Spectroscopy and reaction kinetics of a Criegee intermediate CH_3CHOO using Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry

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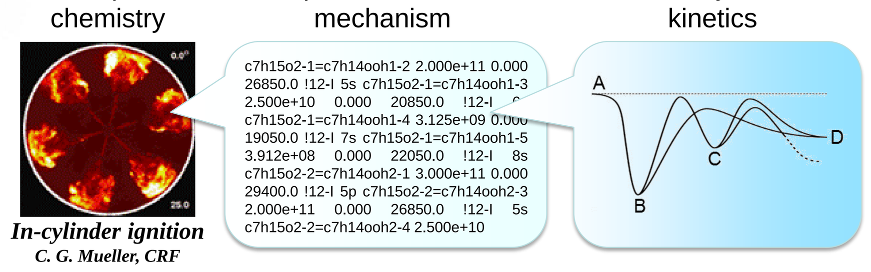
Development of a new spectroscopic method

Motivation

Measurements of important reaction intermediates and products require tailored experimental probe methods

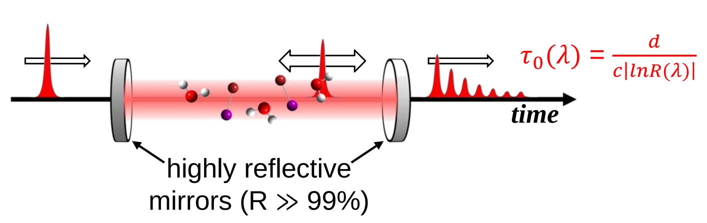


Goal: design a direct optical absorption probe method, optimized for gas-phase kinetics:

- *time-resolved* — *Real-time measurement of concentrations*
- *broadband* — *Multiplexed, many species detected at once*
- *cavity-enhanced* — *Sensitive detection of minor transient species*
- *absorption spectrometry* — *Non-intrusive probe*

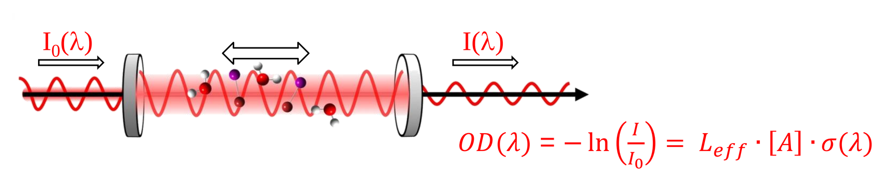
Principles of cavity-enhanced spectroscopy

Pulsed Cavity Ringdown Spectroscopy (CRDS)



- *Input – a single pulse; output – "ringdown" with lifetime τ_0*
- *With absorbers present, $\tau(\lambda)^{-1} = \tau_0(\lambda)^{-1} + c\cdot[A]\cdot\sigma(\lambda)$*
- ***Ringdown time → absorber concentration***

CW Cavity-Enhanced Absorption Spectroscopy (CEAS)



- *Analogous to CRDS – long cavity photon lifetime*
- *Long effective optical path, L_{eff}*
- ***Absorber concentration from Beer's Law***

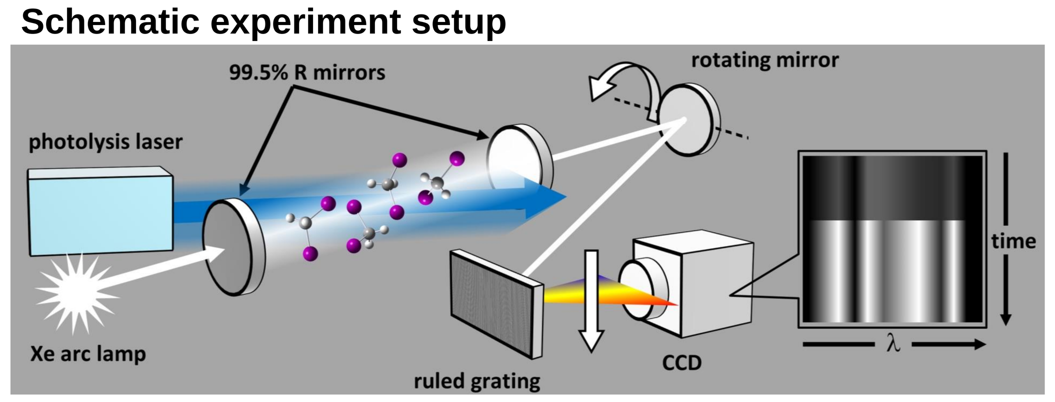
Main disadvantage of existing methods: Typically done at a single wavelength (or narrow wavelength range)

A new approach: time-resolved broadband CEAS

Primary advantages:

- Optimized for kinetics of dilute gas-phase species
- Broadband probing is crucial for complex reactions
- Simple, robust experimental setup
- Total cost (without pump laser) under $50K

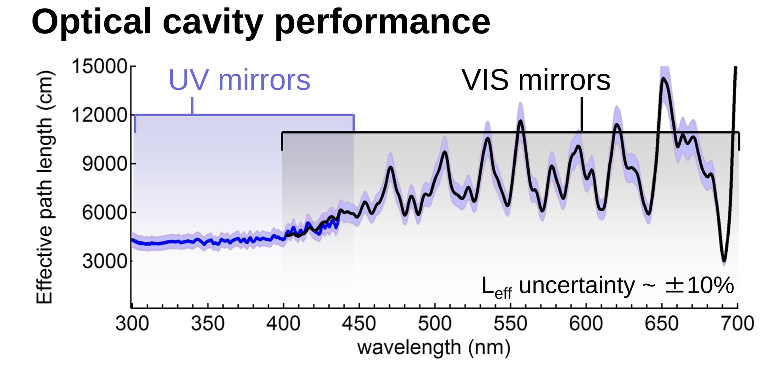
Schematic experiment setup



Experimental strategy

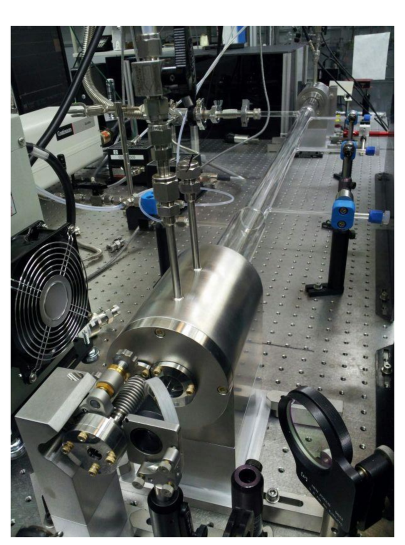
- Moderate-finesse broadband optical resonator integrated with a slow-flow chemical reactor
- Pulsed laser photolysis (pump) initiates reaction
- Xe arc lamp provides CW white-light probe radiation
- 2 sets of R = (99.5±0.2)% mirrors cover UV-VIS range
- Cavity enhancement of ~100x

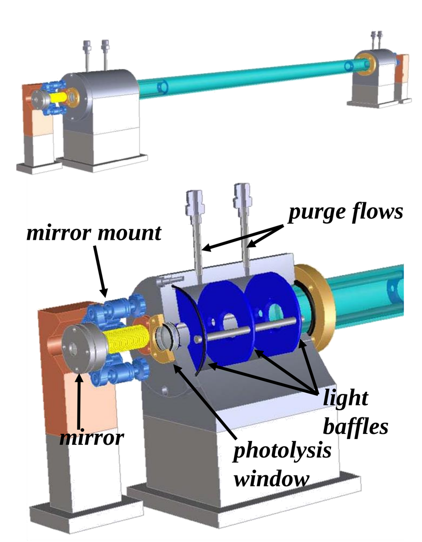
Optical cavity performance



Transient absorption mapped spatially onto CCD detector

- Based on the principle of "ringdown spectral photography" of Scherer *et al.* Scherer, et al., *Appl. Opt.*, **40**, 6725 (2001)
- **X–axis ↔ probe λ** — Ruled grating
- **Y–axis ↔ time** — Phase-locked rotating mirror
- Mirror rotation synchronized with pump laser, allows on-chip averaging in "long exposure" mode





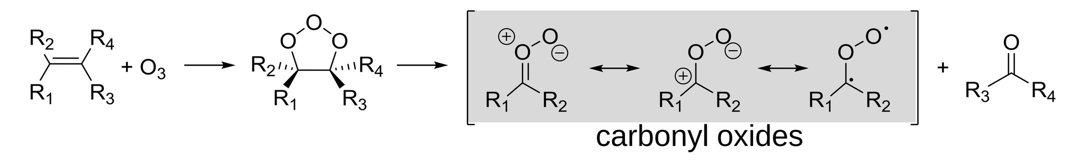
Technical specifications:

- Reactor length = 1.60 m, pump–probe overlap length = 0.80 m
- Spatial resolution ~5 pixels (FWHM) on a 1-Mp CCD sensor
- Time, wavelength resolution ~0.005·full-scale, easily adjustable
- L_{eff} ≥ 4000cm, independently measured using molecular absorption standards – known concentrations of NO_2 and CH_2I_2

Spectroscopy and reaction kinetics of acetaldehyde oxide, CH_3CHOO

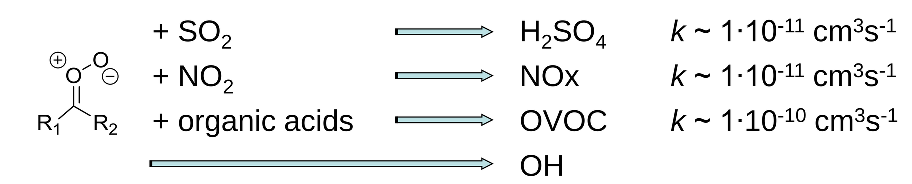
Motivation: role of Criegee intermediates (CI) in atmospheric chemistry

- CI are produced in ozonolysis of unsaturated hydrocarbons

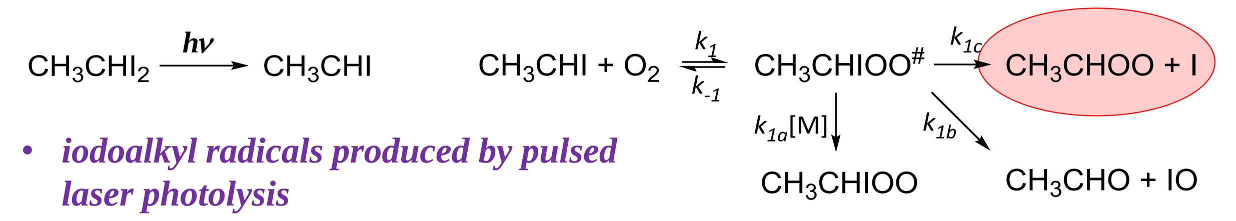


- *highly reactive transients, low steady-state concentrations*

- CI are major oxidants of trace atmospheric species and potential OH sources

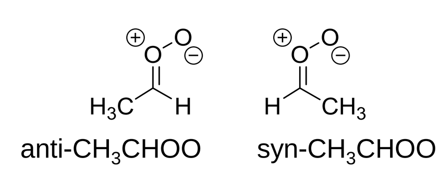


- Reliable source of stabilized CI in the laboratory (Taatjes and co-workers, 2010)



- *iodoalkyl radicals produced by pulsed laser photolysis*
- *high concentration of stabilized CI formed rapidly by iodoalkyl + O_2*
- *well-suited for kinetic and spectroscopic studies*

- CI with single alkyl substituent have conformer-dependent reactivity

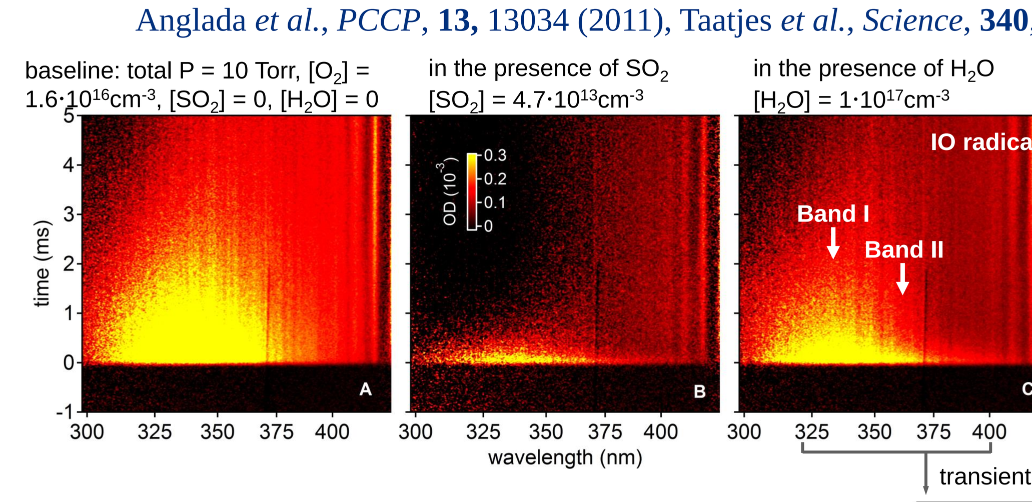


- *Calculations predict that anti-CH_3CHOO reacts faster than syn-CH_3CHOO with many species*
- *Photoionization mass spectrometry probing of CI reactivity confirms predicted trends*

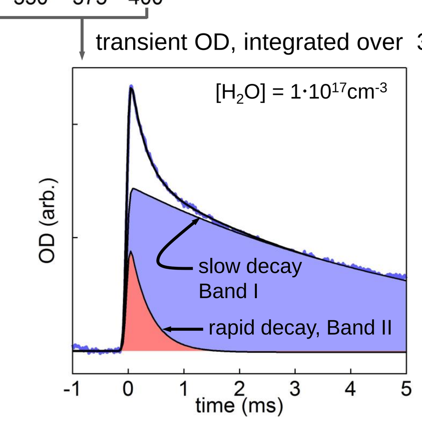
- **We need conformational selectivity to obtain accurate elementary reaction rate coefficients and model the atmospheric impact of Criegee intermediates**

UV absorption spectra of *syn-* and *anti-*CH_3CHOO:

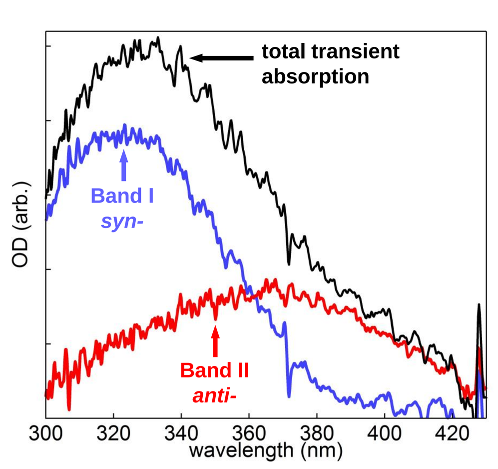
- *Syn-* and *anti-* conformers identified based on reactivity towards SO_2 and H_2O
  Anglada *et al.*, *PCCP*, **13**, 13034 (2011), Taatjes *et al.*, *Science*, **340**, 177 (2013)



- Band I decay depends only on SO_2 → ***syn*-CH_3CHOO**
- Band II decay depends on SO_2 and H_2O → ***anti*-CH_3CHOO**



- Integration of transient absorption (with H_2O) over t = 1 – 5 ms provides spectrum of *syn*-CH_3CHOO
- Subtraction of *syn-* spectrum from total transient OD yields spectrum of *anti*-CH_3CHOO
- All spectra extrapolated to t = 0 based on fitted intensities



Determination of absorption cross-sections

Known quantities:

- Our total initial concentration of CH_3CHOO is ~6·10¹¹cm^{-3}
- σ_{308nm} ~ 1.1·10⁻¹⁷cm^2 (Smith *et al.*, 2014) (due to *syn*-CH_3CHOO, *anti-* contributes little at 308 nm)

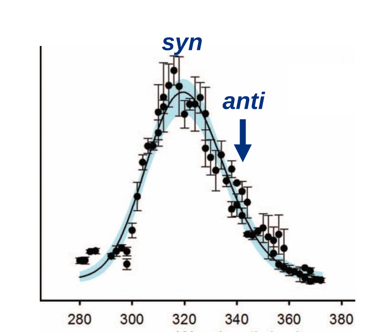
Based on the known quantities, we derive:

- Initial [*syn*-CH_3CHOO] ~4.2·10¹¹cm^{-3} (70% of total)
- Initial [*anti*-CH_3CHOO] ~1.8·10¹¹cm^{-3} (30% of total)
- **Peak σ_{abs}(*syn-*) ~1.2 ·10⁻¹⁷cm^2 at 323 nm (3.8 eV)**
- **Peak σ_{abs}(*anti-*) ~1.2 ·10⁻¹⁷cm^2 at 360 nm (3.4 eV)**

Comparison with previous work:

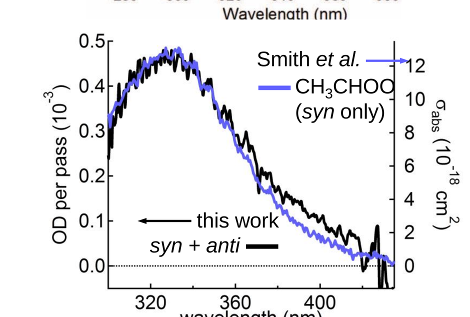
Beames *et al.*, *J. Chem. Phys.*, **138**, 244307 (2013)

- *syn*-CH_3CHOO reported in molecular beam, σ_{max}~ 5·10⁻¹⁷ cm^2 at 322 nm (3.9 eV)
- *anti-* σ_{max} calculated at 0.3 eV lower energy



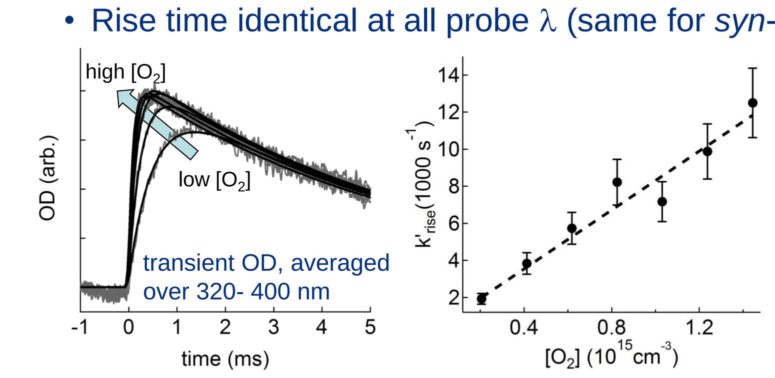
Smith *et al.*, *J. Chem. Phys.*, **141**, 074302 (2014)

- *syn*-CH_3CHOO reported in flow cell at room T, σ_{max}~ 1.27·10⁻¹⁷ cm^2 at 328 nm (3.8 eV)
- *anti-* σ_{max} calculated at 0.35 eV lower energy
- Likely includes unresolved *syn-* and *anti-* spectra



Direct probing of conformer-dependent reactivity

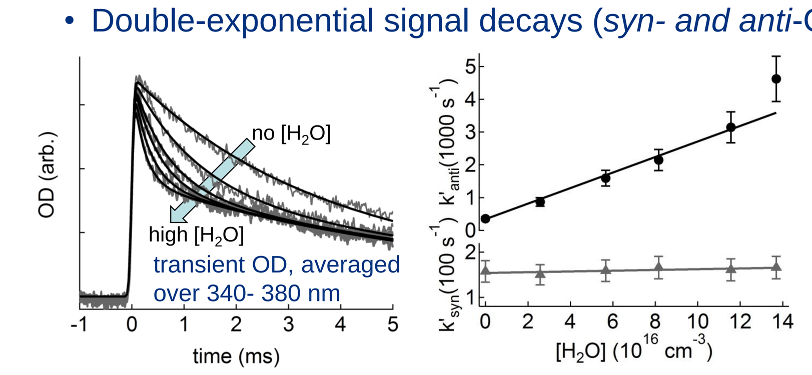
- Reaction $CH_3CHI + O_2$ → products
- Single-exponential signal rise, timescale varies with [O_2]
- Rise time identical at all probe λ (same for *syn-* and *anti*-CH_3CHOO)



- A plot of 1/τ_{rise} vs. [O_2] yields bimolecular reaction coefficient

k($CH_3CHI + O_2$) = (8.0±0.8) ·10⁻¹² cm^3 s^{-1}

- Reaction $CH_3CHOO + H_2O$ → products
- Double-exponential signal decays (*syn- and anti*-CH_3CHOO)



k(*anti*-$CH_3CHOO + H_2O$) = (2.4±0.4) ·10⁻¹⁴ cm^3 s^{-1}

k(*syn*-$CH_3CHOO + H_2O$) < 2·10⁻¹⁶ cm^3 s^{-1}

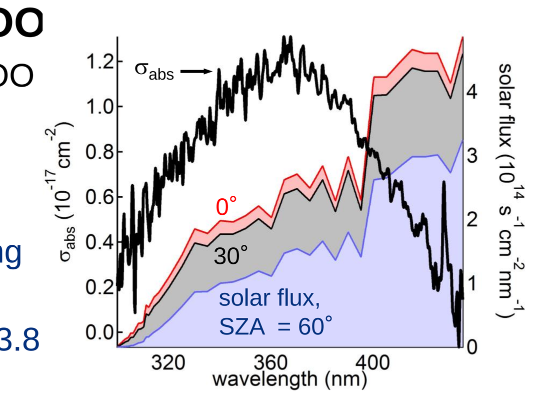
- Trend in reactivity towards H_2O is in qualitative agreement with calculations
  k(*anti*-$CH_3CHOO + H_2O$) = 1.7 ·10⁻¹³ cm^3 s^{-1}
  k(*syn*-$CH_3CHOO + H_2O$) = 2.4 ·10⁻¹⁸ cm^3 s^{-1} — Anglada *et al.*, 2011

  and with photoionization mass spectrometry (PIMS) measurements
  k(*anti*-$CH_3CHOO + H_2O$) = 1 ·10⁻¹⁴ cm^3 s^{-1}
  k(*syn*-$CH_3CHOO + H_2O$) < 4 ·10⁻¹⁵ cm^3 s^{-1} — Taatjes *et al.*, 2011

- UV probing provides greater sensitivity and isomeric selectivity than PIMS for Criegee intermediates, yields improved rate coefficient measurements.

Atmospheric Lifetime of CH_3CHOO

- Photochemical destruction of *anti*-CH_3CHOO
  - Solar actinic flux from NCAR Tropospheric Ultraviolet and Visible (TUV) calculator for solar zenith angles of 0 – 60 degrees
  - Photolytic removal rate calculated assuming a dissociation yield of unity at all λ
  - Photolysis lifetimes of *anti*-CH_3CHOO are 3.8 – 6.6 s



- Similar photochemical lifetime reported for *syn*-CH_3CHOO (Smith *et al.*, 2014)
- For both isomers, removal is dominated by reactions with trace atmospheric species, like H_2O, SO_2, NO_x

For more details, and for additional reactivity measurements of *syn-* and *anti*-CH_3CHOO with SO_2 see Sheps *et al.*, *PCCP*, **16**, 26701 (2014)

COMBUSTION RESEARCH FACILITY — U.S. DEPARTMENT OF ENERGY Office of Science — LDRD — Sandia National Laboratories

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