H. Seinfeld, California Institute of Technology, Pasadena, CA, and approved July 27, 2015 (received for review July 4, 2015)

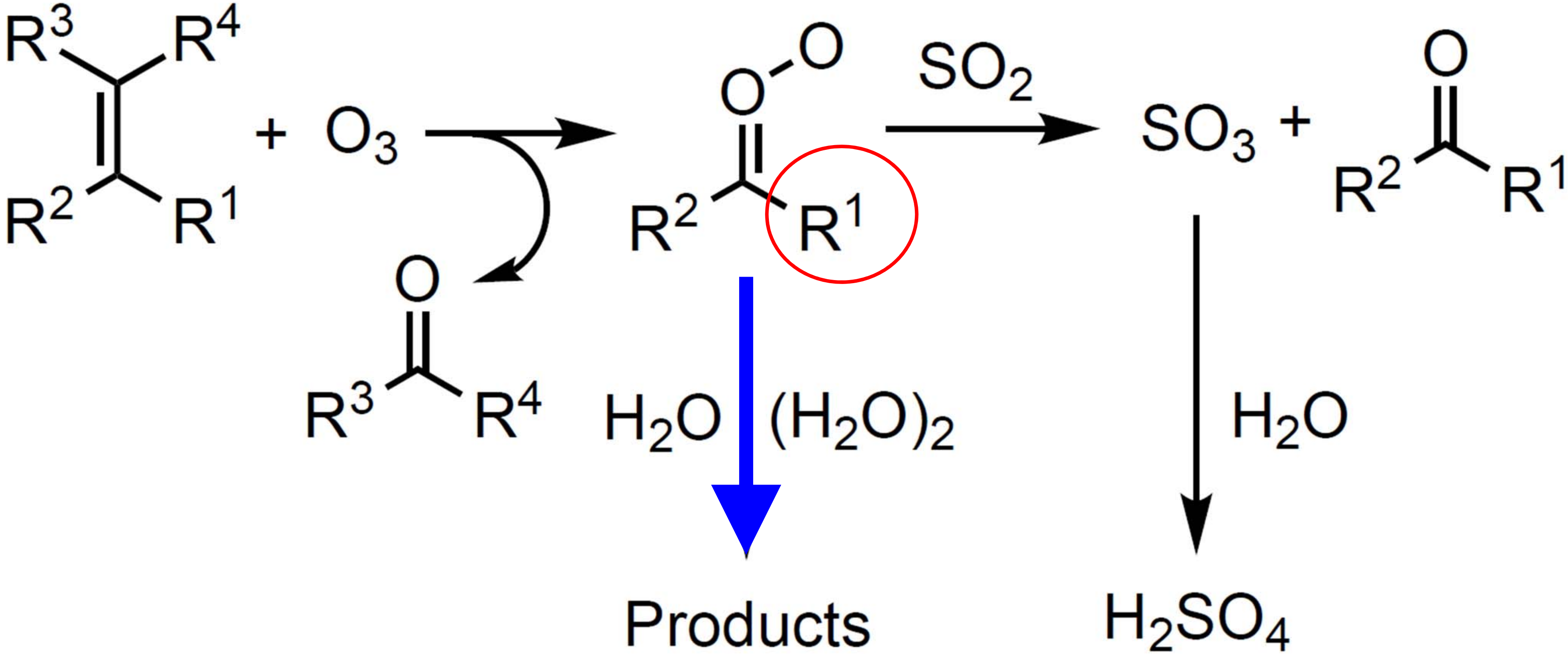
Criegee intermediates are thought to play a role in atmospheric chemistry, in particular, the oxidation of SO_2, which produces SO_3

Typical water concentration in the troposphere (1.3×10^{17} to 8.3×10^{17} cm^{-3} at the dew point of 0–27 °C) is orders of magnitude

Proc. Natl. Acad. Sci. USA, 112 (35), 10857–10862 (2015).

CI	coreactant	[coreactant] /cm^{-3}	k / $cm^3 s^{-1}$	k_{eff} / s^{-1}
CH_2OO	H_2O	5.4×10^{17}	$< 1.5 \times 10^{-15}$	< 810
	$(H_2O)_2$	6.0×10^{14}	6.5×10^{-12}	3900
	SO_2	1.2×10^{12}	3.9×10^{-11}	47
$(CH_3)_2COO$	H_2O	5.4×10^{17}	$< 1.5 \times 10^{-16}$*	< 81*
	$(H_2O)_2$	6.0×10^{14}	$< 1.3 \times 10^{-13}$*	< 78*
	SO_2	1.2×10^{12}	1.3×10^{-10}	160

Proc. Natl. Acad. Sci. USA, 112 (35), 10857–10862 (2015).



fast, if $R^1 = H$

slow, if $R^1 \neq H$

Proc. Natl. Acad. Sci. USA, 112 (35), 10857–10862 (2015).

Brief Summary

Reactivity of Criegee intermediates towards water (dimer) depends strongly on their structures.
Anti forms react with water (dimer) much faster than the syn forms.

$$[CI]_{ss} = \frac{formation\ rate}{k_{decay}}$$

$$k_{\mathrm{decay}} = \boldsymbol{k}_{\mathbf{therm}} + k_{\mathrm{H2O}}[\mathrm{H_2O}] + k_{\mathrm{w2}}[(\mathrm{H_2O})_2] + k_{\mathrm{SO2}}[\mathrm{SO_2}] + k_{\mathrm{NO2}}[\mathrm{NO_2}] + \cdots$$

How to measure thermal decomposition rate?

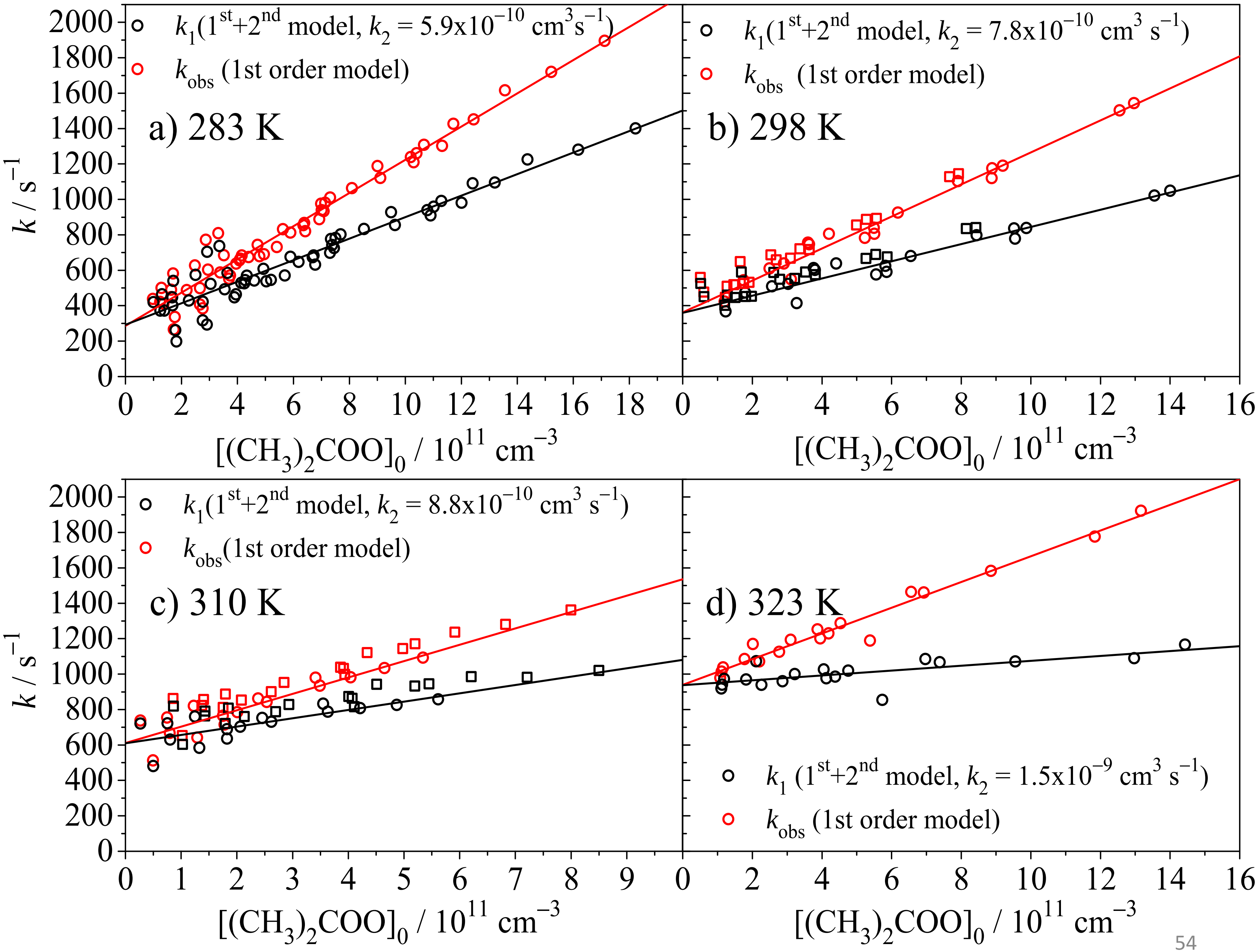
Do nothing but wait. However, there are:

$$CI + CI \rightarrow \text{products}$$

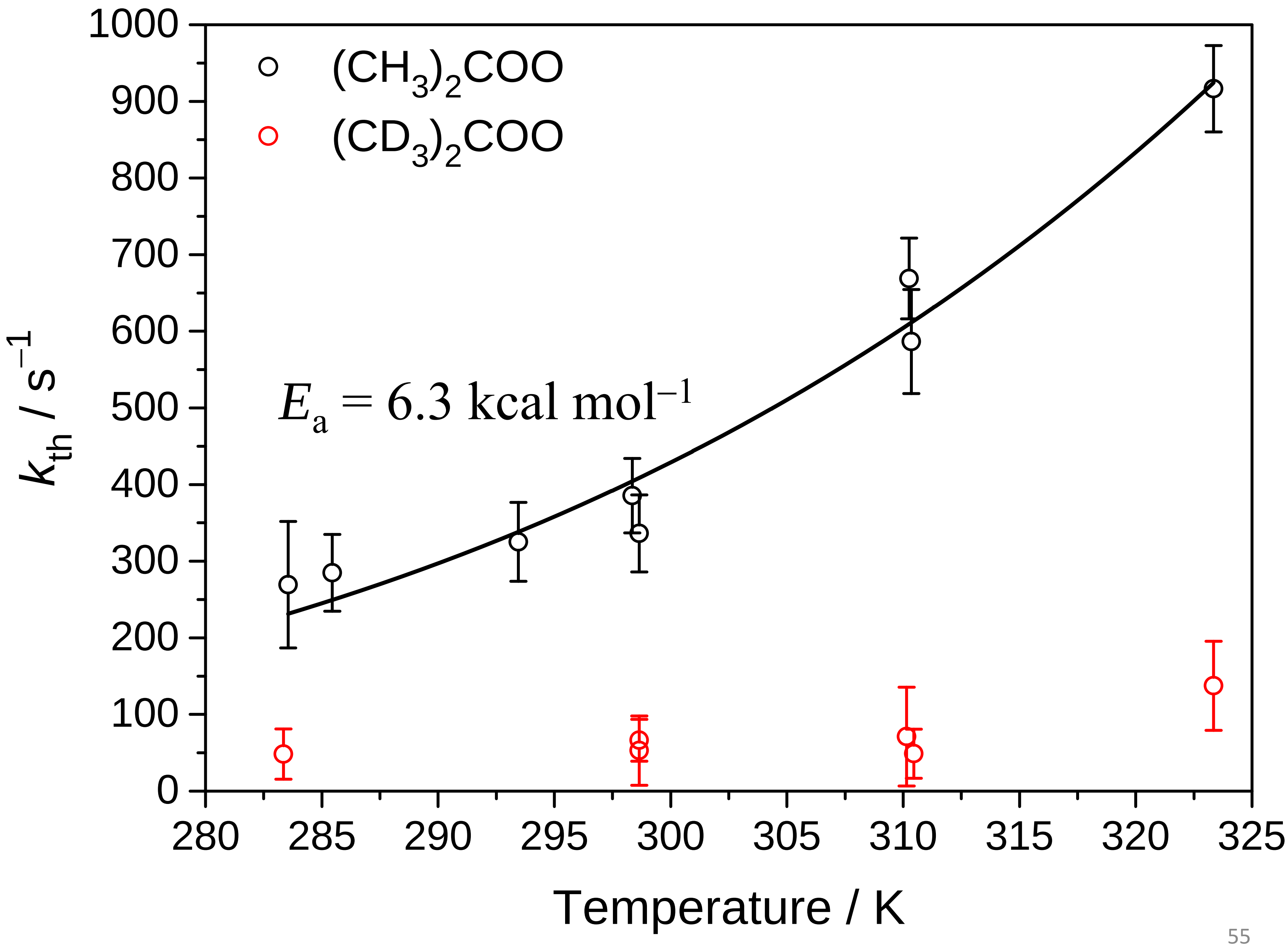
$$CI + I \rightarrow IO + \text{products}$$

$$CI + X \rightarrow \text{products}$$

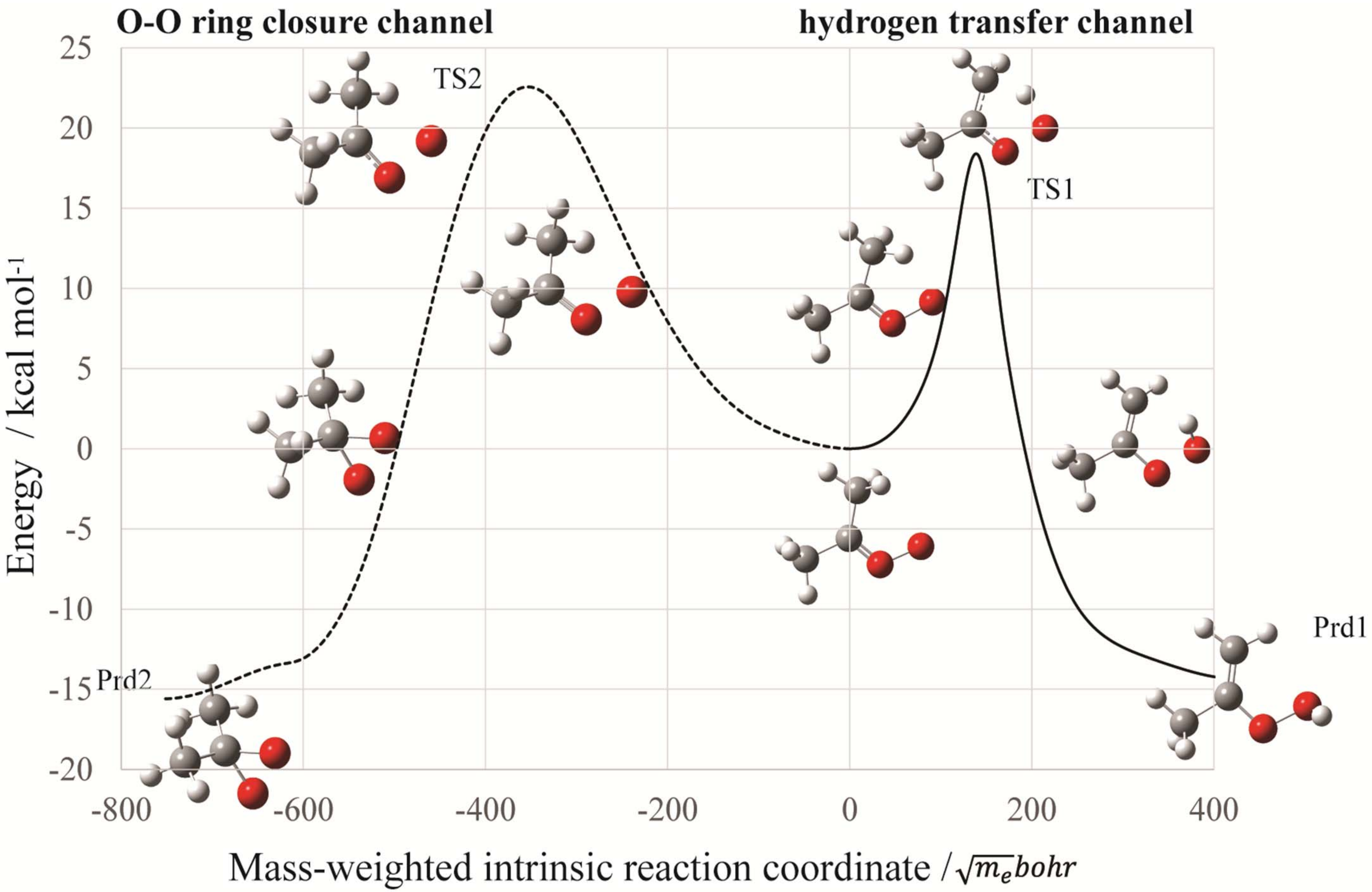
We need the decay rate at zero concentration!



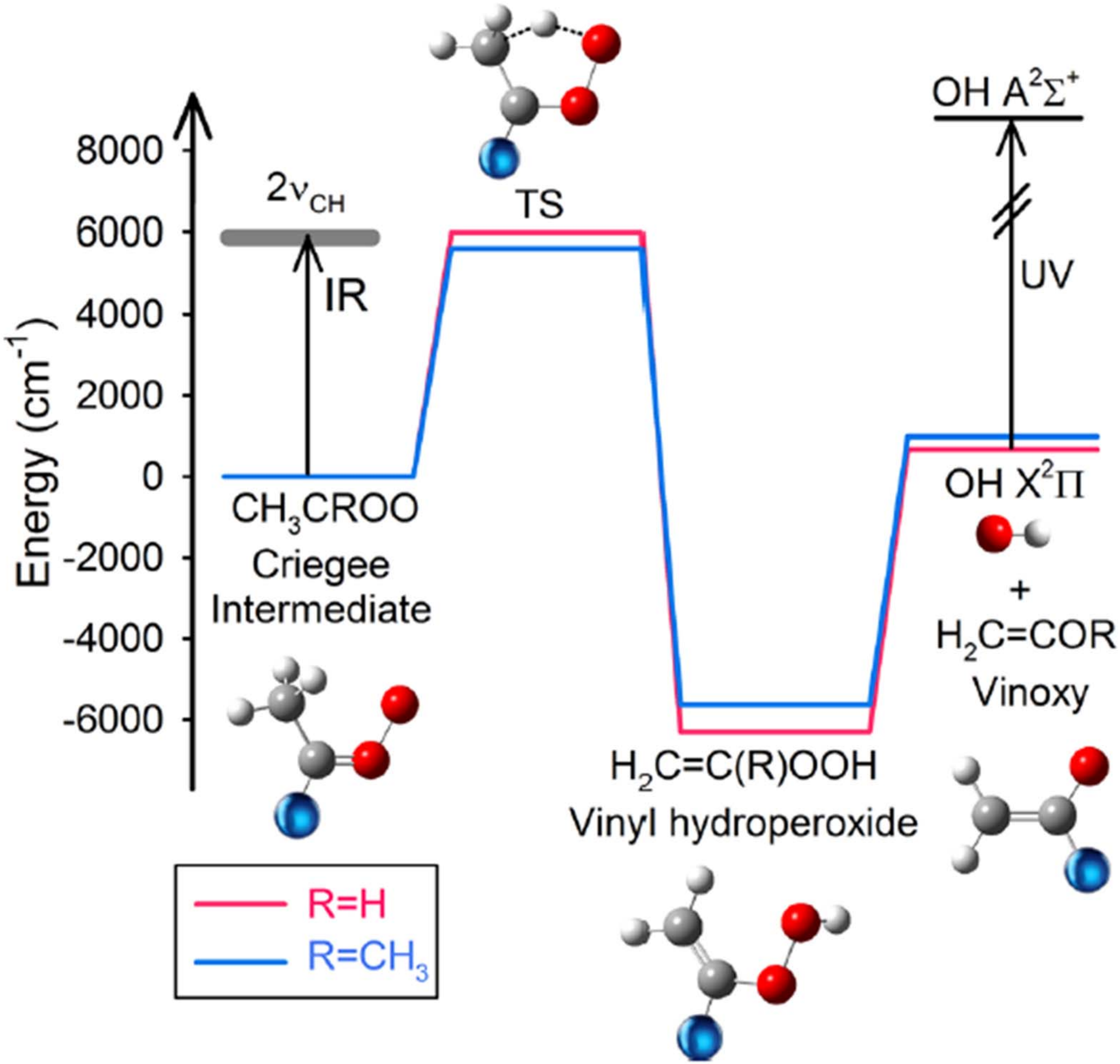
k1(1st+2nd model, k2 = 5.9x10−10 cm3s−1)
kobs (1st order model)
a) 283 K
k1(1st+2nd model, k2 = 7.8x10−10 cm3 s−1)
kobs (1st order model)
b) 298 K
k1(1st+2nd model, k2 = 8.8x10−10 cm3 s−1)
kobs(1st order model)
c) 310 K
d) 323 K
k1 (1st+2nd model, k2 = 1.5x10−9 cm3 s−1)
kobs (1st order model)
k / s−1
[(CH3)2COO]0 / 10^11 cm−3



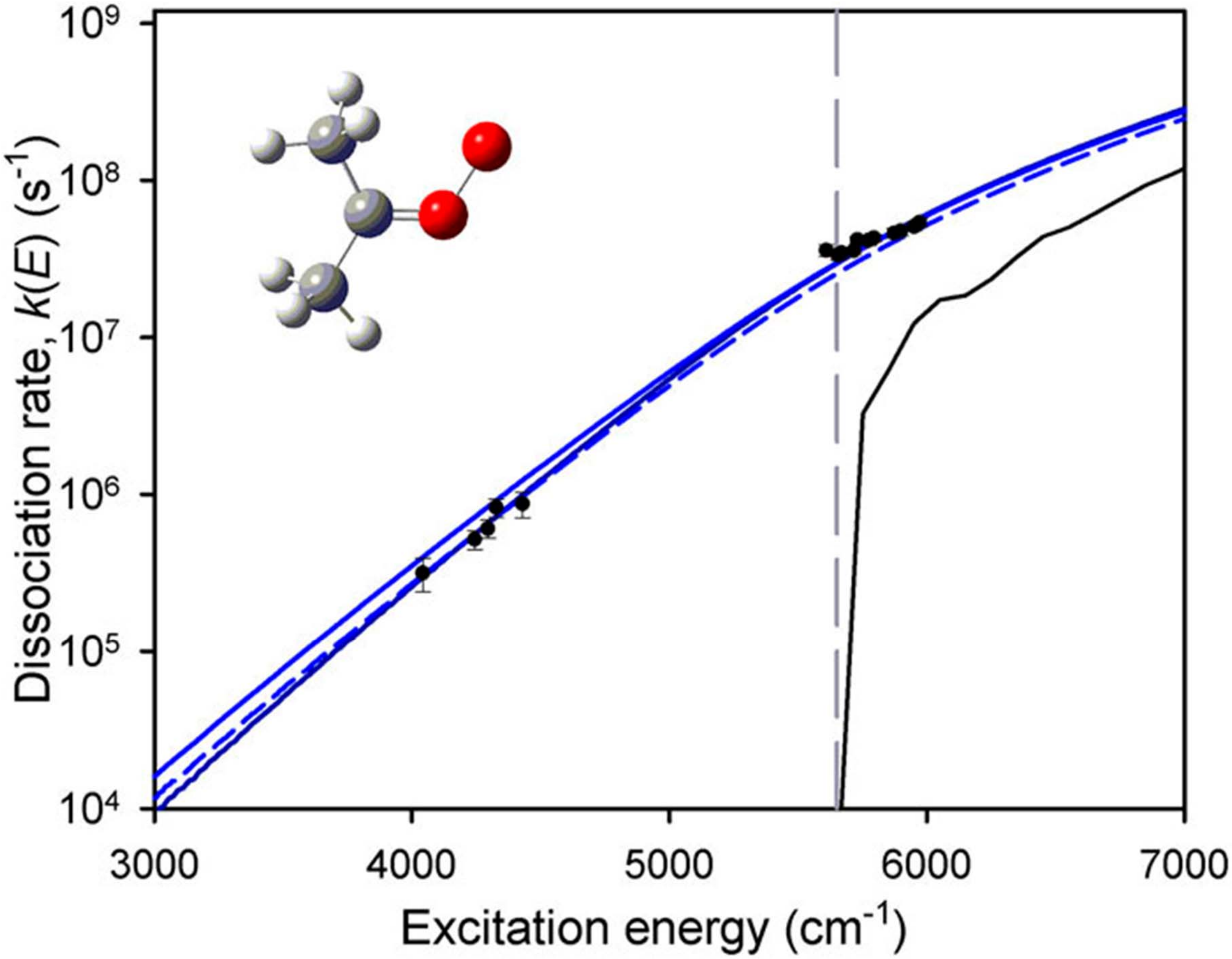
(CH3)2COO
(CD3)2COO
Ea = 6.3 kcal mol−1
kth / s−1
Temperature / K
0
100
200
300
400
500
600
700
800
900
1000
280
285
290
295
300
305
310
315
320
325



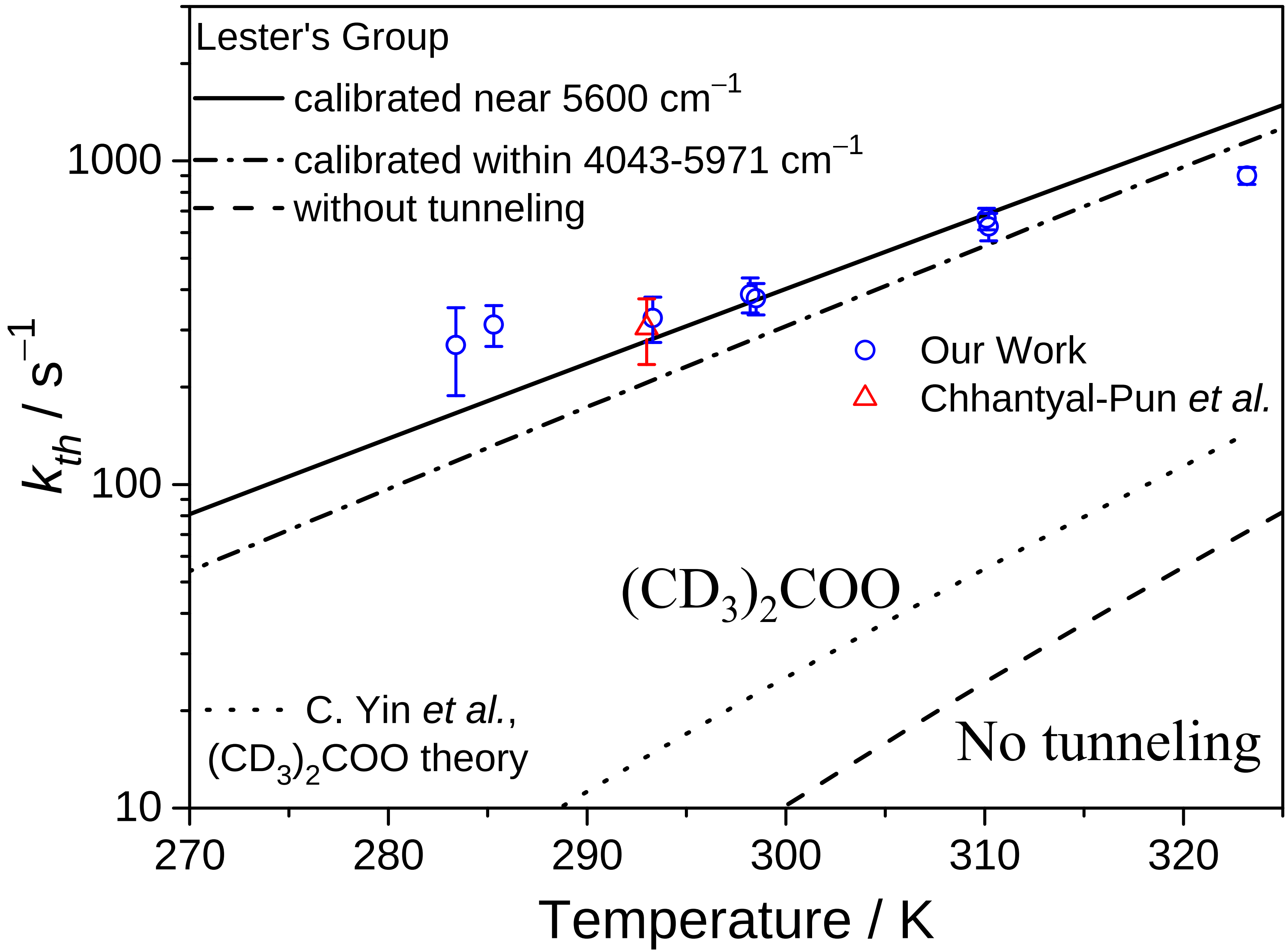
by Kaito Takahashi



Lester & coworkers, J. Chem. Phys. 144, 061102 (2016)

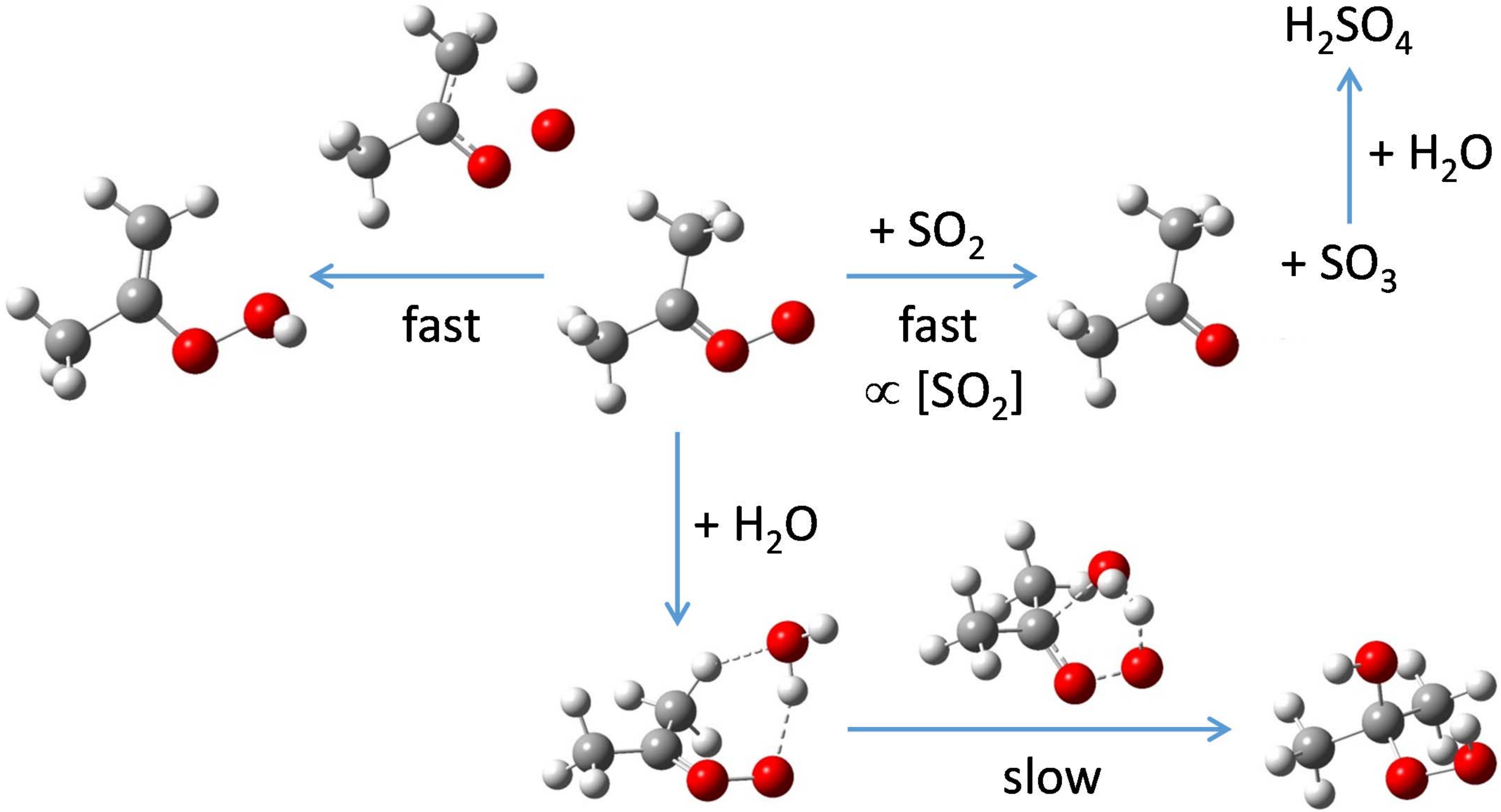


Lester group, J. Chem. Phys., 2017, 146, 134307.



Lester group, J. Chem. Phys., 2017, 146, 134307.

See Poster 4 on Board 1, especially data of CD_3CHOO



Kaito Takahashi, IAMS

Summary & more

Reactivity of Criegee intermediates towards water (dimer) depends strongly on their structures.

Anti forms react quickly with water (dimer).

Simple ***syn*** forms have significant thermal decomposition rates.

Can CI has enough concentration and oxidize atmospheric SO_2? Need More Complicated Structures.

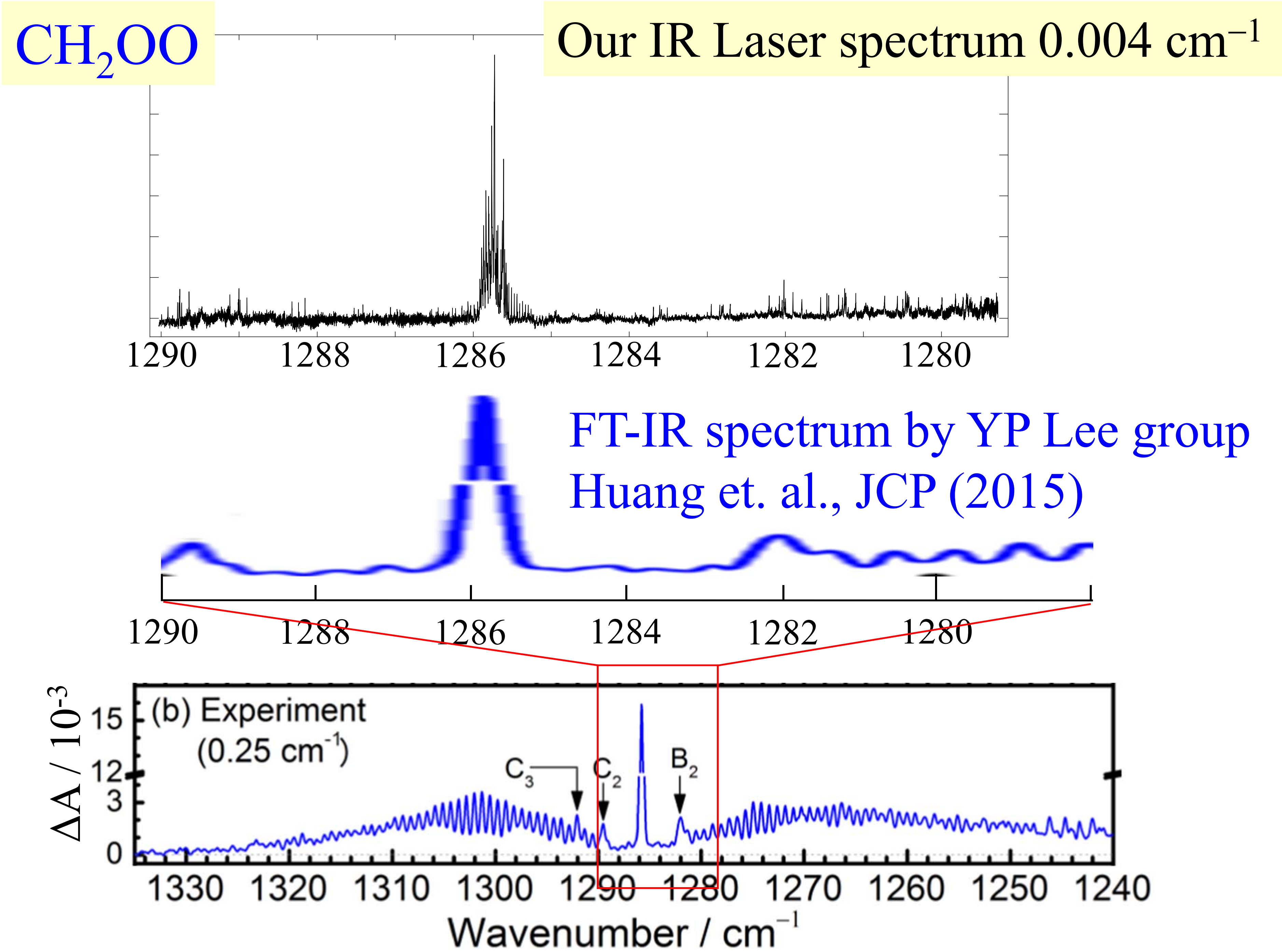
$CH_2OO + O_3$ reaction

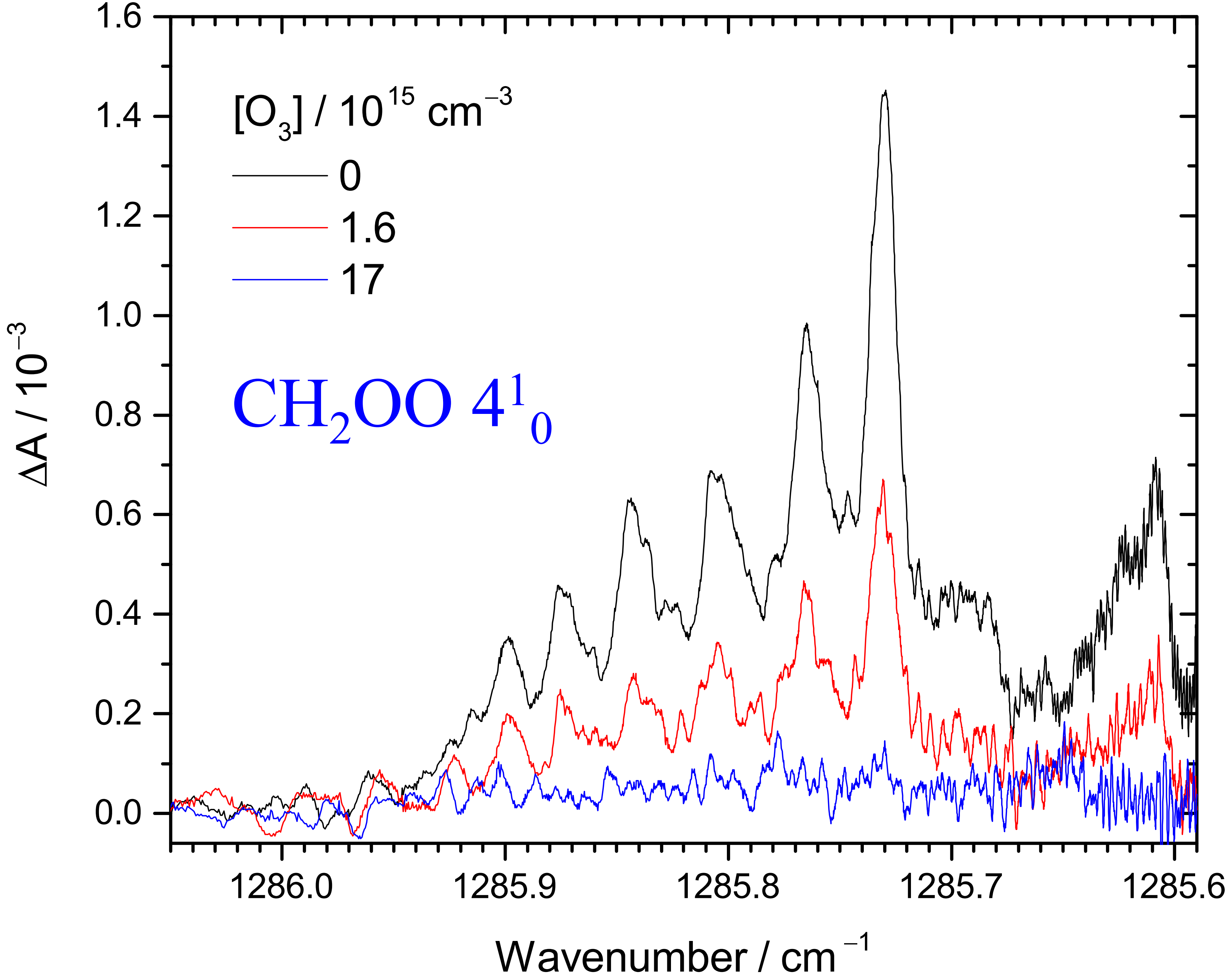
probed by

high resolution IR quantum cascade laser

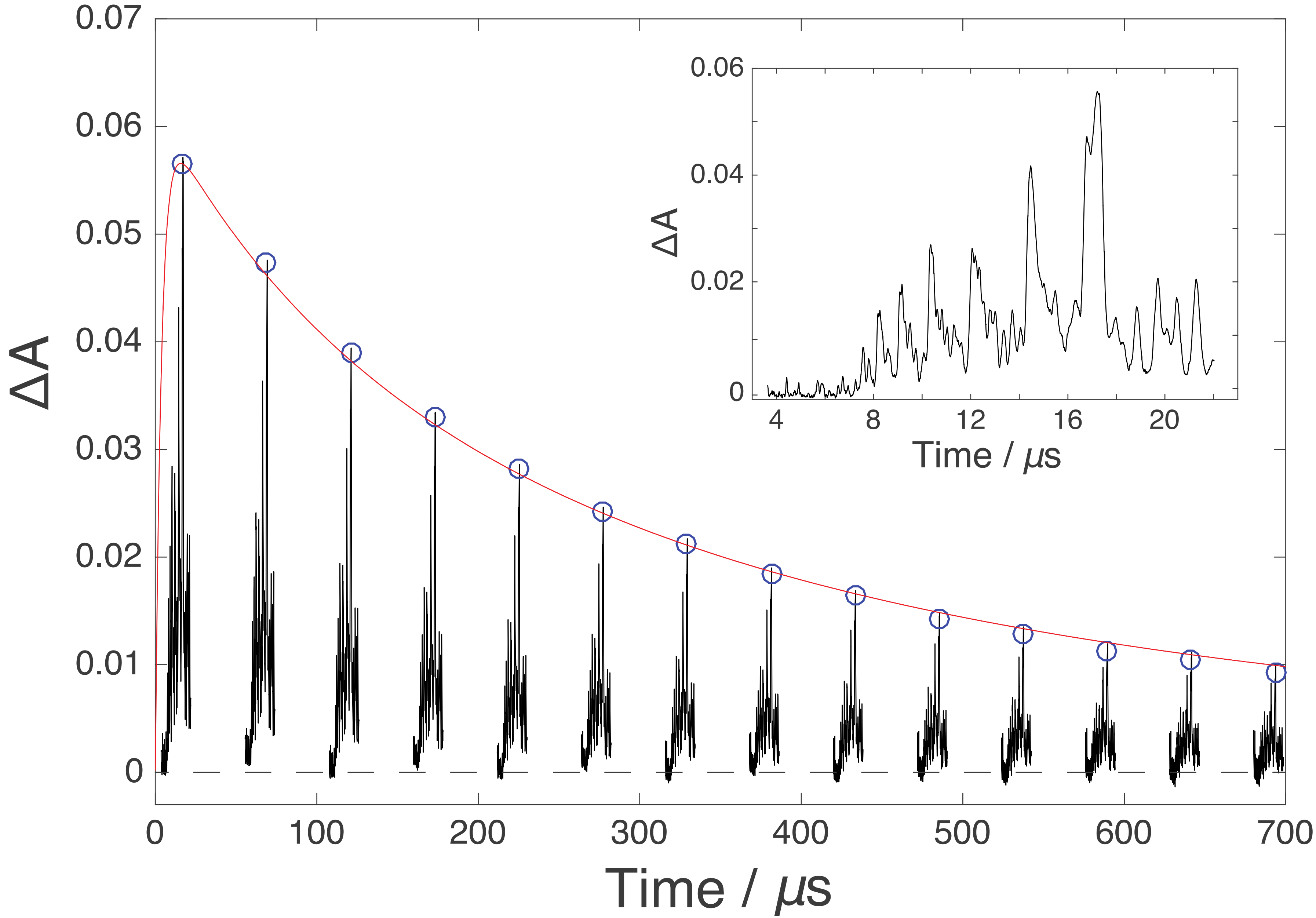
with Dr. Yuan-Pin Chang

Manuscript in preparation

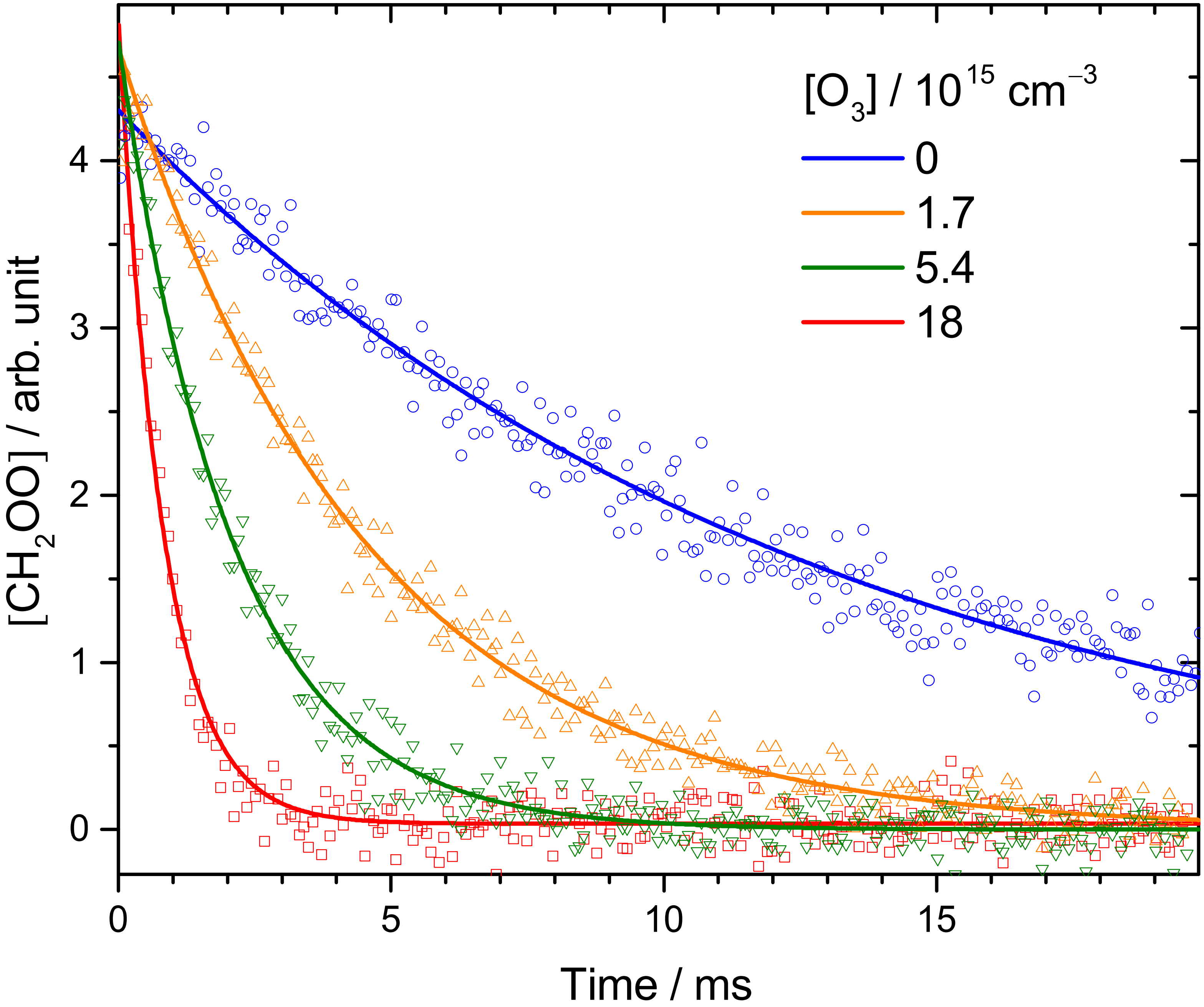

CH2OO
Our IR Laser spectrum 0.004 cm−1
1290
1288
1286
1284
1282
1280
FT-IR spectrum by YP Lee group
Huang et. al., JCP (2015)
1290
1288
1286
1284
1282
1280
(b) Experiment
(0.25 cm-1)
C3
C2
B2
ΔA / 10-3
15
12
3
0
1330
1320
1310
1300
1290
1280
1270
1260
1250
1240
Wavenumber / cm−1

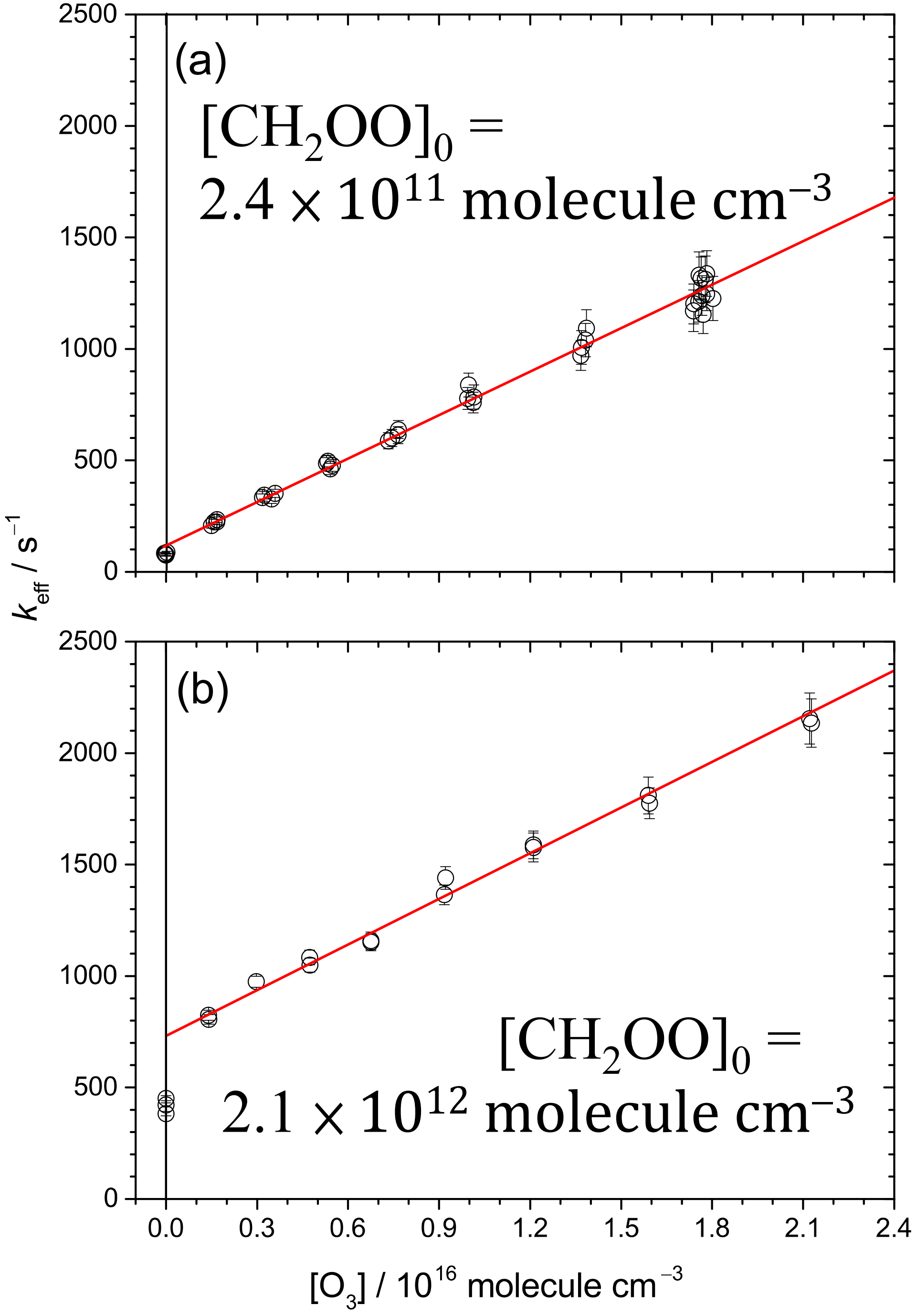


[O3] / 10^15 cm^−3
0
1.6
17
CH2OO 4^1_0
ΔA / 10^−3
Wavenumber / cm^−1
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1286.0
1285.9
1285.8
1285.7
1285.6



YP Chang et al., JCP 146, 244302 (2017)


[O3] / 10^15 cm^-3
0
1.7
5.4
18
[CH2OO] / arb. unit
0
1
2
3
4
0
5
10
15
Time / ms



Pseudo-1st-order kinetics

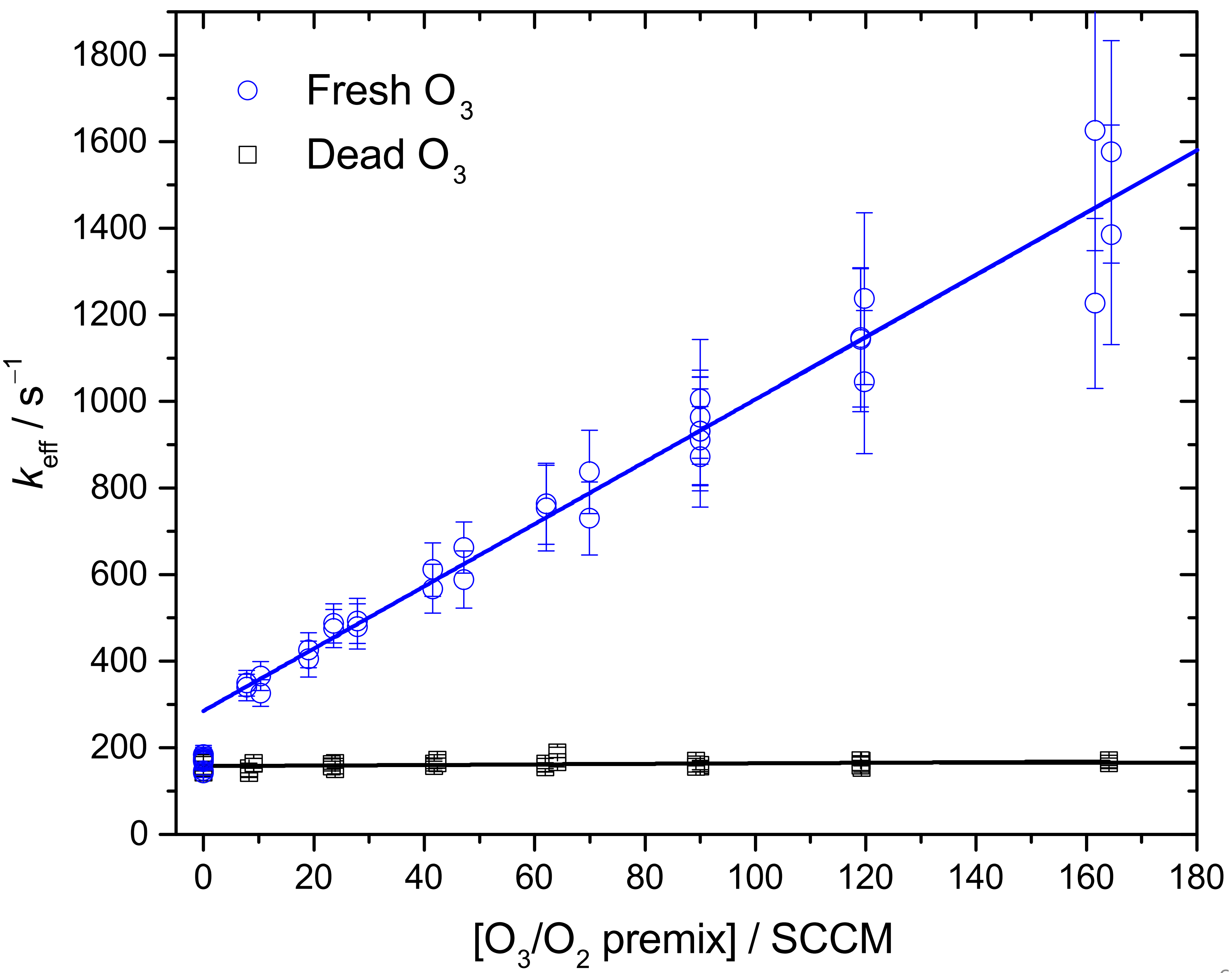
$$-d[CH_2OO]/dt$$

$$= k_0 [CH_2OO]$$

$$+ k_{O3} [O_3][CH_2OO]$$

$$\text{slope} = k_{O3}$$

$$= 6.7 \times 10^{-14}\ cm^3\ s^{-1}$$


Fresh O_3
Dead O_3
k_{eff} / s^{-1}
[O_3/O_2 premix] / SCCM
0
200
400
600
800
1000
1200
1400
1600
1800
0
20
40
60
80
100
120
140
160
180

$$CH_2I_2 + h\nu \rightarrow CH_2I + I$$

$$CH_2I + O_2 \rightarrow CH_2OO + I$$

$$O_3 + I \rightarrow \mathbf{IO} + O_2 \qquad k_8 = 1.28 \times 10^{-12}$$

$$O_3 + CH_2OO \rightarrow CH_2O + 2O_2 \qquad k_9 = 6.83 \times 10^{-14}$$

$$\mathbf{IO} + CH_2OO \rightarrow CH_2O + IO_2 \qquad k_{10} = 1.5 \times 10^{-10}\ ?$$

Method	k / $cm^3\ s^{-1}$	reference
CCSD(T)/aug-Schwartz(DT)	1.0×10^{-12}	Vereecken et. al., PCCP (2014)
ROCCSD(T)/Schwartz6(DTQ)	4.0×10^{-13}	Vereecken et. al., PCCP (2015)
Experiment	$(6.69 \pm 0.31) \times 10^{-14}$	This work
RB3LYP/aVTZ	3.98×10^{-16}	Kjaergaard et. al., JPCL (2013)
RHF-RCCSD(T)/aVTZ	2.60×10^{-17}	Kjaergaard et. al., JPCL (2013)
RHF-UCCSD(T)-F12A/VDZ-F12	5.73×10^{-18}	Kjaergaard et. al., JPCL (2013)
RHF-RCCSDT/cc-pVDZ	1.19×10^{-18}	Kjaergaard et. al., JPCL (2013)

$$$: Academia Sinica, Ministry of Science and Technology, Taiwan

Coworkers: Man-Nung Su, Wei-Lun Ting, Ying-Hsuan Chen, Mica C. Smith, Chun-Hung Chang, Jun-Ting Hsieh, Liang-Chun Lin, Hao-Li Huang, Hung-Tzu Chang, Chien-Hsun Chang, Yuan-Pin Chang, Hsun-Hui Chang

Collaborators: YP Lee, K Takahashi, YT Lee

Thank You for Your Attention