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UV Spectroscopy and Reaction Kinetics of Criegee Intermediates: CH_2OO and CH_3CHOO

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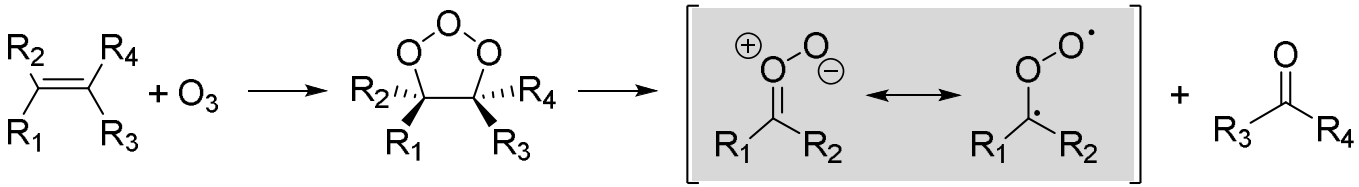
A very brief history of Criegee intermediates

1949 R. Criegee postulated that carbonyl oxides are intermediates in ozonolysis



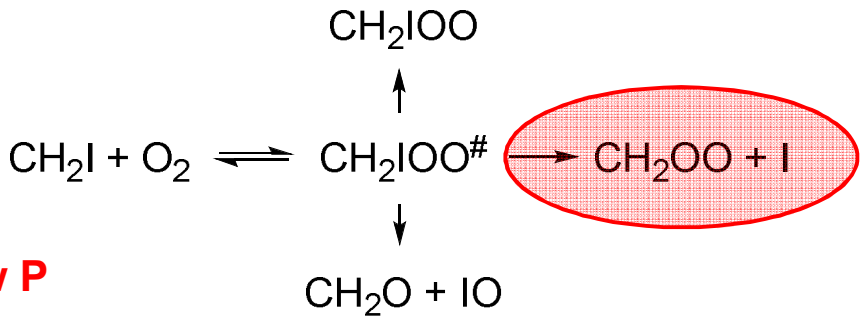
carbonyl oxides

Numerous indirect reactivity studies

No direct detection in the gas phase

2008 Direct detection of CH_2OO from DMSO oxidation by photoionization mass spectrometry (PIMS) *Taatjes and co-workers*

2012 **A simple new method of CI production in the lab:** *Welz et al.*



CH_2OO formation dominates at low P
Yield approaches 1 (!)

A very brief history of Criegee intermediates

2012 – 2014

Direct kinetic studies are now possible

- Reaction products (OH, CH_2O) — *The Leeds group, Sander and co-workers*
- CI detection by PIMS — *Taatjes, Osborn, Percival, Shalcross et al.*
- IR Spectroscopy — *Y.-P. Lee and co-workers*

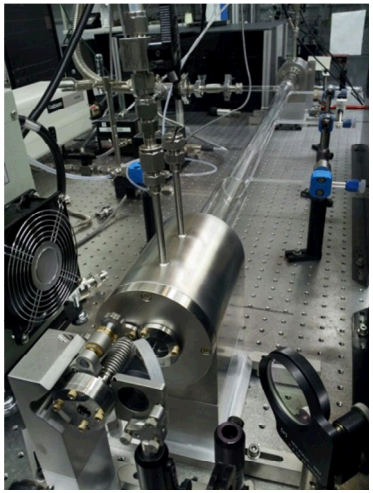
Intense interest in the spectroscopy of CI

- IR spectrum of CH_2OO — *Y.-P. Lee and co-workers*
- MW spectra of CH_2OO and syn-CH_3CHOO — *Nakajima and Endo, McCarthy et al.*
- UV (*B*-state) spectra of C1–C3 CI — *M. I. Lester and co-workers*

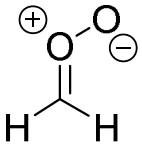
What about UV probing of kinetics?

Outline:

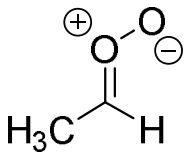
I. A new experimental tool for gas-phase chemical kinetics
Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry



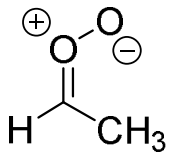
II. UV spectroscopy and reaction kinetics of CH_2OO



III. The search for UV spectrum of CH_3CHOO



anti-



syn-

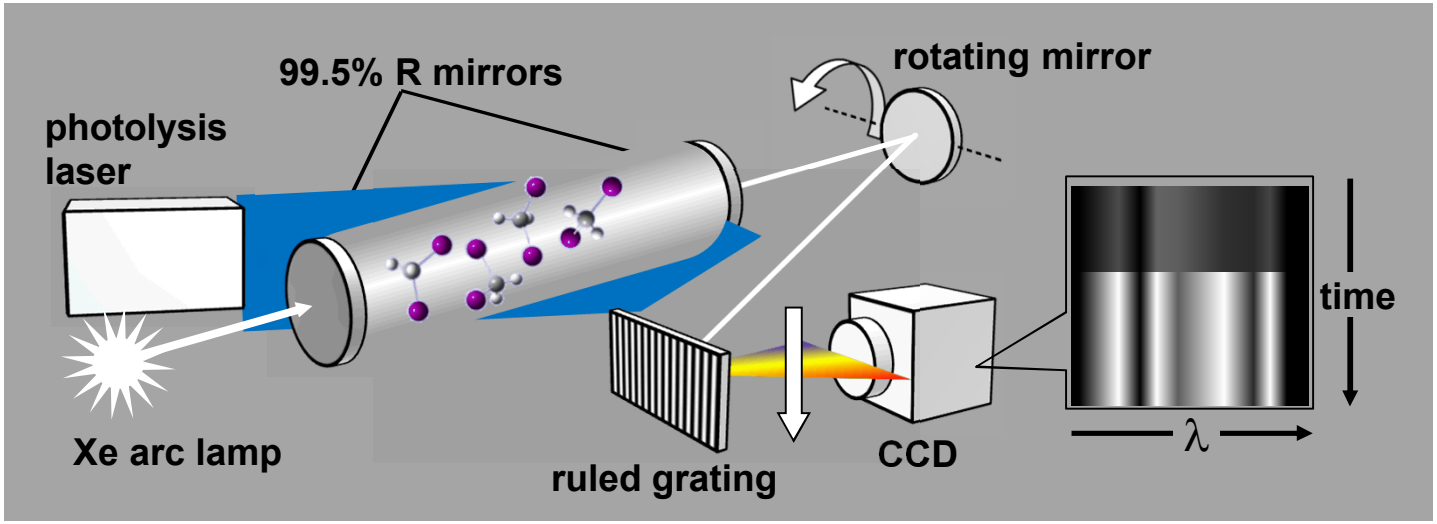
Development of a new tool for gas-phase chemical kinetics

Experimental capabilities needed for direct measurement of gas-phase kinetics:

- Real-time measurement of concentrations
- Multiplexed, many species detected at once
- Sensitive detection under dilute conditions
- Non-intrusive, *in situ* probe

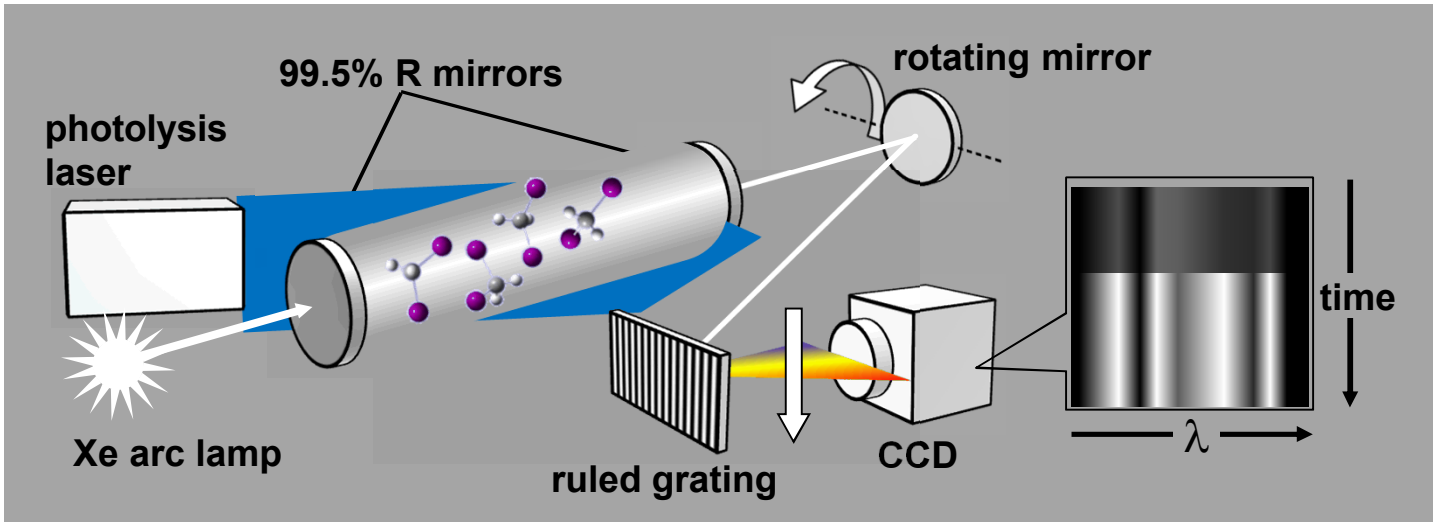
- ➢ **time-resolved**
- ➢ **broadband**
- ➢ **cavity-enhanced**
- ➢ **absorption spectrometry**

Time-Resolved Broadband Cavity-Enhanced Absorption Spectroscopy



- **"White light" probe radiation source**
- **Broadband optical cavity (300 – 700 nm),**
  Factor of ~ 100x path length enhancement
- **Laser photolysis reactor integrated into cavity**
- **Custom time-resolved spectrometer**
  Transient absorption is spatially mapped onto CCD
  - **X–axis ↔ probe λ**
  - **Y–axis ↔ time**

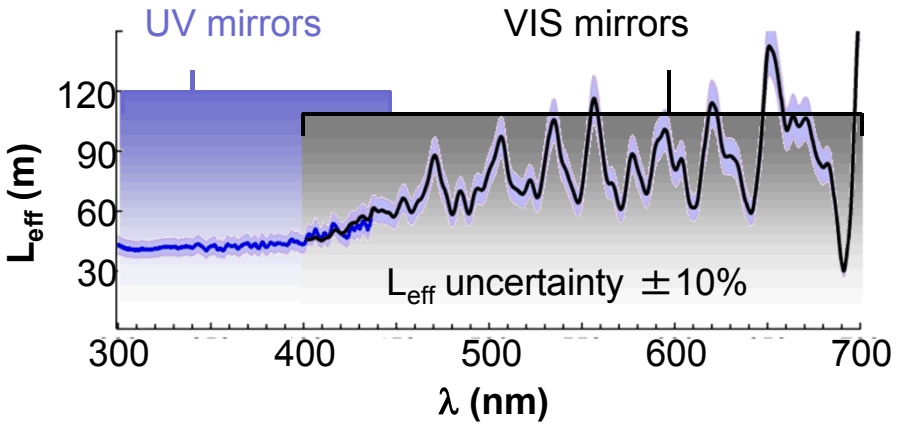
Time-Resolved Broadband Cavity-Enhanced Absorption Spectroscopy



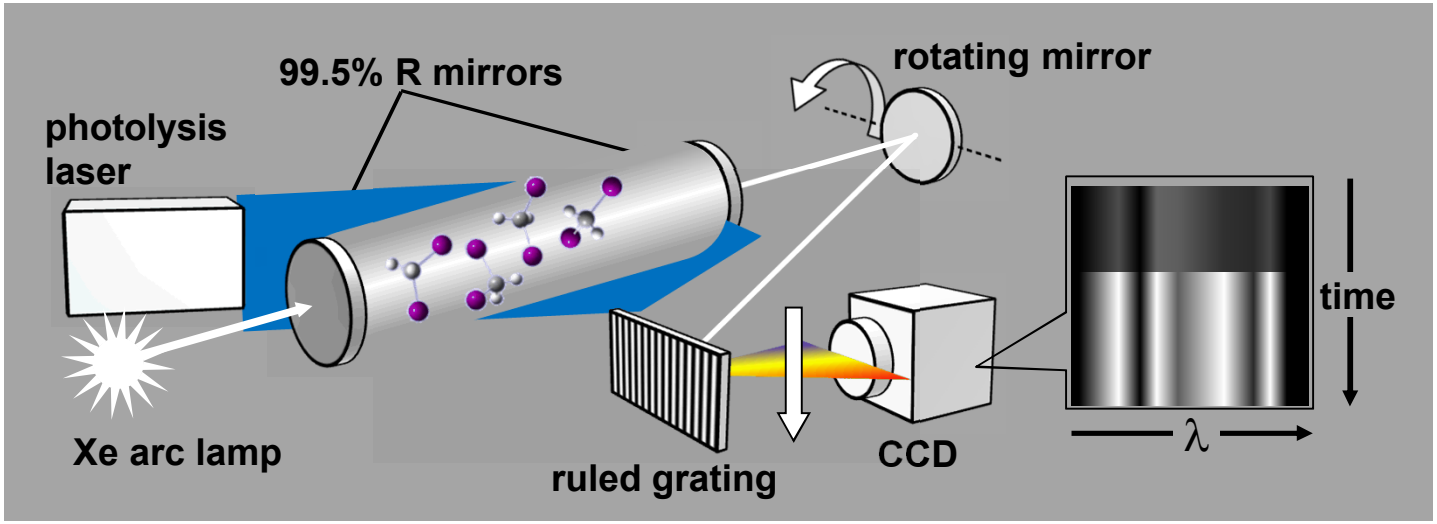
Effective path length

- L_{eff} (λ) must be measured using absorption "standards" – NO_2 and CH_2I_2

  L_{eff} ≥ 40 m over the UV-VIS range



Time-Resolved Broadband Cavity-Enhanced Absorption Spectroscopy



Instrument resolution

- In this study: wavelength resolution ~ 1 nm, full-scale range ~ 200 nm
  time resolution ~ 30 μs, full-scale range ~ 7 ms.

Accessible experimental conditions

Current Study:

- P = 1 – 30 torr
- T ~ 295 K

Design limitations:

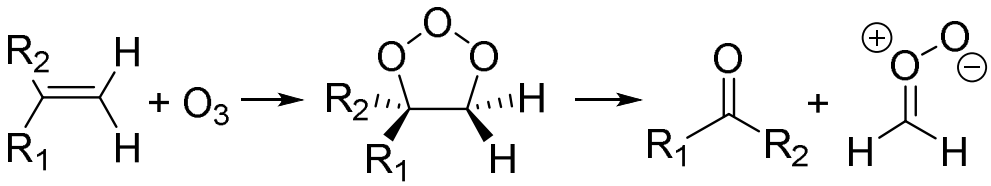
- Turbulence-free conditions at P up to 760 torr
- Heating jacket installed, capable of T up to 700 K

Price tag: ~$40K (excluding photolysis laser)

Formaldehyde oxide, CH_2OO – a prototypical Criegee intermediate

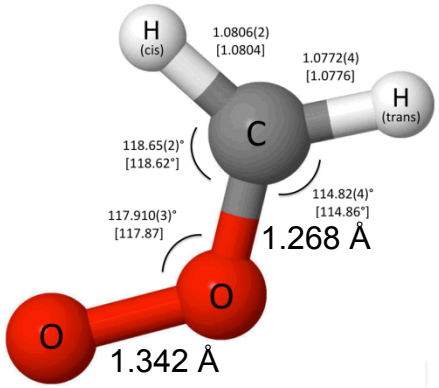
Smallest possible CI

- Terminal C=C bonds



(X $^1A'$) state well-characterized

- IR spectroscopy *Su et al.*
- MW spectroscopy *McCarthy et al., Endo et al.*
- *Ab initio* calculations *Stanton et al., Li et al., Lee et al.*
  - Equilibrium geometry
  - Electronic structure (zwitterionic character)

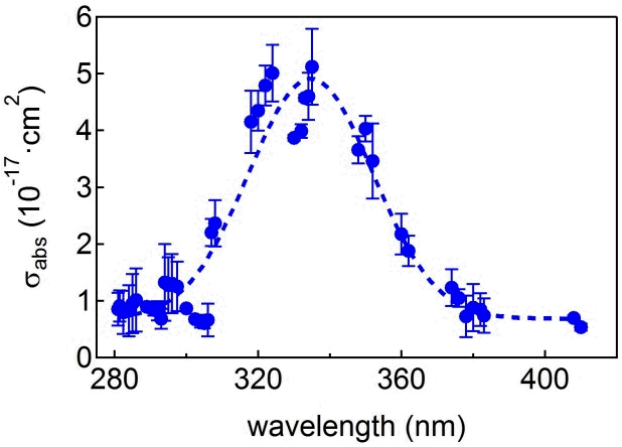


from McCarthy *et al.*, 2013

Excited states are less well understood

- 4 low-lying excited states predicted
- Strong absorption to B $^1A'$ state, ~4 eV

- Beames *et al.* observed B state by CH_2OO^+ ion depletion (photoionization mass spec)



from Beames *et al.*, 2012

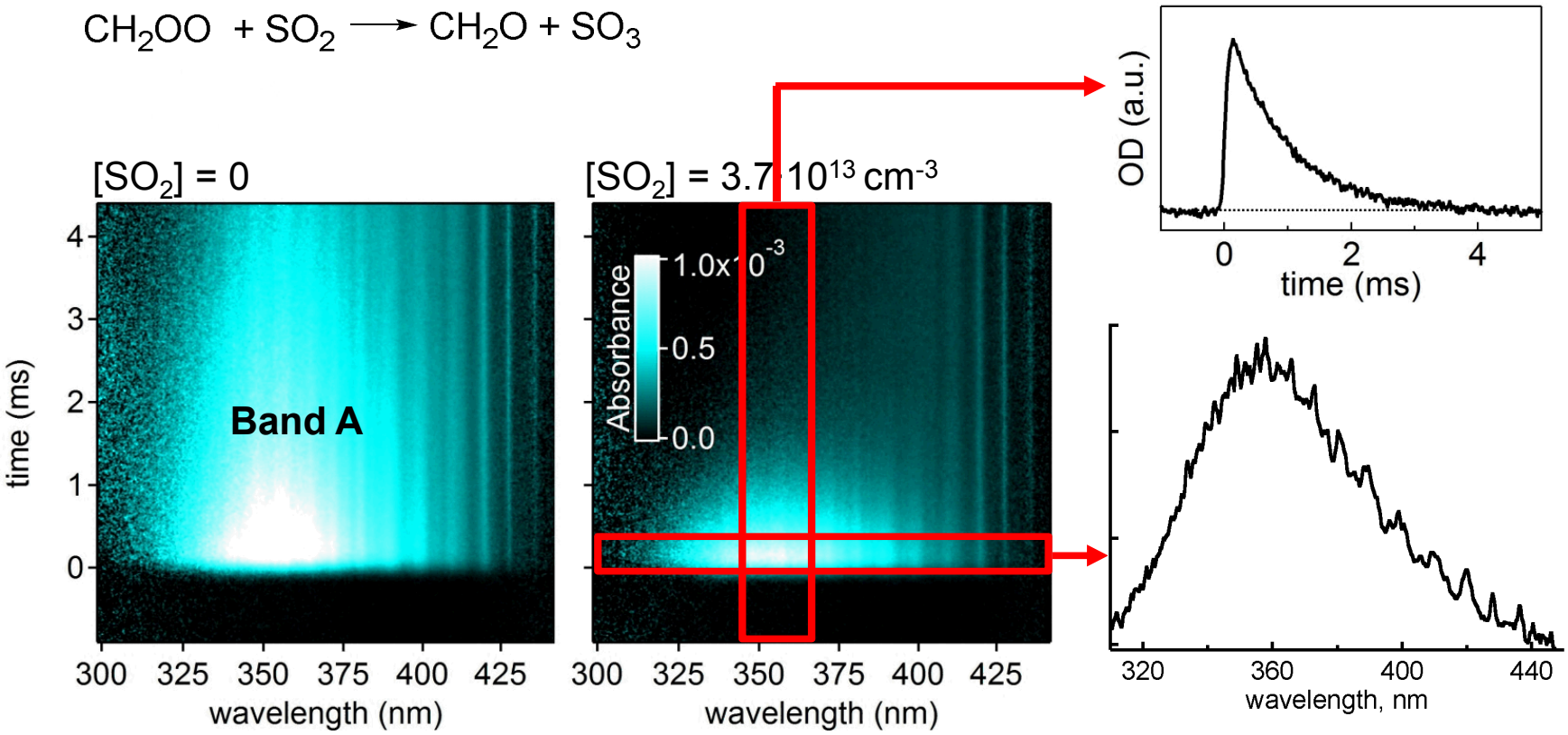
Could this strong UV absorption be used for kinetics measurements?

Identification of the CH_2OO UV absorption spectrum

CH_2OO produced by 266-nm photolysis of CH_2I_2 in the presence of O_2

$$CH_2I_2 \xrightarrow{h\nu} CH_2I + I$$
$$CH_2I + O_2 \longrightarrow CH_2OO + I$$
$$CH_2OO + SO_2 \longrightarrow CH_2O + SO_3$$

P = 5.1 torr, T = 295 K, He buffer gas
$[CH_2I]_0 \sim 5\cdot10^{11}cm^{-3}$, $[O_2] \sim 8.4\cdot10^{15}cm^{-3}$



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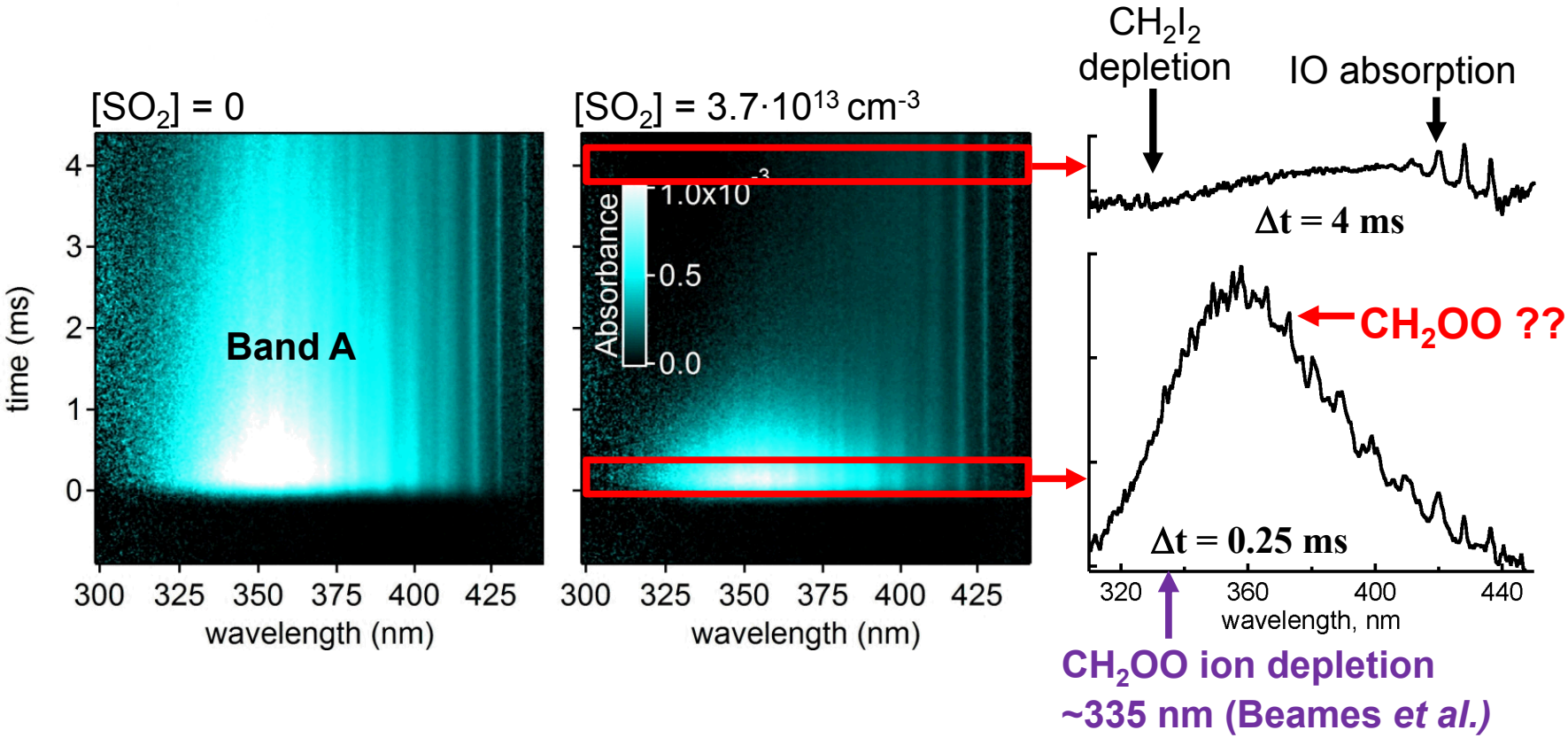
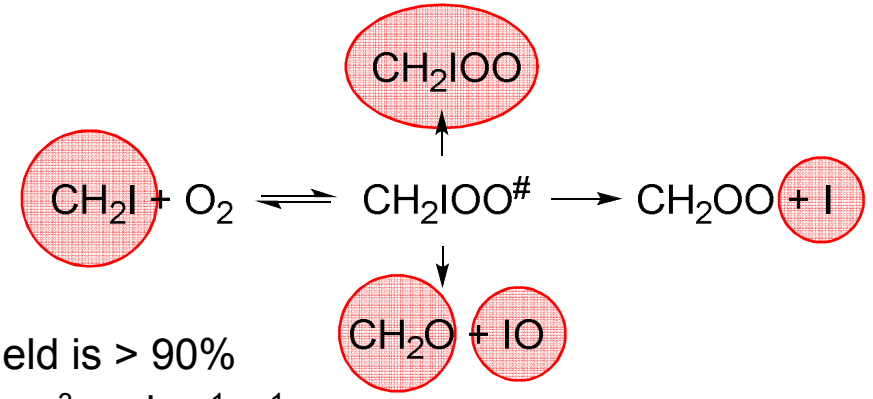


UV probing of the formation kinetics of CH_2OO

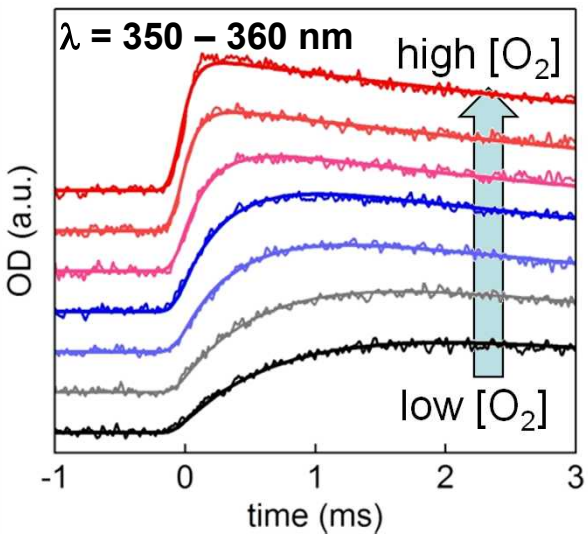
$CH_2I + O_2$ has been studied before

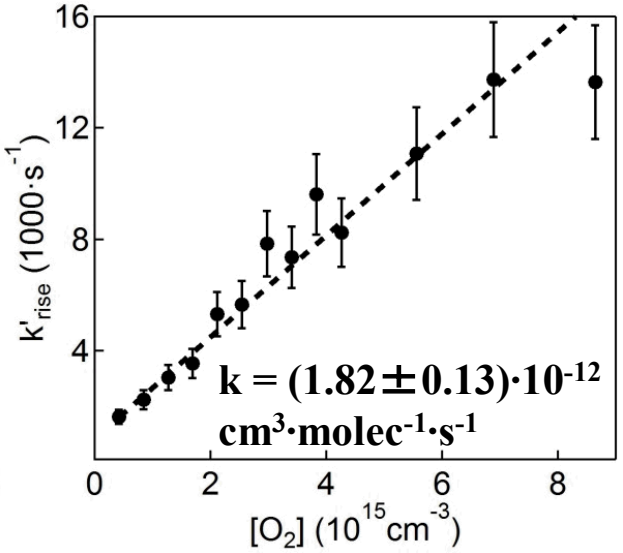
- Masaki *et al.*
- Eskola *et al.*
- Huang *et al.*
- Gravestock *et al.*
- Stone *et al.*



- At low P used in this study CH_2OO yield is > 90%
- Rate coefficient $k_1 = (1.6 \pm 0.2) \cdot 10^{-12}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$

Using UV absorption





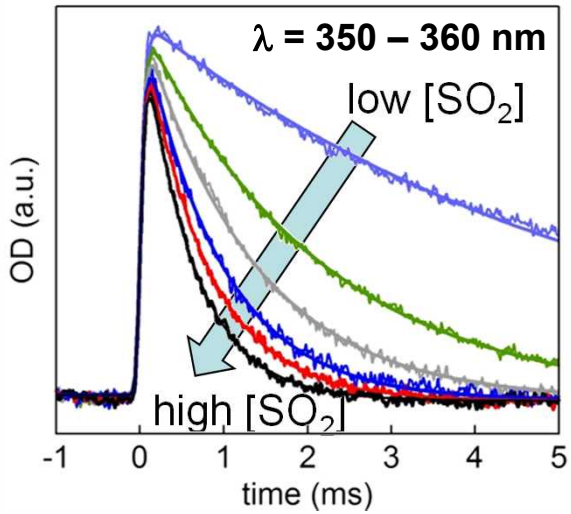
- Fit to single component with exponential rise and decay
- Rate coefficient matches the established value

Reaction of CH_2OO with SO_2

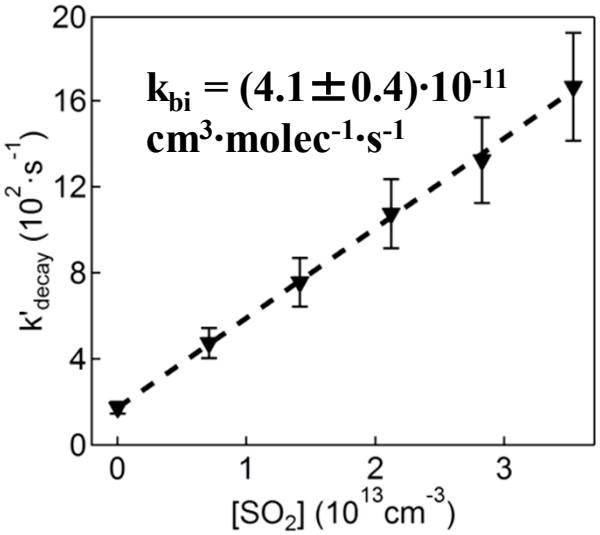
Recent experimental determinations of bimolecular rate coefficient

- Welz *et al.*, P = 4 torr
  CH_2OO detection by PIMS
  $k_2 = (3.9 \pm 0.7) \cdot 10^{-11}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$
- Stone *et al.*, P = 1.5 – 450 torr
  CH_2OO (PIMS) and CH_2O (LIF)
  $k_2 = (3.6 \pm 0.5) \cdot 10^{-11}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$

Using UV absorption



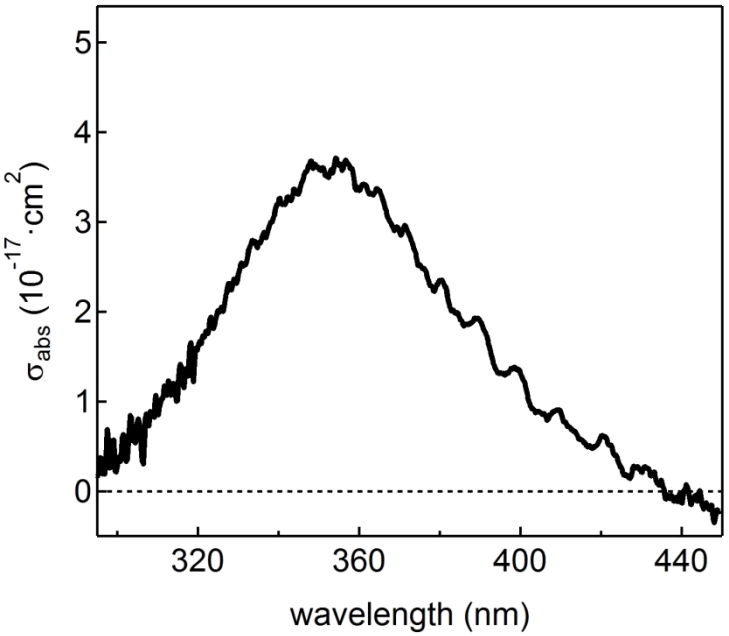
- Fit to exponential rise and decay



➢ Rate coefficient matches the literature values

Identification of the CH_2OO UV absorption spectrum

UV absorption spectrum (CH_2I_2 and IO signals subtracted)



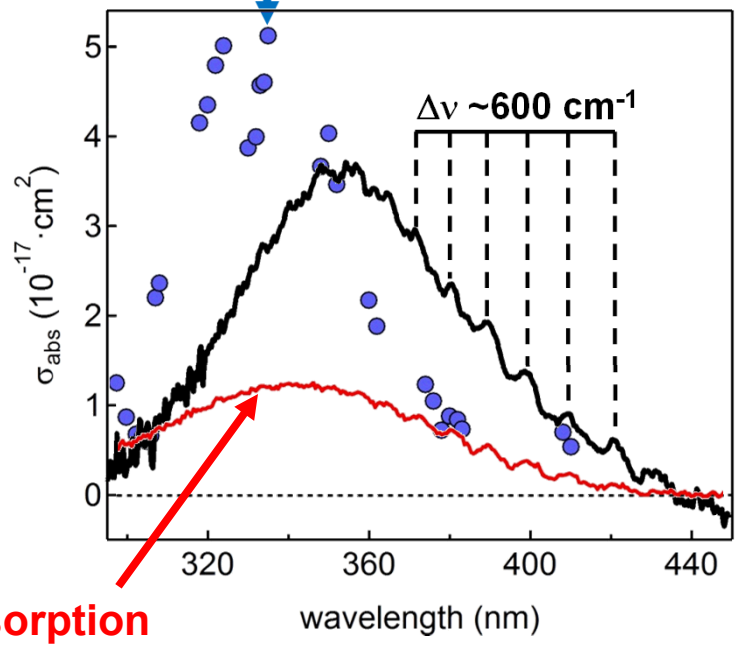
***J. Phys. Chem. Letters*, 4, 4201 (2013)**

Summary of the evidence…

- Intense UV absorption similar to that measured in a molecular beam by CH_2OO^+ (m/z = 46) ion depletion by Beames *et al.*
- Other possible species (CH_2I, IO, CH_2IO_2, I_2) can be excluded
- Formation and decay kinetics match published rate coefficients
- Kinetics are the same at all probe λ
  - ➢ **CH_2OO dominates this UV spectrum**
- $[CH_2I]$ at t=0 is $(5\pm1)\cdot10^{11}$ cm^{-3}
  - ➢ Peak σ_{abs} ~$(3.6\pm0.9)\cdot10^{-17}$ cm^2

Identification of the CH_2OO UV absorption spectrum

Ground-state depletion (Beames *et al.*)



Absorption (Ting *et al.*)

Differences from ground-state depletion spectrum of Beames *et al.*

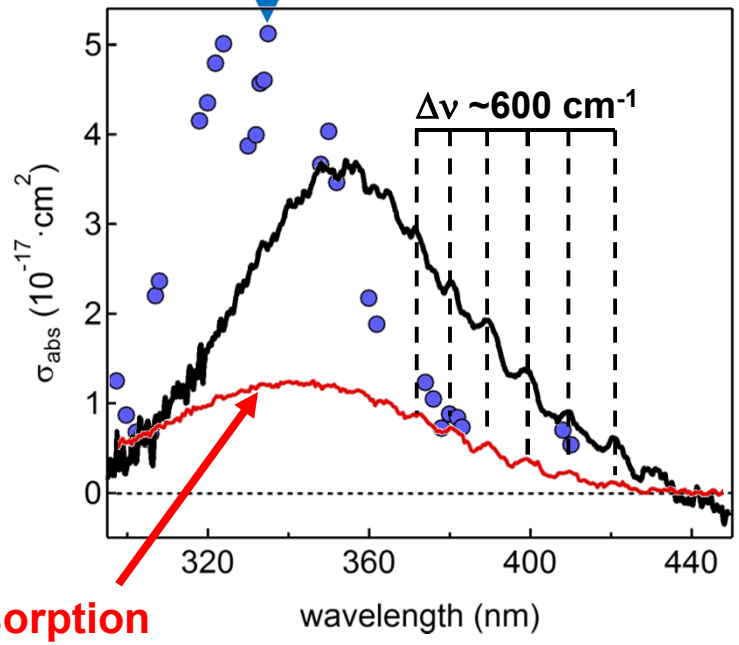
- Differences in T?
- (Quasi)-bound vibrational states?

Differences from UV spectrum of Ting *et al.*

- Peak σ_{abs} ~$1.3 \cdot 10^{-17}$ cm^2

Identification of the CH_2OO UV absorption spectrum

Ground-state depletion (Beames *et al.*)



Absorption (Ting *et al.*)

Differences from ground-state depletion spectrum of Beames *et al.*

- Differences in T?
- (Quasi)-bound vibrational states?

Differences from UV spectrum of Ting *et al.*

- Peak σ_{abs} ~$1.3 \cdot 10^{-17}$ cm^2
- However, the vibrational structure between 360 – 400 nm is confirmed

- **Significant discrepancies in the spectra that need to be resolved**
- **UV absorption is a good choice for direct CH_2OO detection in kinetic measurements**

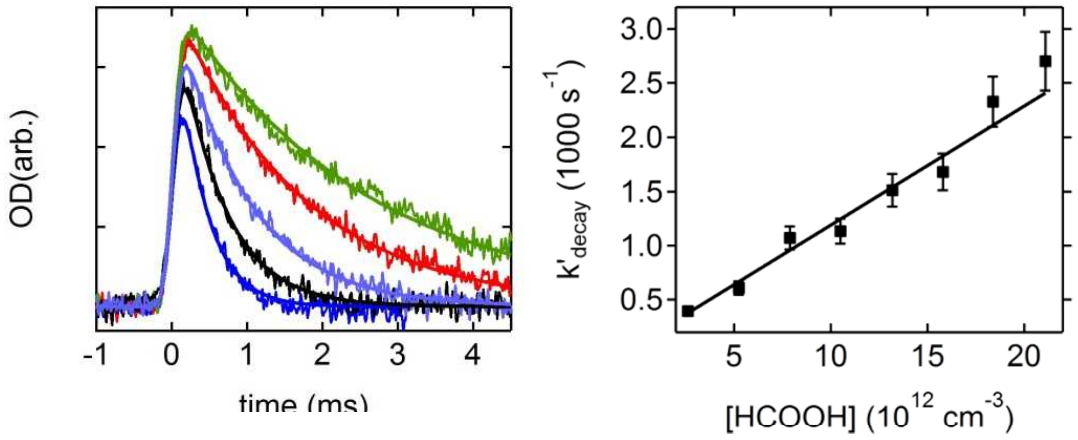
Reaction of CH_2OO with small organic acids

Done in collaboration with Taatjes, Percival, Shallcross, Osborn, others

Welz *et al.*, *Angew. Chem.*, 126, 4635 (2014)

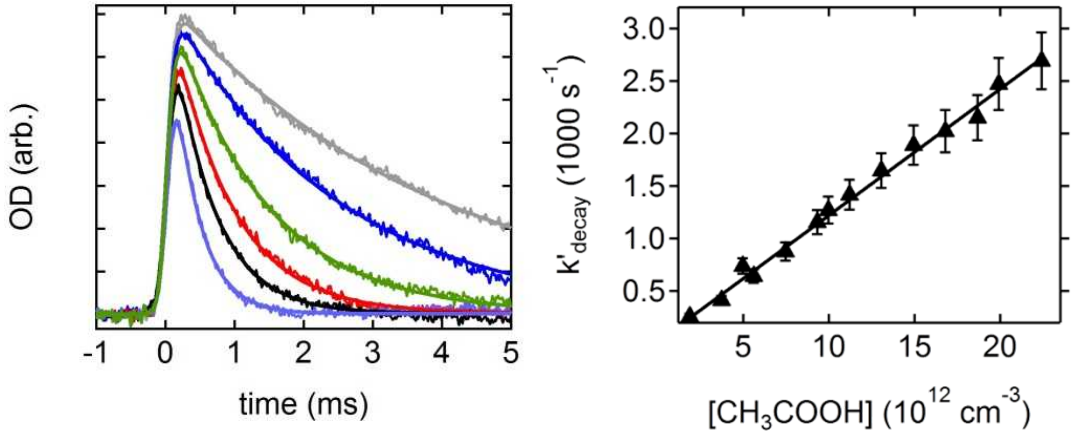
$CH_2OO + HCOOH$

- $k_{295K} = (1.1 \pm 0.1) \cdot 10^{-10}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$



$CH_2OO + CH_3COOH$

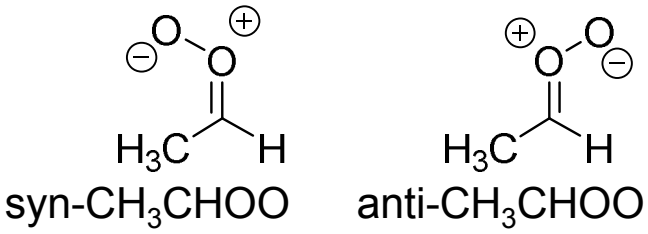
- $k_{295K} = (1.25 \pm 0.1) \cdot 10^{-10}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$



- Reaction rate coefficients by PIMS and UV agree to within < 10%

Acetaldehyde oxide, CH_3CHOO – a step up in complexity

Smallest Criegee intermediate with structural isomers



Expected to have different impact

- *Syn-* should be more stable than *anti* by ~3.3 kcal/mol Kuwata *et al.* (2010)
- Distinct decomposition pathways and reactivity

  anti- should be much more reactive towards H_2O (factor of 10^5), unsaturated hydrocarbons factors of ~10^3 – 10^4), etc.

Kinetic measurements

- *Syn-* and *anti-* identified by PIMS based on differences in ionization E

  Taatjes *et al., Science, 340, 177 (2013)*
- *Anti*-CH_3CHOO contribution estimated at ~10% at room T, P = 4 torr
- Found conformer-dependent reactivity

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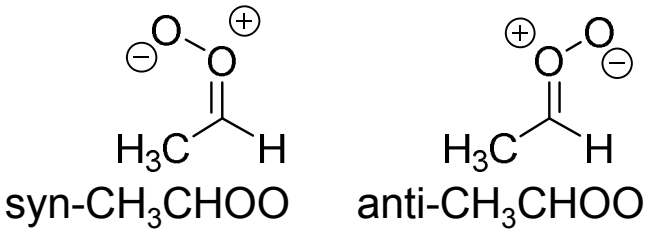
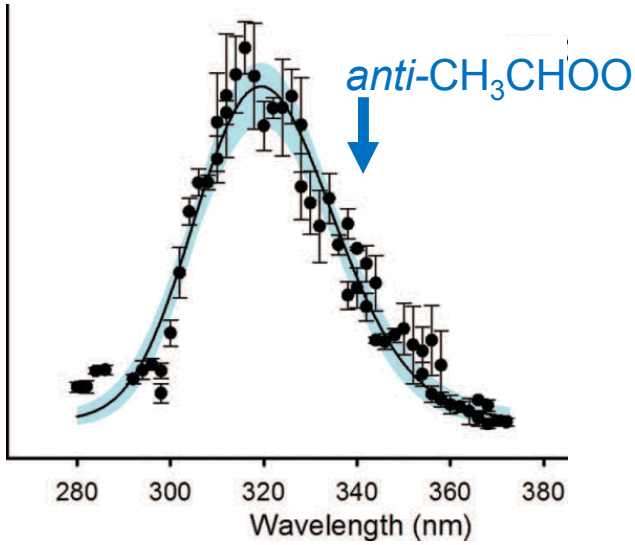


UV spectroscopic measurements

- UV depletion spectrum of *syn*-CH_3CHOO **(Beames *et al.*, 2013)**
- Peak absorption at ~322 nm (3.9 eV), blue-shifted from CH_2OO
- Very strong UV cross-section, ~$5 \cdot 10^{-17}$ cm^2

- *anti*-CH_3CHOO not observed
- Calculations suggest *anti*- band maximum near ~3.6 eV (345nm)



UV spectroscopic detection of CH_3CHOO

$$CH_3CHI_2 \xrightarrow{h\nu} CH_3CHI + I$$

$$CH_3CHI + O_2 \longrightarrow I + \textit{syn}\text{-}CH_3CHOO \xrightarrow{+ SO_2} \text{products}$$

$$\textit{anti}\text{-}CH_3CHOO \longrightarrow \text{products}$$

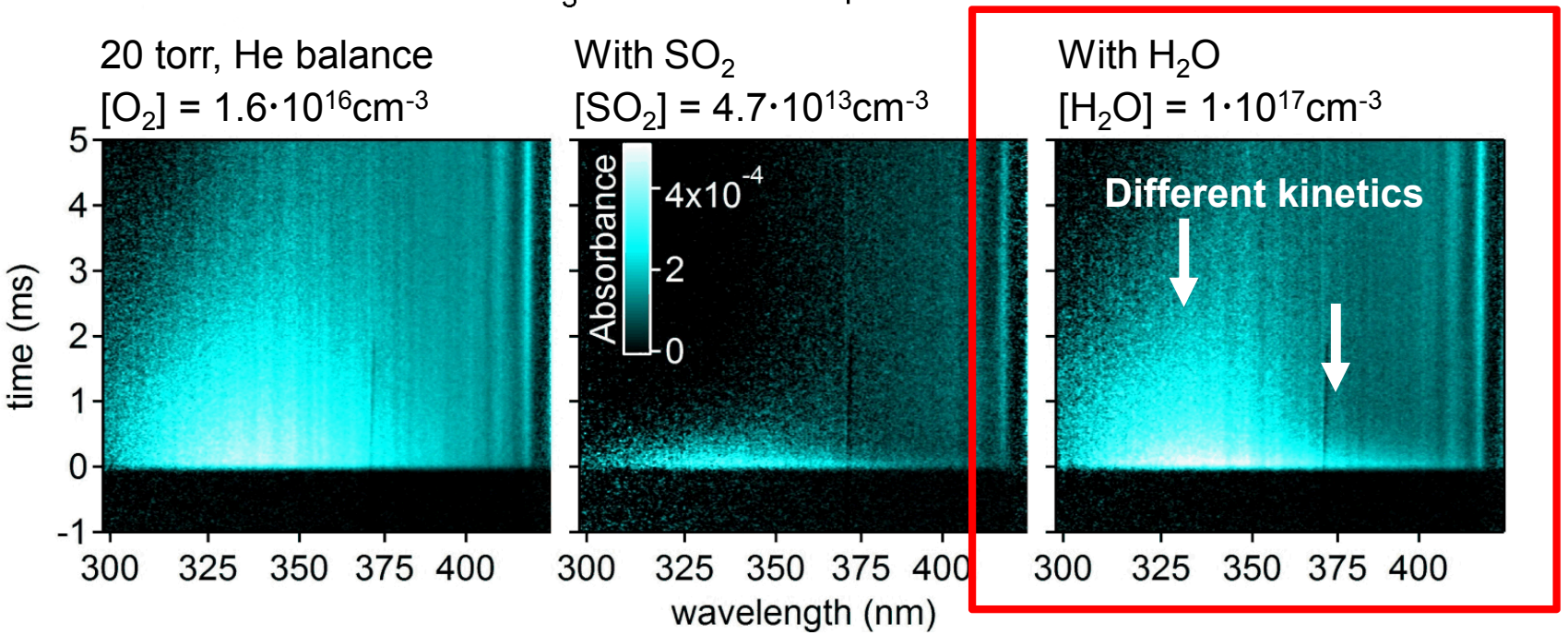
$$\textit{syn}\text{-}CH_3CHOO \xrightarrow{+ H_2O} \text{products}$$

$$\textit{anti}\text{-}CH_3CHOO \longrightarrow \text{products}$$

predicted rate coefficients:

$k \sim 1 \cdot 10^{-18}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$

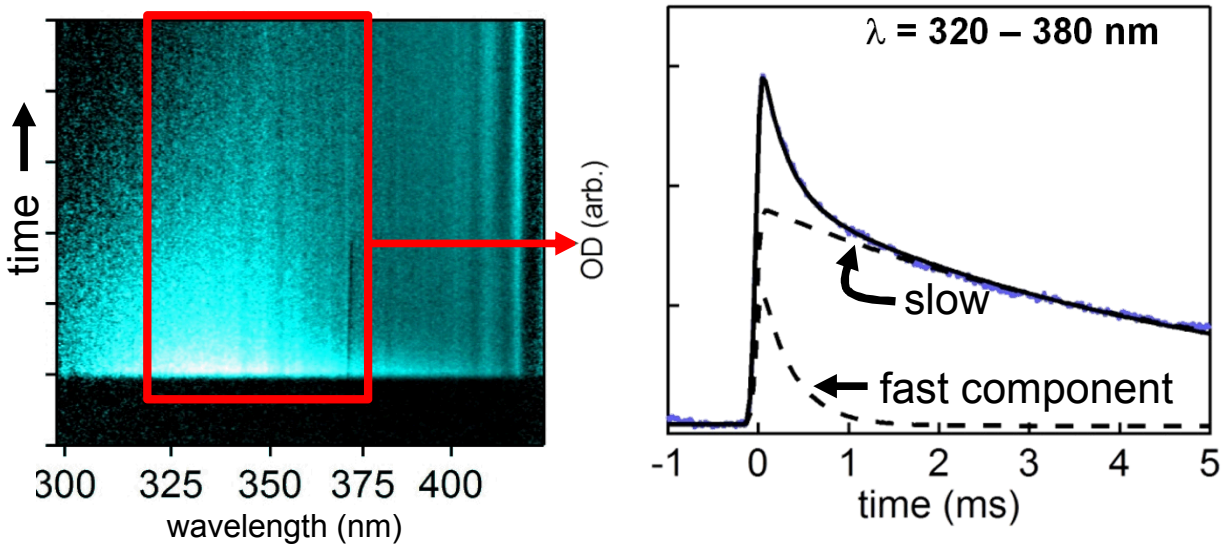
$k \sim 1 \cdot 10^{-13}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$



- Two transient bands in the UV spectra
- Both react quickly with SO_2, but only one with H_2O

Identification of *syn*- and *anti*-CH_3CHOO UV spectra

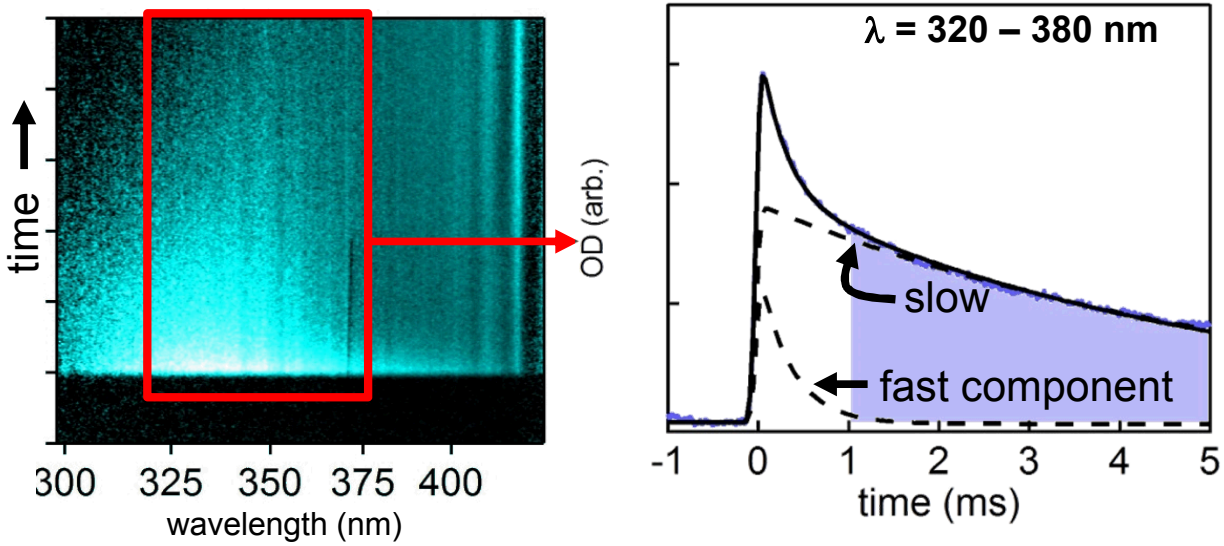
Transient absorption in the presence of H_2O



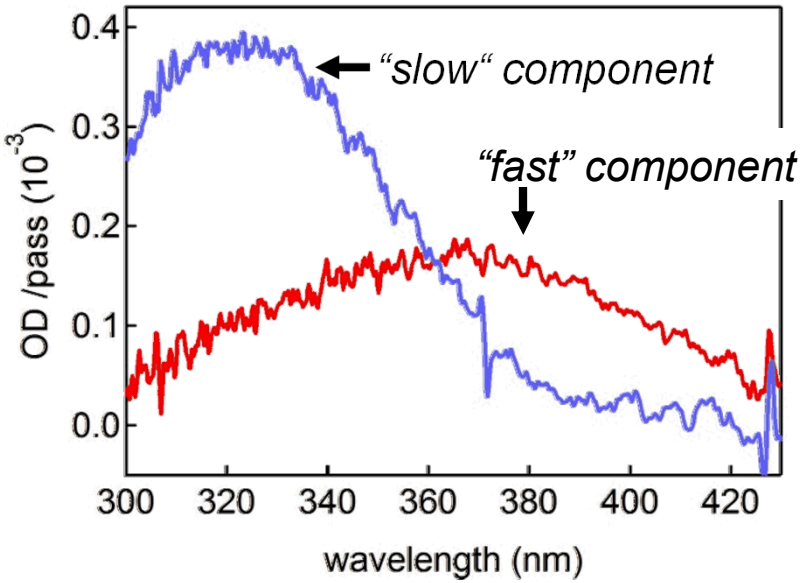
- Two kinetic components, each with exponential rise and decay

Identification of *syn*- and *anti*-CH_3CHOO UV spectra

Transient absorption in the presence of H_2O



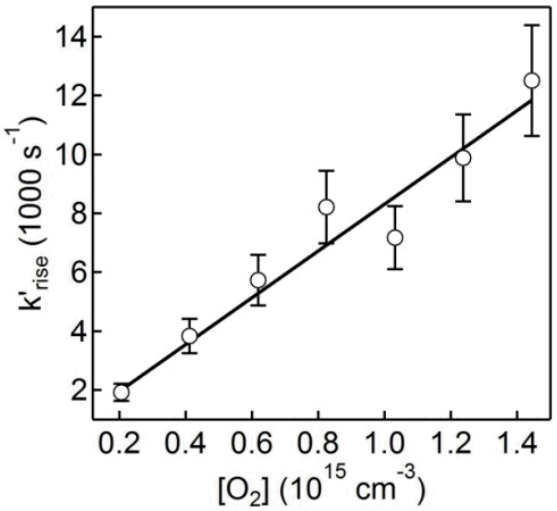
- Two kinetic components, each with exponential rise and decay
- Integrating over t > 1 ms yields the spectrum of the "slow" component, peaked at ~325 nm
- Subtraction of "slow" component yields the spectrum of the "fast" component, peaked at ~360 nm



Identification of *syn*- and *anti*-CH_3CHOO UV spectra

Kinetics of formation from $CH_3CHI + O_2$

- Time traces fit simultaneously to sum of 2 components
- No $[O_2]$ dependence: Amplitudes A1 and A2, decay rates k'_{slow} and k'_{fast}
- $1/\tau_{rise}$ linear vs. $[O_2]$



Signal rise times are the same at all probe λ

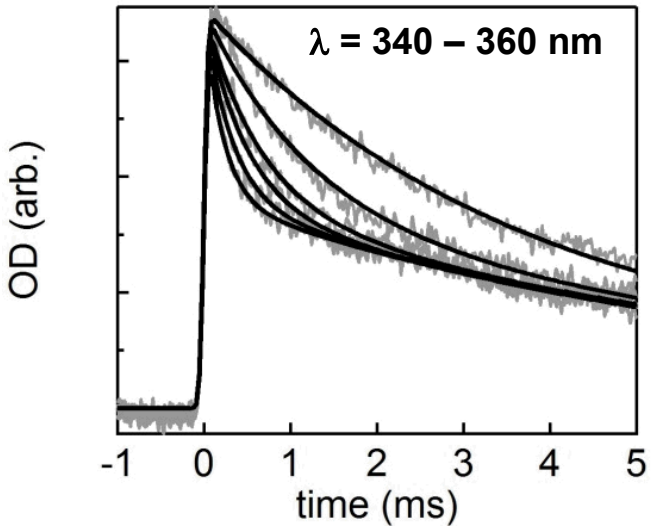
➢ We expect both isomers, *syn*- and *anti*-CH_3CHOO, to be formed with the same rate

$k_{bi} = (8 \pm 0.8) \cdot 10^{-12}$ $cm^{-3} \cdot molec^{-1} \cdot s^{-1}$

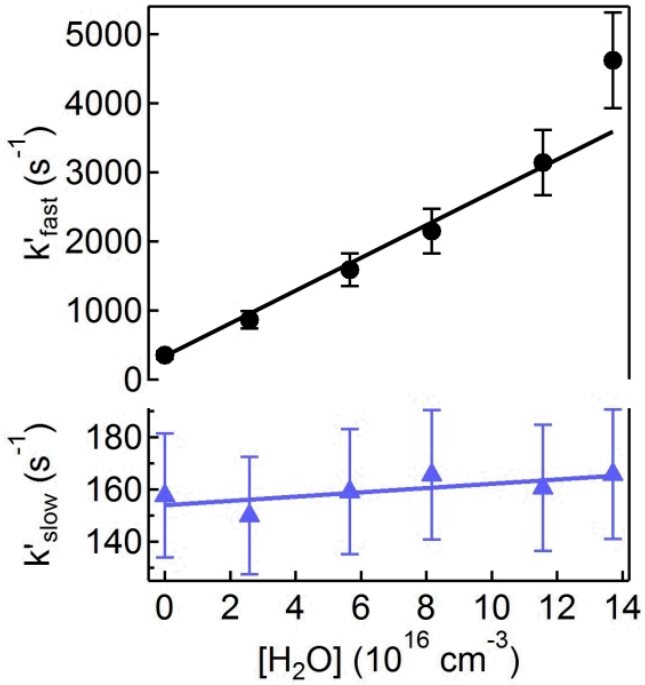
Higher than for the analogous reaction $CH_2I + O_2$, but in general reasonable

Identification of *syn*- and *anti*-CH_3CHOO UV spectra

Reaction with H_2O



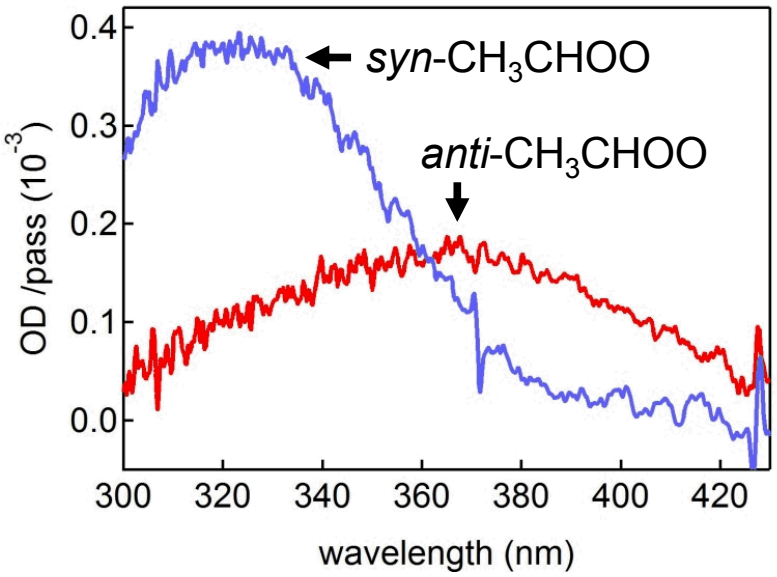
- Sum of 2 kinetic components
- Only k'_{fast} depends on $[H_2O]$



The bimolecular rate coefficients:

- $k_{fast} = (2.4 \pm 0.4) \cdot 10^{-14}$ cm^{-3}·molec^{-1}·s^{-1}
- $k_{slow} < 1 \cdot 10^{-16}$ cm^{-3}·molec^{-1}·s^{-1}

Identification of *syn*- and *anti*-CH_3CHOO UV spectra



Summary of the evidence…

- Two intense, broad UV absorption bands
- Kinetics also show two independent species
- 325-nm band is similar to UV depletion measurement by Beames *et al.*
- Formation and decay kinetics agree with expectations for *syn*-CH_3CHOO
- 360-nm band in qualitative agreement with calculations by Beames *et al.*
- Formed at the same rate as *syn*- isomer
- Decay kinetics agree with expectations for *anti*-CH_3CHOO

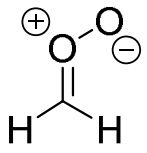
- Cross-section determination is not possible, because the *syn*- vs. *anti*- isomer branching ratio is not known.
  - ➢ Qualitatively, σ_{abs} ~1 - $2 \cdot 10^{-17}$ cm^2

Conclusions:

Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry

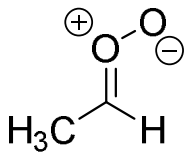
- Broadband probing is key to de-convolve kinetics

UV spectroscopy and reaction kinetics of CH_2OO

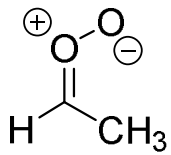


- UV absorption probing yields reliable kinetic measurements
- Currently working on reactions of CH_2OO + alkenes

The search for UV spectrum of CH_3CHOO



anti-



syn-

- Distinct UV spectra of *syn-* and *anti-*CH_3CHOO
- Conformer-dependent reactivity with H_2O
- Also working on CH_3CHOO + SO_2, alkenes

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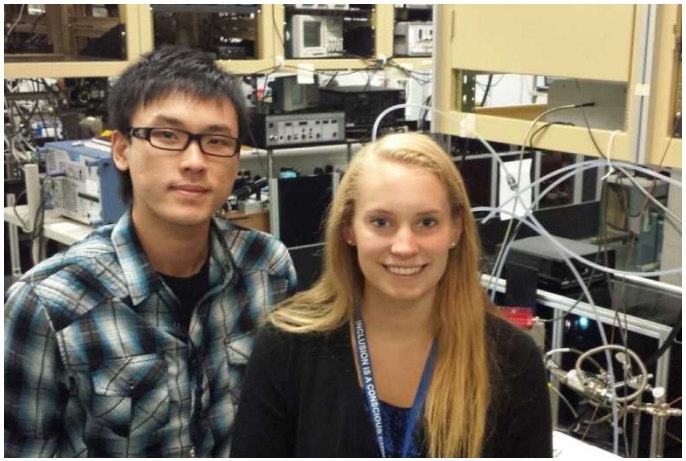
Development of TR-BB-CEAS experimental apparatus

LDRD Laboratory Directed Research & Development



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