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Direct kinetic measurement of the reaction of the simplest Criegee intermediate with water vapor

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Carbonyl oxides or Criegee intermediates are important transient species formed in the reactions of unsaturated hydrocarbons with ozone. Although direct detection of Criegee intermediates has recently been realized, the main atmospheric sink of Criegee intermediates remains unclear. Here we report ultraviolet absorption spectroscopic measurements of the lifetime of the simplest Criegee intermediate CH_2OO at various relative humidity levels up to 85% at 298 Kelvin. An extremely fast decay rate (~ 5000 per second) of CH_2OO was observed at high humidity. The observed quadratic dependence of the decay rate on water concentration implied a predominant reaction with water dimer. Based on the water dimer equilibrium constant, the effective rate coefficient of the $CH_2OO + (H_2O)_2$ reaction was determined to be $(6.5 \pm 0.8) \times 10^{-12}$ cm^3 s^{-1}. This work would help modelers to better constrain the atmospheric concentrations of CH_2OO.

authors did not observe any significant reaction of CH_2OO with water (rxn. 1) and set an upper bound for the rate coefficient k_1 of 4×10^{-15} cm^3 s^{-1} (*1*). Using similar technique, Taatjes *et al.* measured the rate coefficient of the reaction of *anti*-CH_3CHOO with water to be $(1.0 \pm 0.4) \times 10^{-14}$ cm^3 s^{-1}, but still could not observe the reactions of water with CH_2OO and *syn*-CH_3CHOO (*2*). Stone *et al.* reported $k_1 < 9 \times 10^{-17}$ cm^3 s^{-1} by measuring the laser-induced fluorescence of H_2CO, a product in the CH_2OO reaction system (*7*). Ouyang *et al.* reported $k_1 = (2.5 \pm 1) \times 10^{-17}$ cm^3 sec^{-1}, determined in a relative rate experiment monitoring NO_3 production (*8*).

Evidence for significant reactivity of CH_2OO with water has been reported in C_2H_4 ozonolysis experiments (*9*, *10*), despite a large scatter in the reported rate coefficient (10^{-17} to 10^{-12} cm^3 s^{-1}) (*11–13*). Berndt *et al.* (*14*) investigated H_2SO_4 formation from SO_2 oxidation in C_2H_4 ozonolysis at

Abstract 1

- **Direct kinetic measurement of the reaction of the simplest Criegee intermediate with water vapor**
  Wen Chao, Jun-Ting Hsieh, Chun-Hung Chang, and Jim Jr-Min Lin
  Science 1261549Published online 1 January 2015
  »Abstract »Full Text »Full Text (PDF) »Supplementary Materials

Abstract 2

- **Infrared-driven unimolecular reaction of CH_3CHOO Criegee intermediates to OH radical products**
  Fang Liu, Joseph M. Beames, Andrew S. Petit, Anne B. McCoy, and Marsha I. Lester
  Science 26 September 2014: 1596-1598.
  »Abstract »Full Text »Full Text (PDF) »Supplementary Materials

Abstract 3

- **Infrared Absorption Spectrum of the Simplest Criegee Intermediate CH_2OO**
  Yu-Te Su, Yu-Hsuan Huang, Henryk A. Witek, and Yuan-Pern Lee
  Science 12 April 2013: 174-176.
  »Abstract »Full Text »Full Text (PDF) »Supplementary Materials

Abstract 4

- **Direct Measurements of Conformer-Dependent Reactivity of the Criegee Intermediate CH_3CHOO**
  Craig A. Taatjes, Oliver Welz, Arkke J. Eskola, John D. Savee, Adam M. Scheer, Dudley E. Shallcross, Brandon Rotavera, Edmond P. F. Lee, John M. Dyke, Daniel K. W. Mok, David L. Osborn, and Carl J. Percival
  Science 12 April 2013: 177-180.
  »Abstract »Full Text »Full Text (PDF) »Supplementary Materials

Abstract 5

- **Direct Kinetic Measurements of Criegee Intermediate (CH_2OO) Formed by Reaction of CH_2I with O_2**
  Oliver Welz, John D. Savee, David L. Osborn, Subith S. Vasu, Carl J. Percival, Dudley E. Shallcross, and Craig A. Taatjes
  Science 13 January 2012: 204-207.
  »Abstract »Full Text »Full Text (PDF) »Supporting Online Material

Direct kinetic measurement of the reaction of the simplest Criegee intermediate with water vapor

Wen Chao (趙玄),[1,2] Jun-Ting Hsieh (謝郡庭),[1,3]

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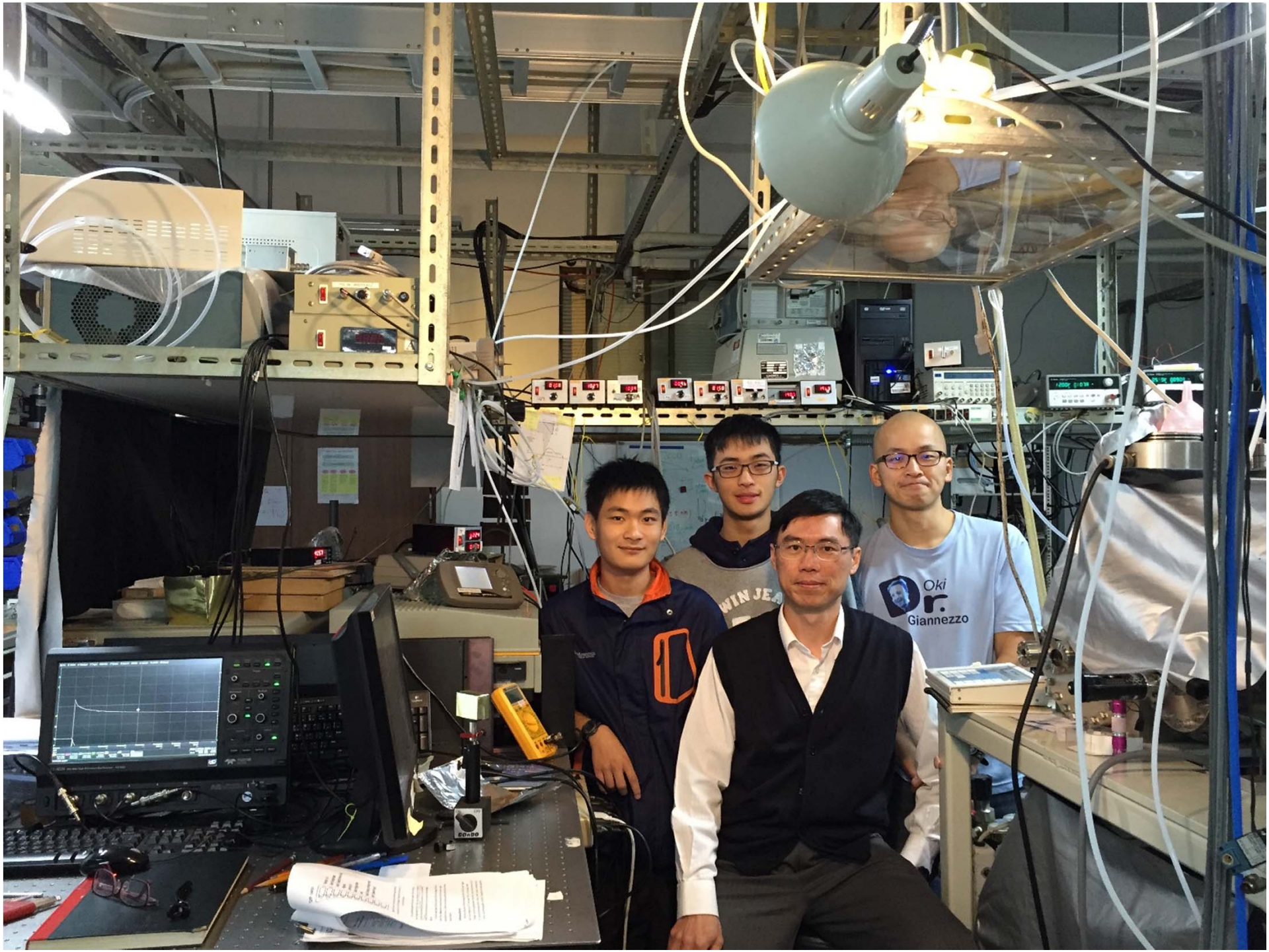
2. 國立臺灣大學化學系

3. 美國史丹佛大學

4. 國立交通大學應用化學系


Oki
Dr.
Giannezzo

中央研究院
原子與分子科學研究所

科學家在玩什麼？

系列演講暨體驗活動

http://playsci.iams.sinica.edu.tw/

趙彣 (花中高二)

謝郡庭 (升建中)

2010 種子小老師訓練營

乙烯、丙烯、異戊二烯・・・

臭氧 ＋ 不飽和碳氫化合物

「克里奇中間體」(Criegee Intermediates)

「克里奇中間體」(Criegee Intermediates, 簡稱 CIs)

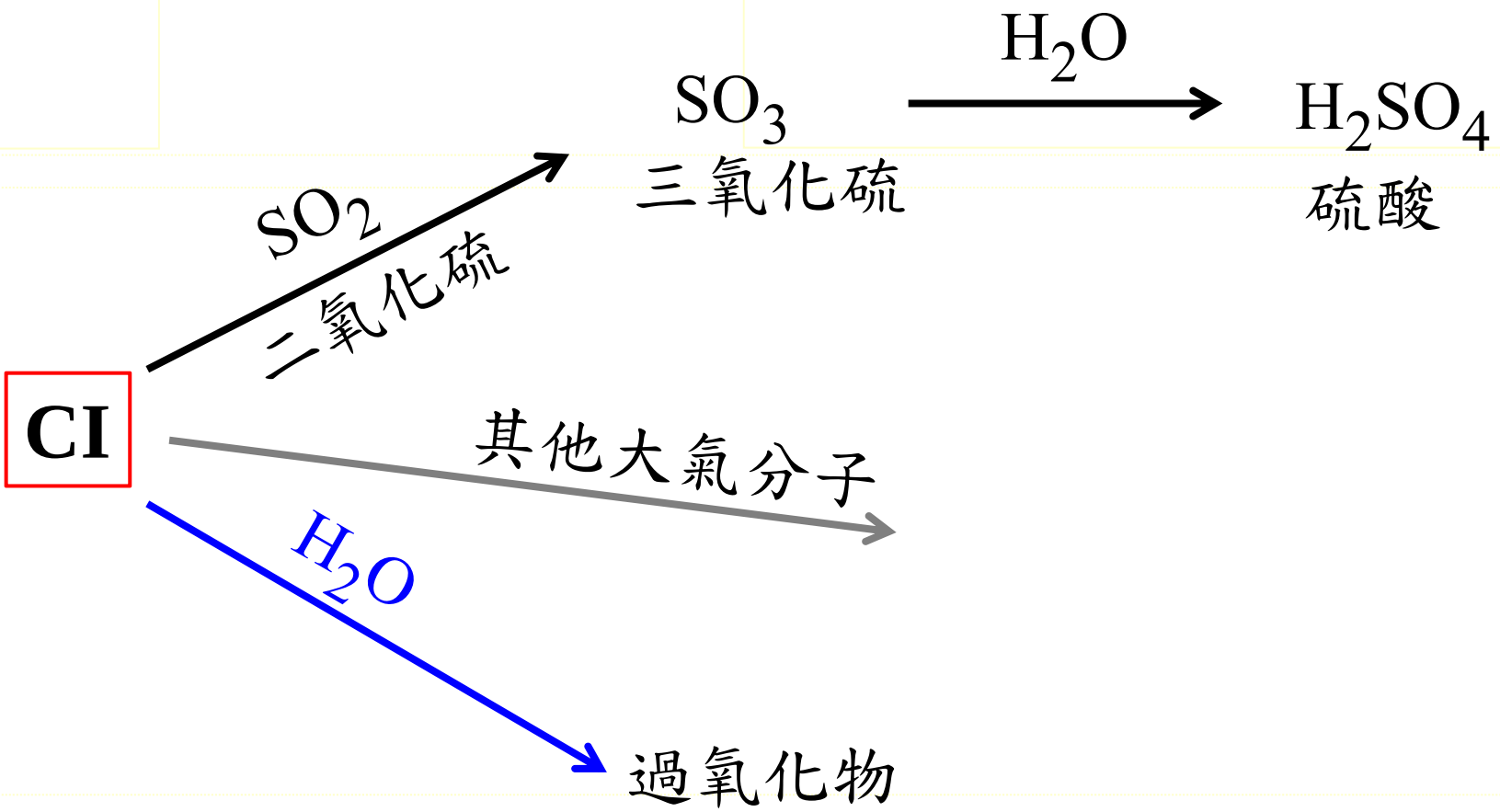
是一系列化合物的統稱，例如

CH_2OO (甲醛氧化物)

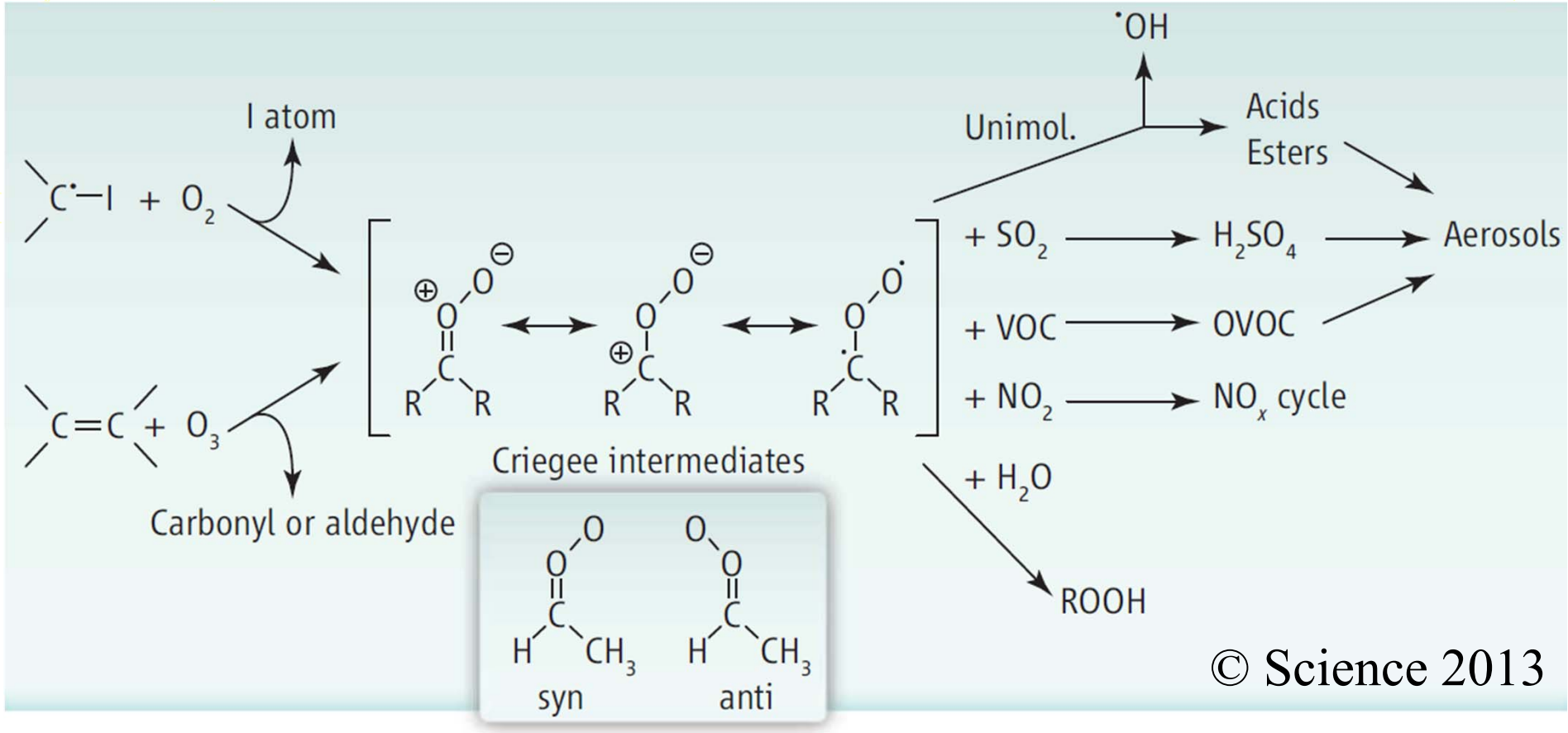
CH_3CHOO (乙醛氧化物)

$(CH_3)_2COO$ (丙酮氧化物), …

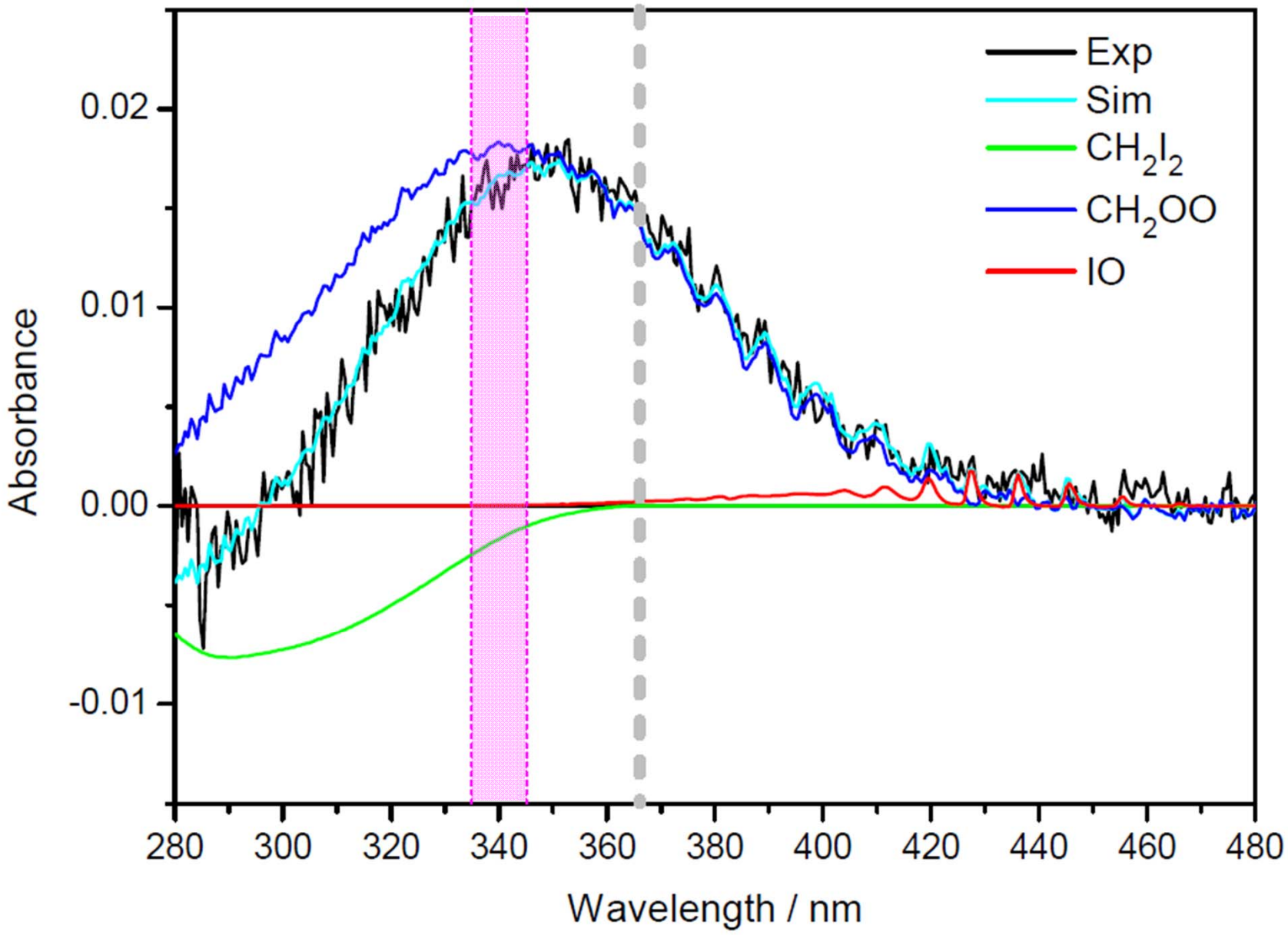
「克里奇中間體」 (Criegee Intermediate, 簡稱 **CI**)



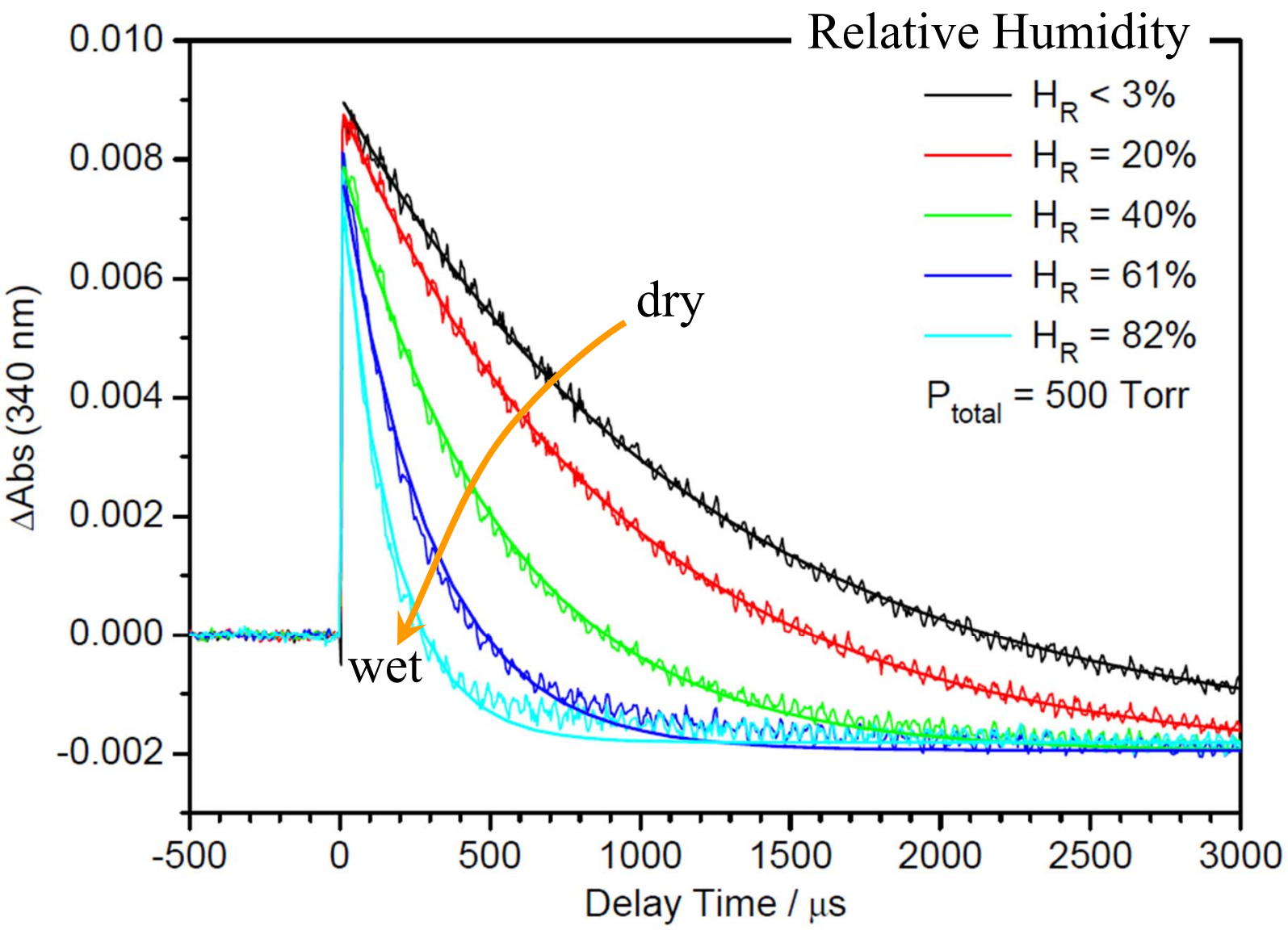
Criegee Intermediates

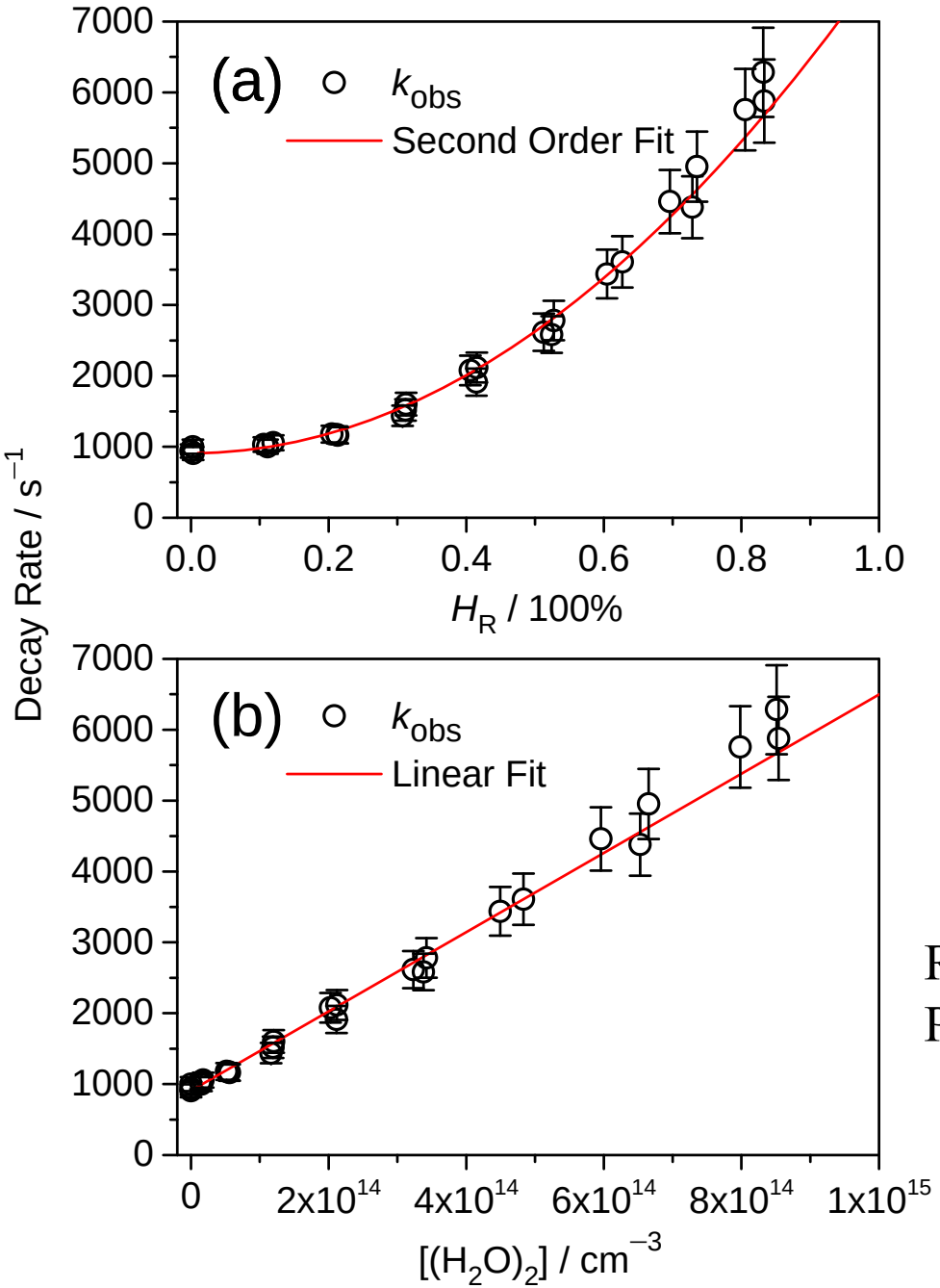


紫外吸收光譜偵測CH_2OO

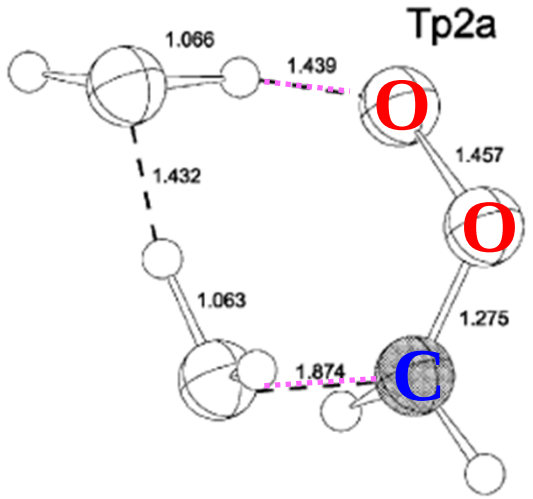


在不同溼度下CH_2OO的濃度隨時間之變化





Reaction with water dimer predominates for tropospheric CH_2OO!



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

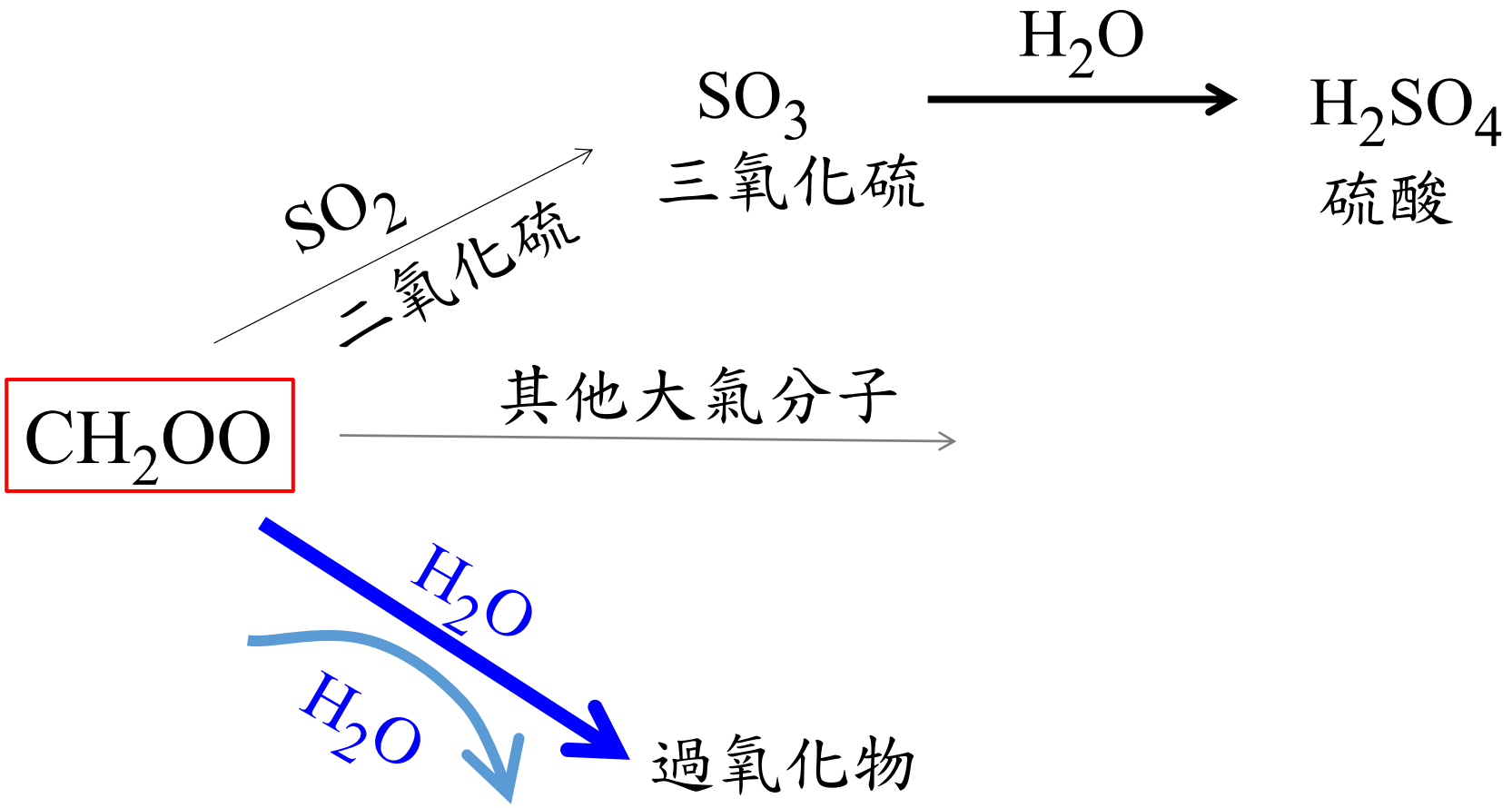
Possible atmospheric sinks of CH_2OO

Co-reactant	k_{rxn} (cm^3 sec^{-1})	Assumed Concentration[d]	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

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

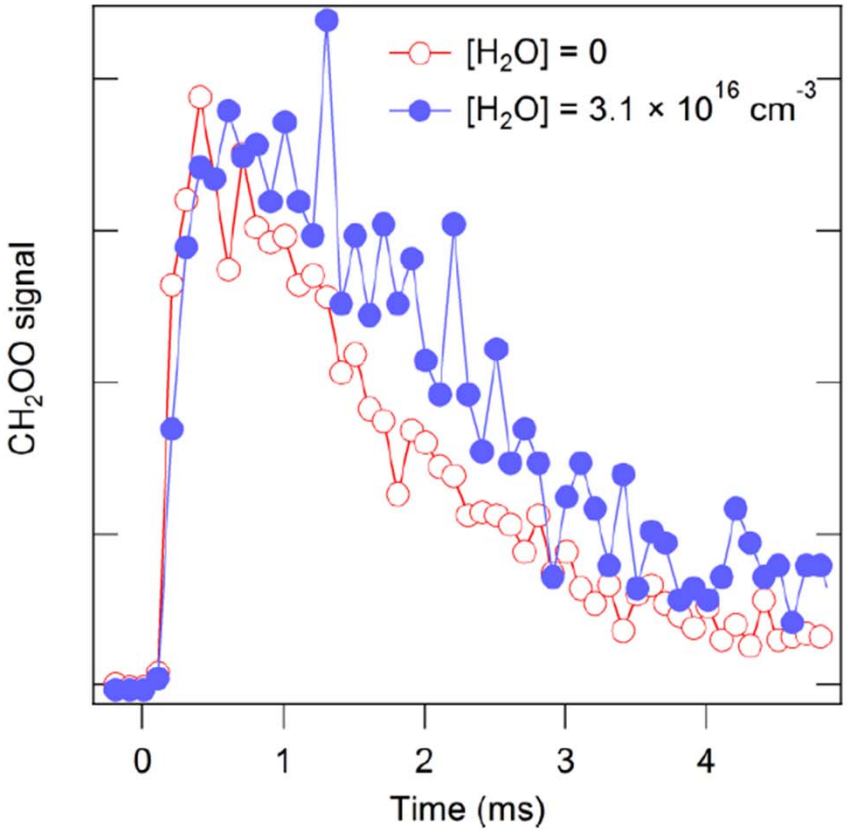
[c] O. Welz et al. *Angew. Chem. Int. Ed.* **53**, 4547-4550 (2014).

Simplest **CI**: 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);
DOI: 10.1126/science.1213229



受限於實驗氣壓

未觀察到**CI** 與

水蒸氣之反應

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 $[H_2O]$.

經驗的累積是成功的關鍵

但年輕人原本缺乏經驗

給年輕人機會累積經驗

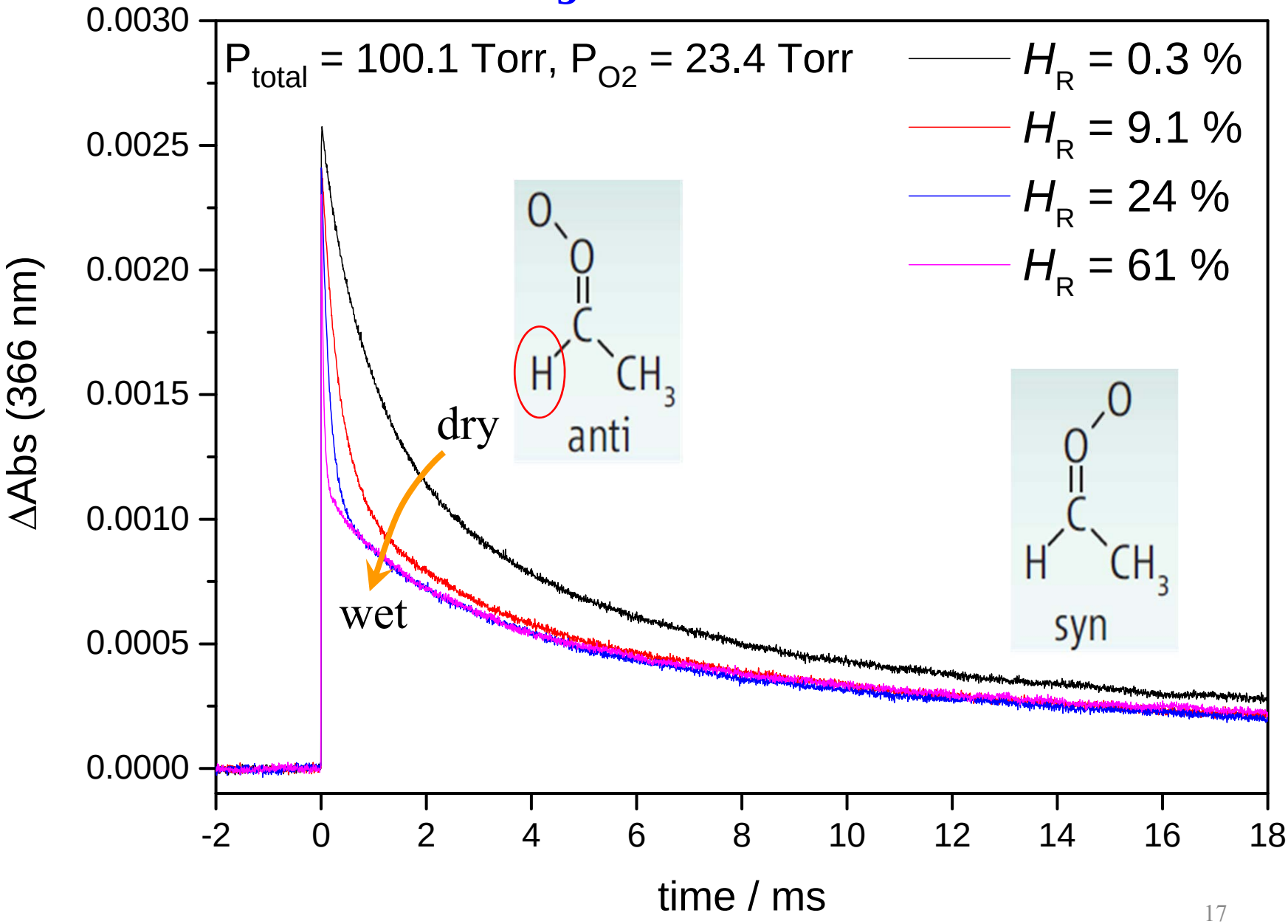
年輕人主動積極累積經驗

完成任務 做出貢獻

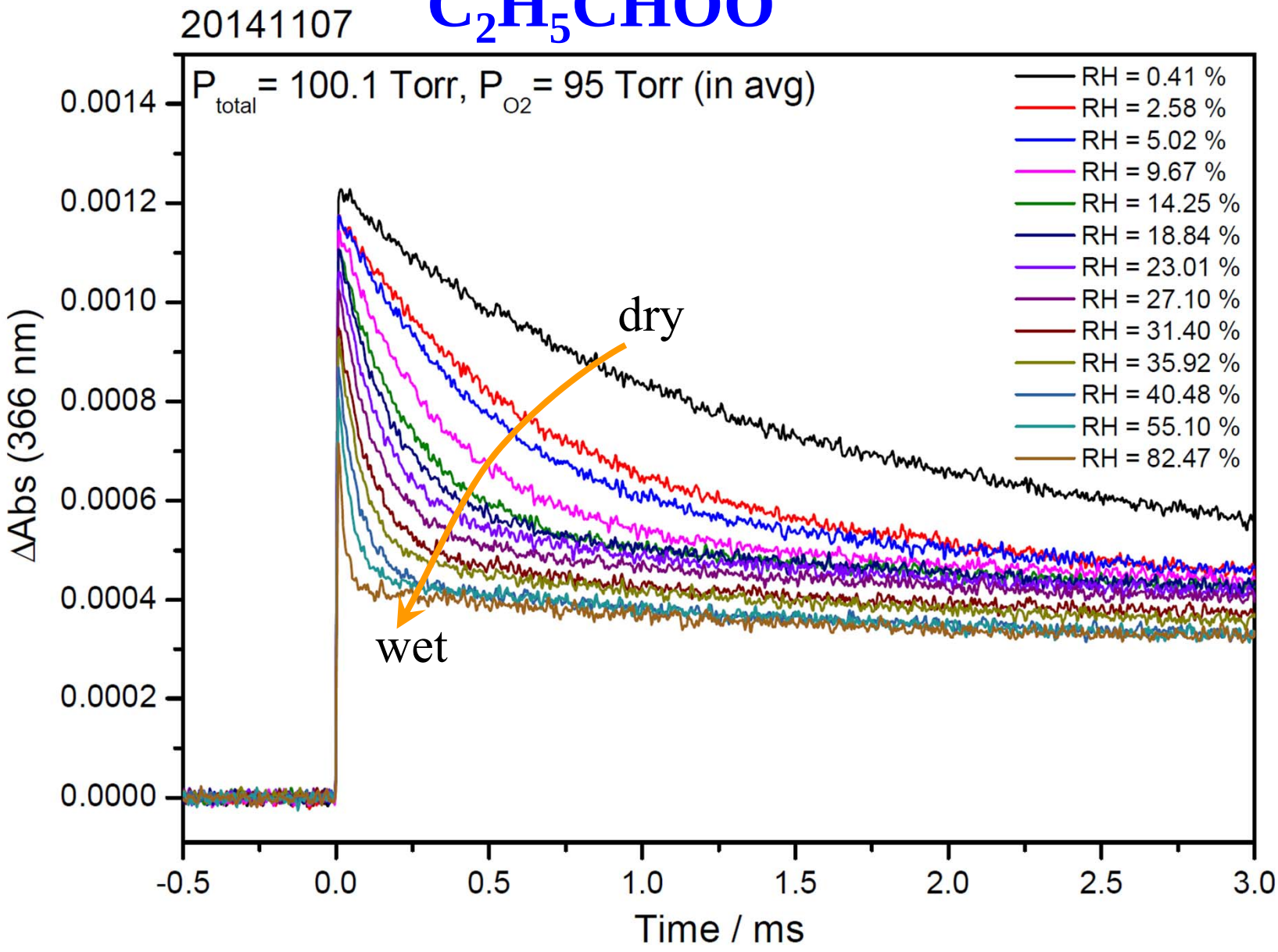
成就感 實踐感 自信

有時超越期待

CH_3CHOO


20141029
P_total = 100.1 Torr, P_O2 = 23.4 Torr
H_R = 0.3 %
H_R = 9.1 %
H_R = 24 %
H_R = 61 %
dry
wet
anti
syn
ΔAbs (366 nm)
time / ms
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

C_2H_5CHOO


20141107
P total = 100.1 Torr, P O2 = 95 Torr (in avg)
RH = 0.41 %
RH = 2.58 %
RH = 5.02 %
RH = 9.67 %
RH = 14.25 %
RH = 18.84 %
RH = 23.01 %
RH = 27.10 %
RH = 31.40 %
RH = 35.92 %
RH = 40.48 %
RH = 55.10 %
RH = 82.47 %
dry
wet
ΔAbs (366 nm)
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Time / ms

Thank You for Your Attention