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Reaction Kinetics of a Prototypical Criegee Intermediate, Formaldehyde Oxide (CH_2OO), with Isoprene

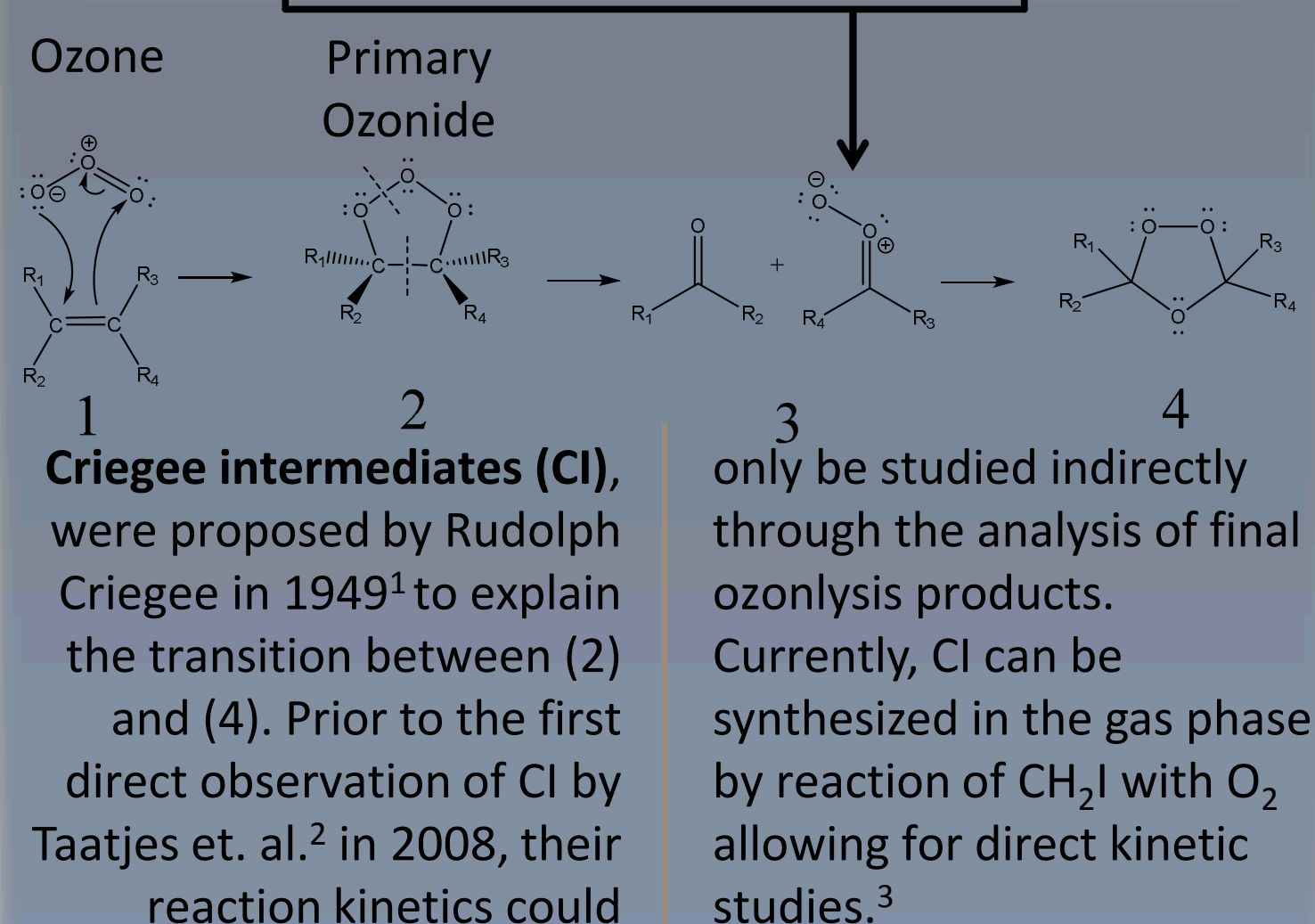
Zachary Decker*, Kendrew Au[‡], Leonid Sheps[‡]

*Department of Chemistry New College of Florida, Sarasota, FL, 34243

[‡]Sandia National Laboratories Combustion Research Facility, Org: 8353

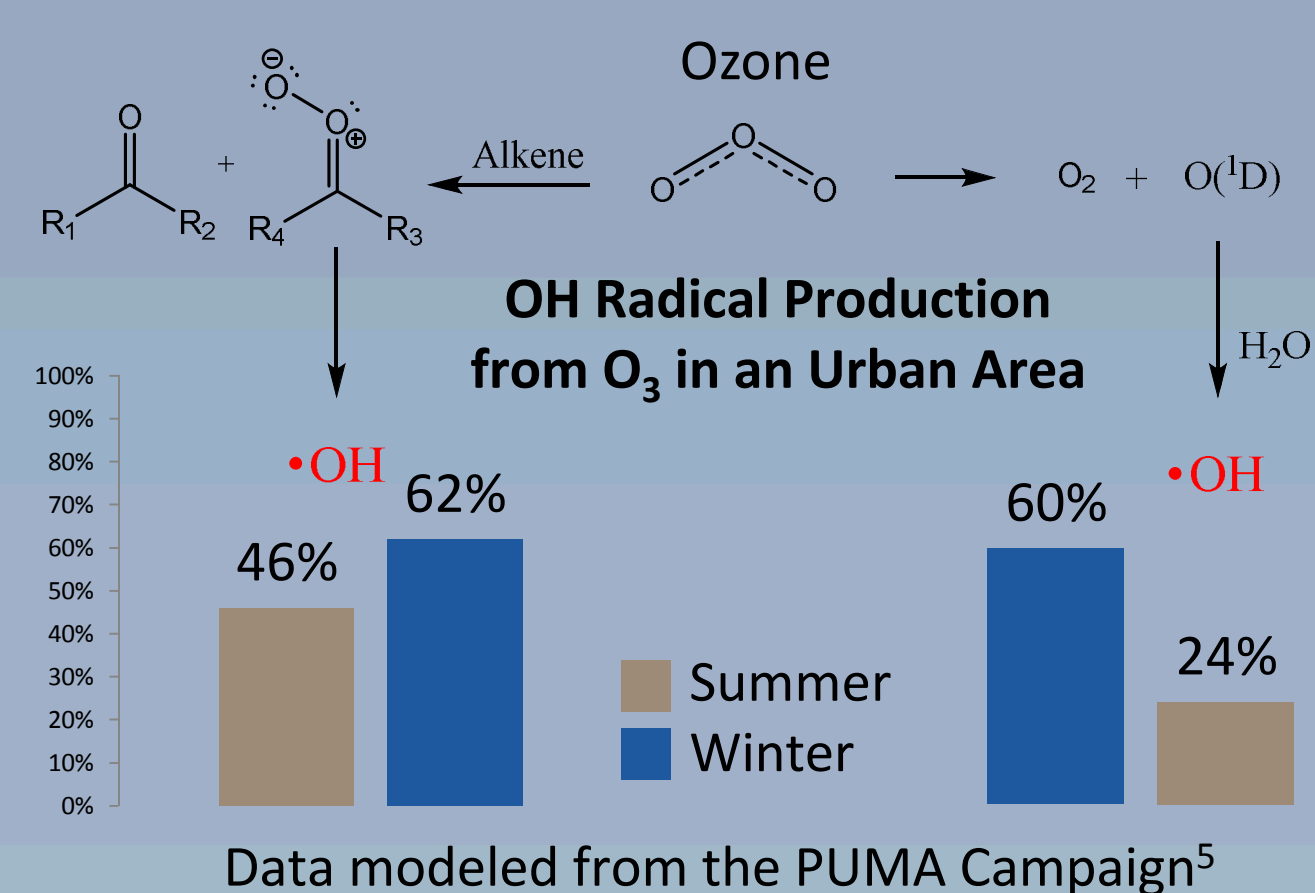
Introduction

Criegee Intermediates



Importance of Criegee Intermediates

The Ozone (O_3) layer fills the stratosphere about 12 km above the earth's surface and is beneficial for its ability to block UV radiation. In contrast to O_3 in the stratosphere, O_3 in the troposphere (lowest 10 km) is a highly reactive component of smog⁴. Here, O_3 reacts with sunlight and water vapor to produce OH radicals, a principal oxidant in the troposphere. Most volatile organic compounds in the atmosphere are oxidized by OH. It is believed that O_3 + alkene reactions dominate night time OH production through decomposition of CI.

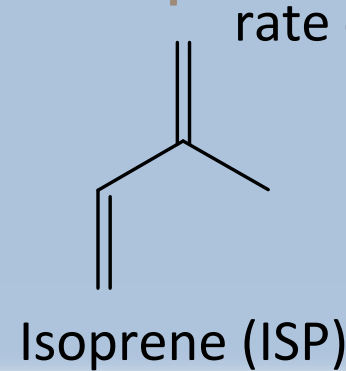


Organic acid formation may also be attributed to CI. Leather et al. suggest that CH_2OO can decompose into formic acid. Furthermore, they find that formic acid formation increases with increasing concentration of water vapor, suggesting that CI reaction with water could be the leading formic acid producer.

Reactions of CI with Isoprene

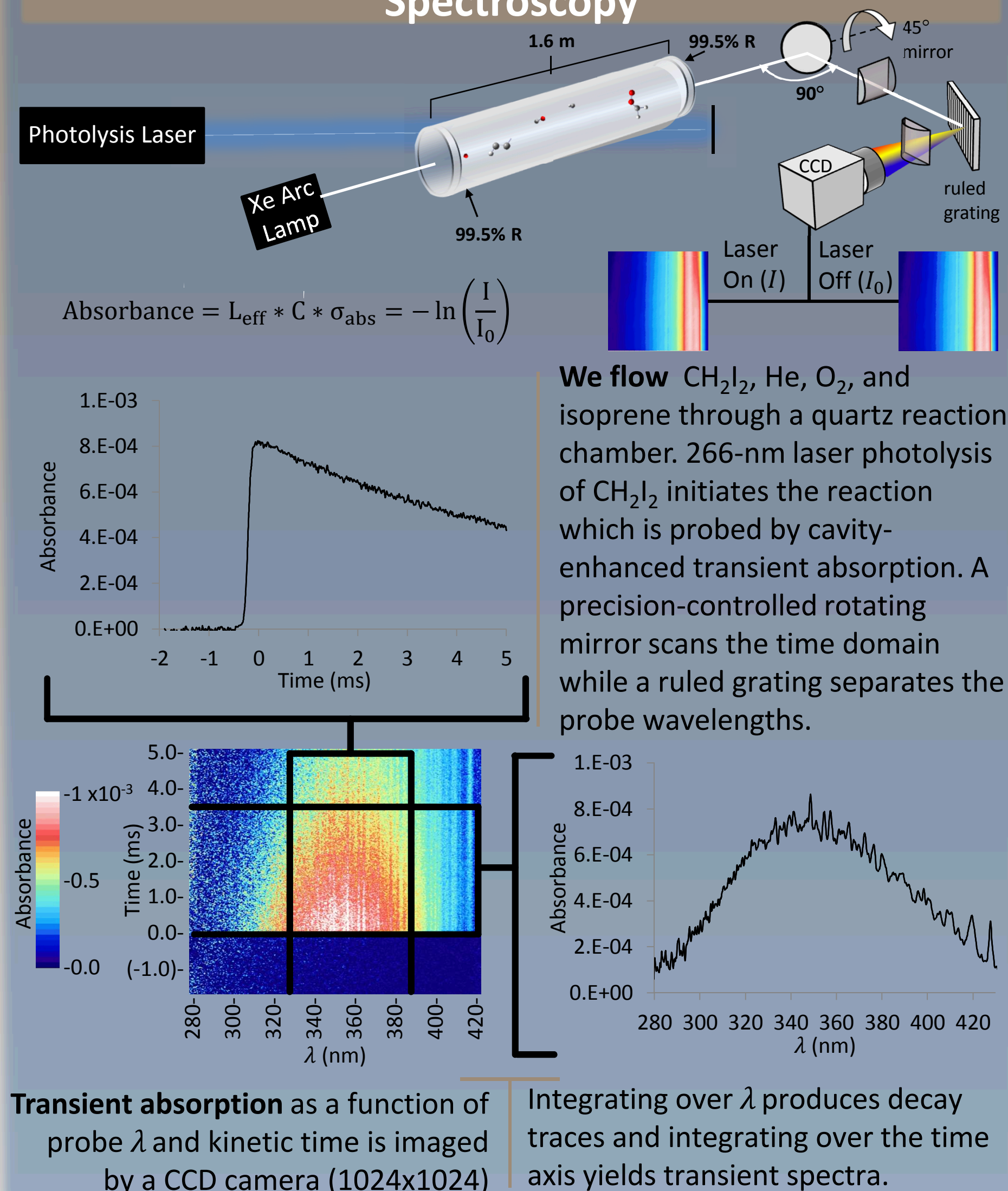
Isoprene is a prototypical unsaturated volatile organic compound (VOC) with a system of conjugated C=C double bonds. It is also emitted in high quantities into the atmosphere (500–750 Tg, mostly by biogenic sources, annually)⁶.

We examine the reaction kinetics of CH_2OO with isoprene using transient UV spectroscopy. We measure the decay of CH_2OO in the presence of varying concentrations of isoprene and extract from this T-dependent reaction rate coefficients.



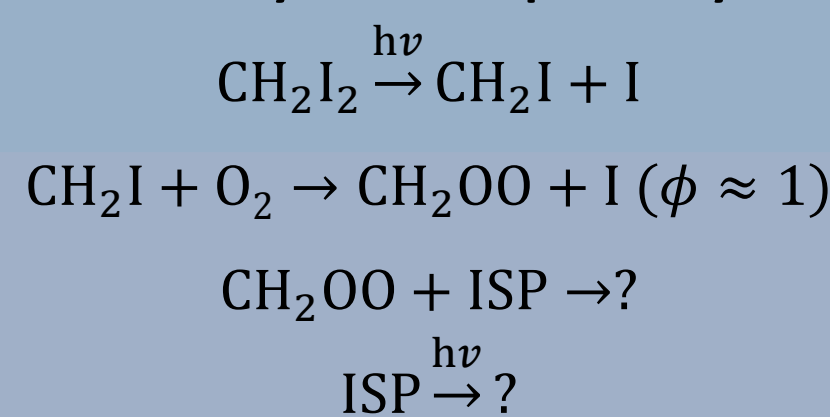
Methods

Time Resolved-Cavity Enhanced Absorption Spectroscopy



UV probing of the reaction of CH_2OO + ISP

Primary reaction pathways:



UV absorption of CH_2OO

- CH_2OO is the dominant absorber in the near-UV spectral region.
- Broad, intense spectrum centered near $\lambda = 350$ nm

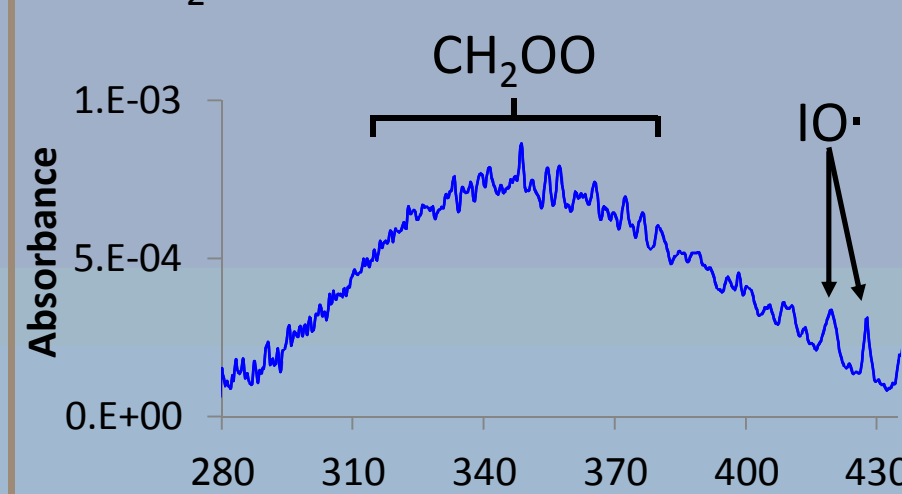
Interfering absorption signals

- Interference from IO (a product of secondary chemistry) present at $\lambda \sim 400 - 430$ nm
- Interference from unknown products of isoprene photolysis present at two broad spectral regions

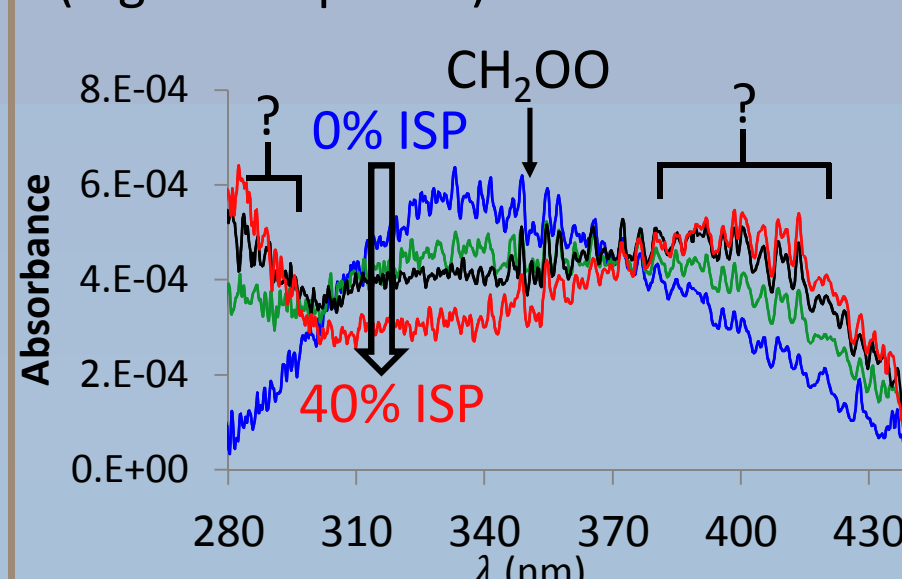
Strategy for eliminating interfering absorption signals

- IO absorption is spectrally well isolated from CH_2OO ; integration over $\lambda = 330 - 390$ nm avoids IO signals
- ISP photolysis is minimized by reducing laser power.
 - Sufficient signal from CH_2OO is ensured even with reduced laser power by maintaining appropriate concentration of the precursor, CH_2I_2

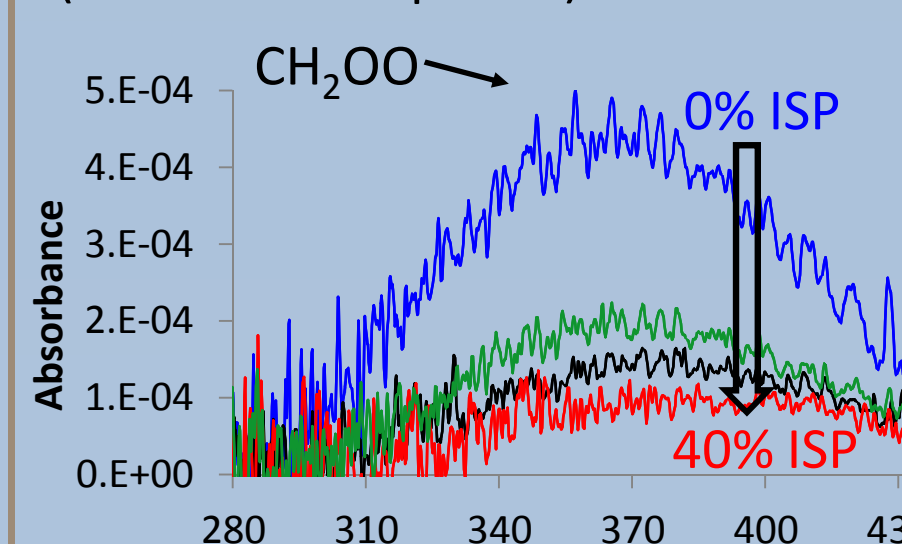
Transient UV spectrum (0–3 ms) of CH_2OO in the absence of ISP



Transient spectra (0–2 ms) as a function of ISP concentration (high laser power)

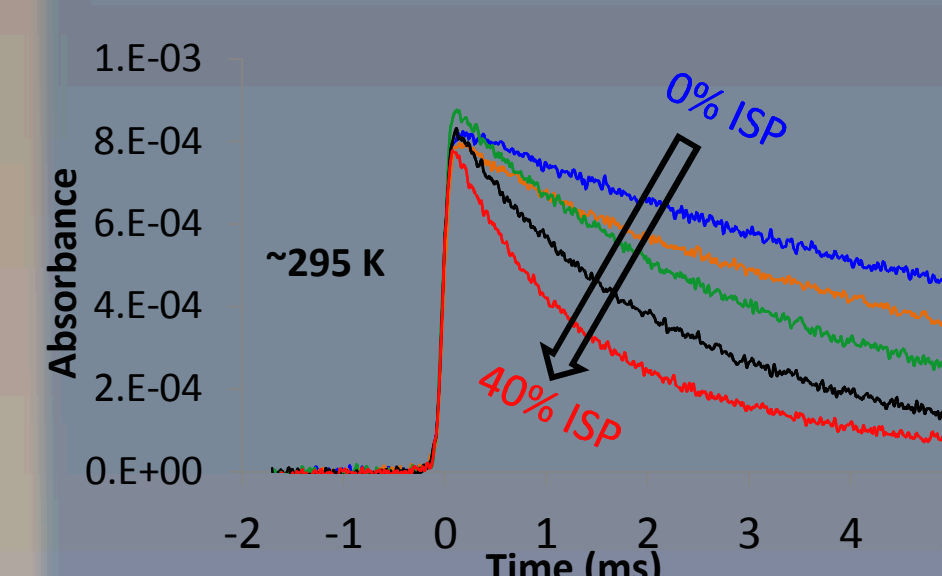


Transient spectra (0–3 ms) as a function of ISP concentration (reduced laser power)

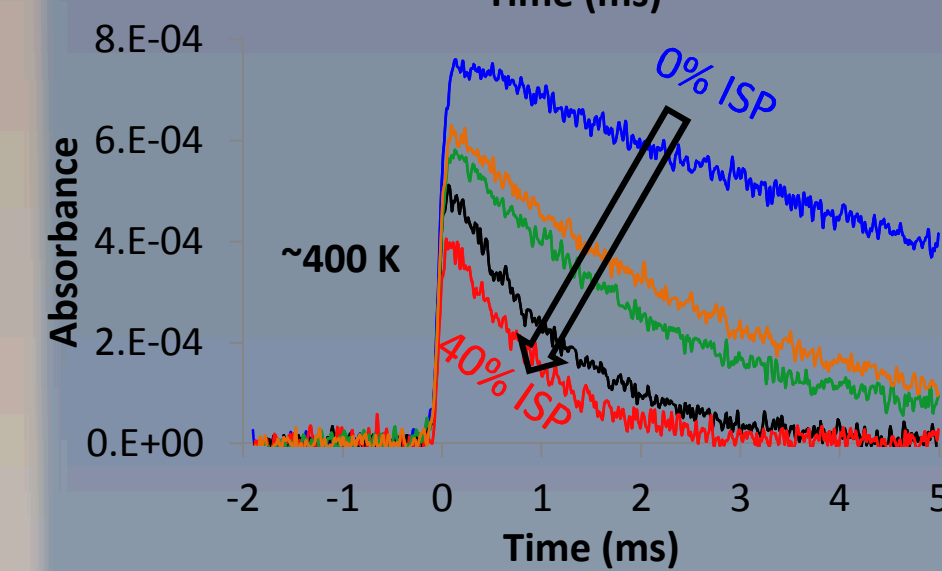


Results

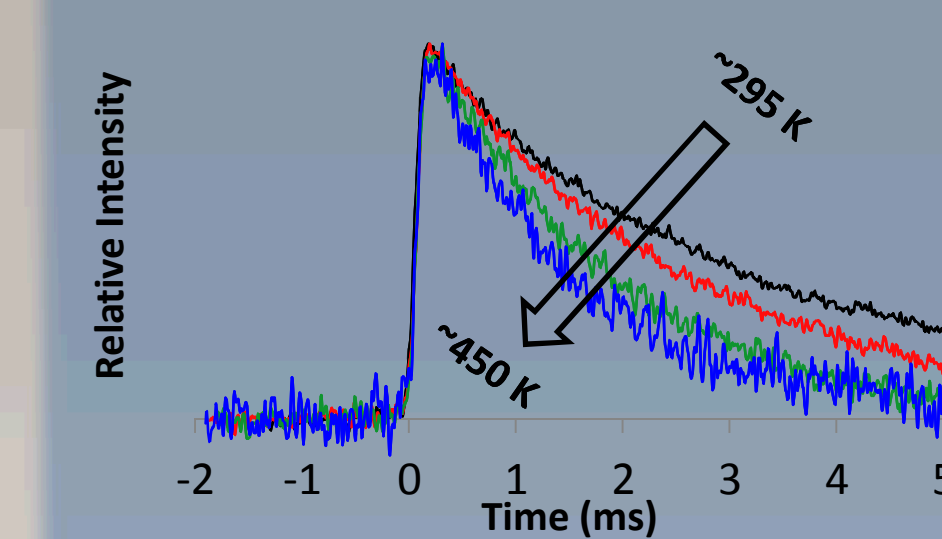
CH_2OO + ISP & Barrier Heights



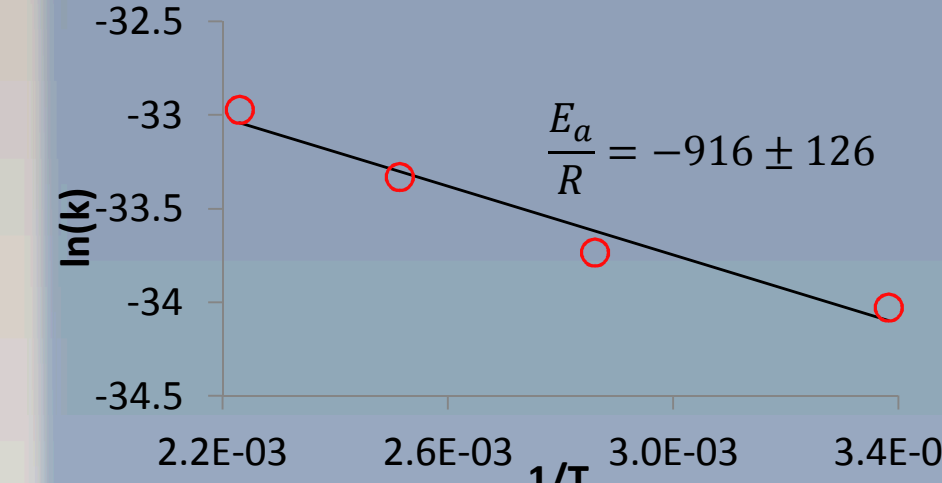
Room-temperature studies show single-exponential CH_2OO decays that become more rapid at higher [isoprene] (top).



High-temperature studies show increased CH_2OO decay constants (relative to room temperature), suggesting the reaction of CH_2OO with isoprene has positive temperature dependence (middle).



A reaction barrier height is obtained by fits of the reaction rate coefficient to the Arrhenius equation. Our data suggest a barrier of ~ 100 (J/mol) (bottom).



Preliminary Conclusions

- Transient UV absorption probes the CH_2OO concentration in the gas phase and is an excellent means for direct measurements of its reaction kinetics.
- Careful choice of experimental conditions is necessary to minimize interferences due to products of secondary reactions of CH_2OO and of direct isoprene photolysis.
- Temperature-dependent measurements of the reaction rate coefficients of CH_2OO + isoprene suggest a reaction barrier of ~ 100 (J/mol).

Ongoing Work:

- We plan to continue experiments to reliably elucidate the reaction kinetics of CH_2OO + isoprene, including possible pressure-dependence of the reaction rate coefficient.
- We are conducting quantum chemical calculations of the reaction barrier for CH_2OO + isoprene for comparison with experimental data.

References

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