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Investigating Combustion and Atmospheric Chemistry Intermediates with Photoionization Mass Spectrometry

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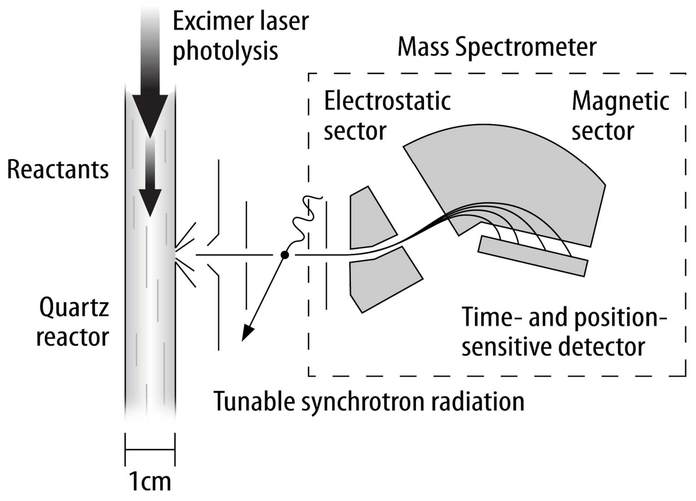
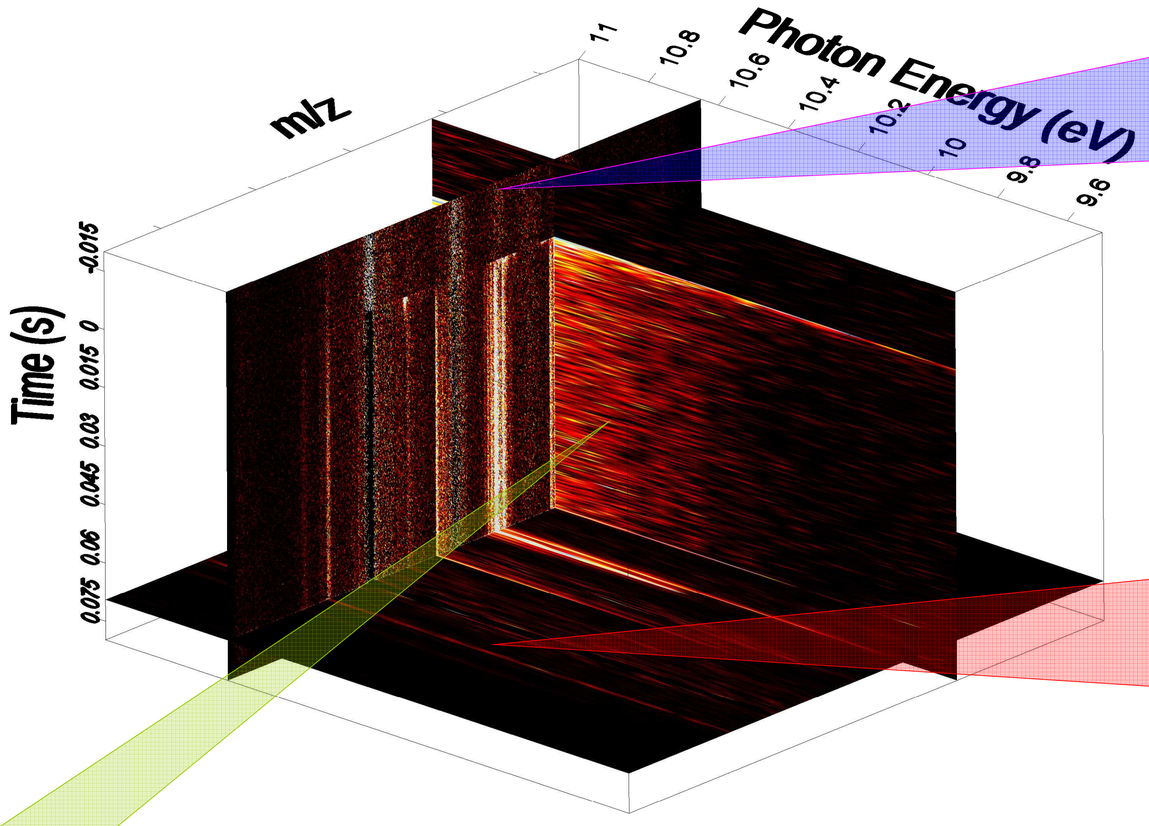
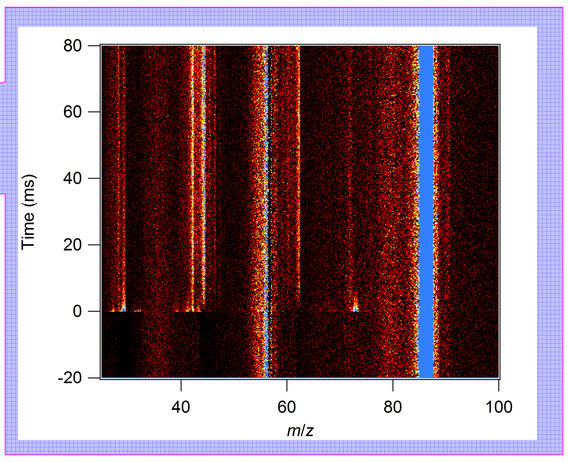
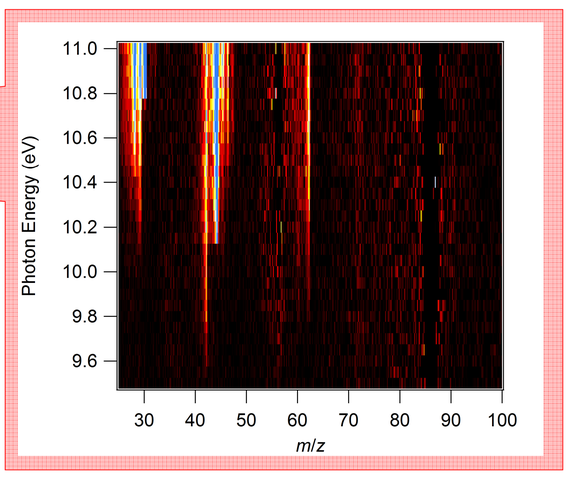


The Multiplexed Chemical Kinetics Reactor permits identification of time-resolved isomeric composition of laser-initiated reaction systems.



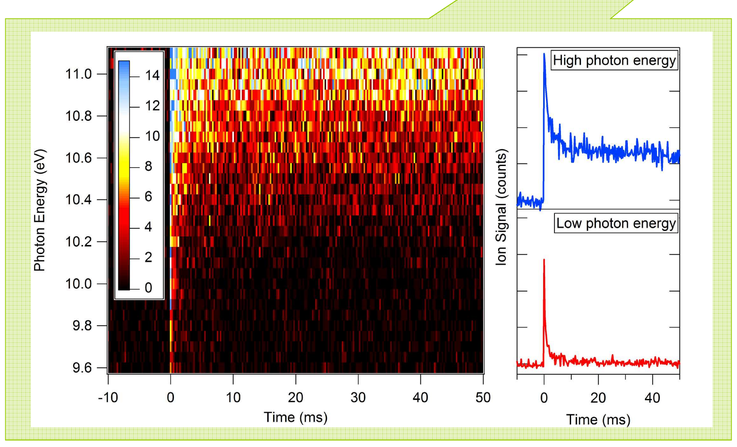


Mass Spectrum vs. Reaction Time

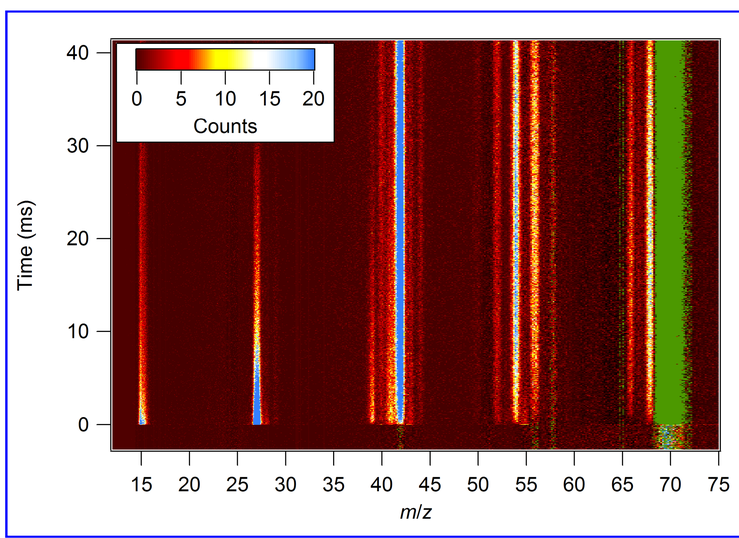


Photoionization Efficiency vs. Mass

Multiple-mass detection and the ease of tunability of synchrotron radiation make it possible to acquire full sets of data as a function of mass, photon energy, and time after reaction initiation. The data can be quantitatively correlated and integrated along any of several dimensions to compare to traditional measurements such as time profiles of individual chemical species, but it can also be directly interpreted in image form. (Taatjes, C. A.; Hansen, N.; Osborn, D. L.; Kohse-Höinghaus, K.; Cool, T. A.; Westmoreland, P. R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 20)



Single-Mass Photoionization Efficiency Spectrum vs. Reaction Time

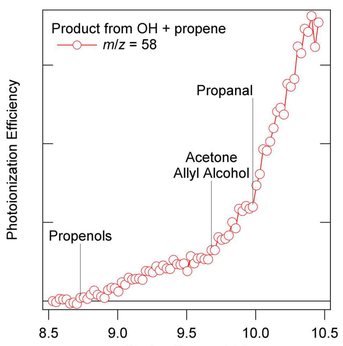


The collection of full multidimensional data is particularly powerful in discovering unexpected pathways. The vinyl + vinyl reaction has been previously measured to produce both 1,3-butadiene and ethene + acetylene. At right is a section of the mass spectrum taken at 10.2 eV photon energy following 193 nm photolysis of methyl vinyl ketone. Clear signal at *m*/*z* = 39, attributable to the propargyl radical, is observed, and closer inspection reveals a clearly discernable risetime, indicating that it is not a direct photolysis product. The shape of the propargyl signal is well-modeled by assuming it is a product of the self-reaction of vinyl radicals, indicating substantial branching of the reaction to propargyl + methyl.

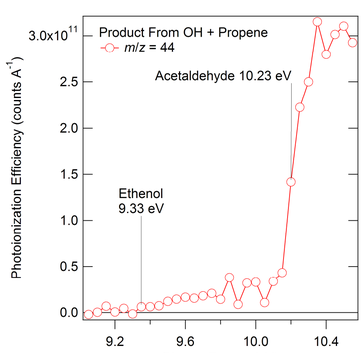
Enols have been observed in hydrocarbon flames and might play a role in tropospheric acid formation. Enols have been calculated to be produced in OH + alkene reactions. Enols have now been experimentally observed in the reactions of OH with several alkenes.

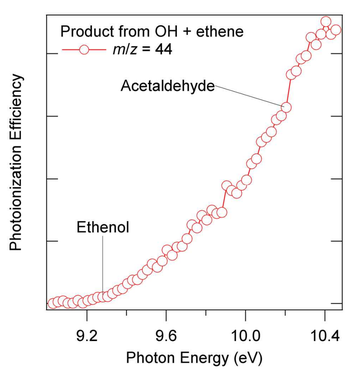
OH + propene produces C_2H_4O and C_3H_6O products:

m/*z* = 58 is propenol



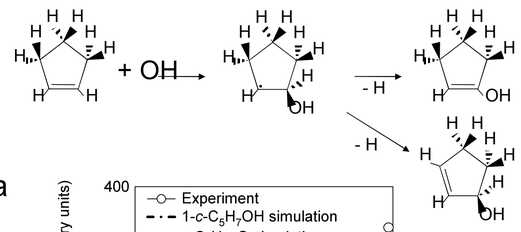
m/*z* = 44 is acetaldehyde

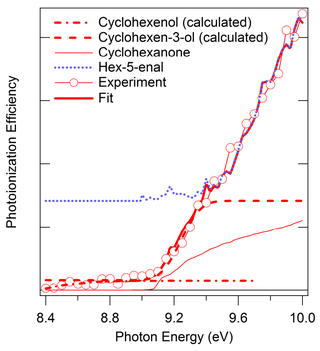




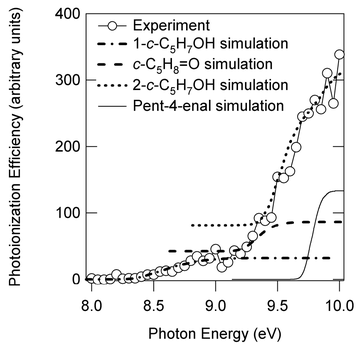
Substantial ethenol is observed from OH + ethene

The OH-initiated oxidation of cyclopentene shows similar products of OH addition and (possibly O_2 mediated) H-atom loss to those observed in OH + ethene and propene. Only cyclic C_5H_8O isomers are observed.





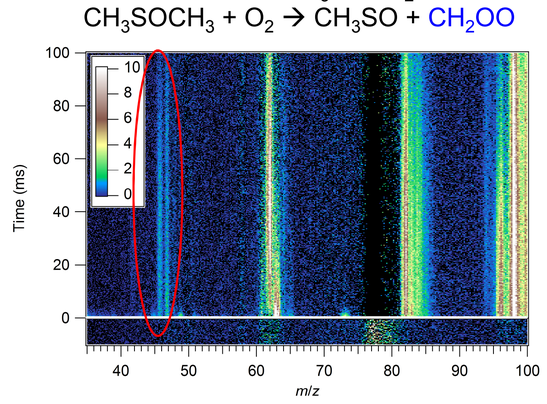
However, in OH-initiated oxidation of cyclohexene and 1,4-cyclohexadiene a significant contribution from ring-opening is seen. The mechanism for this process remains unclear, but ring opening appears more facile from the six-carbon species.



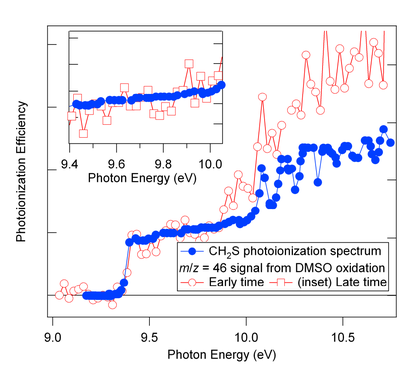
Reaction with ozone is an important tropospheric removal mechanism for unsaturated hydrocarbons. As first proposed by Rudolf Criegee, ozonolysis is generally accepted to occur via carbonyl oxide intermediates. Although gas-phase carbonyl oxides had never been directly observed, these “Criegee intermediates” are recognized as key species in, for example, tropospheric formation of organic acids and hydroperoxides.

Cl + DMSO → CH_3SOCH_2 + HCl

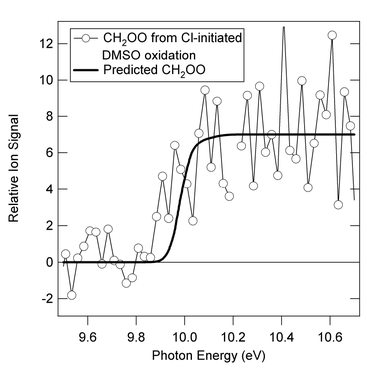
CH_3SOCH_3 + O_2 → CH_3SO + CH_2OO



We have measured the product mass spectrum from Cl-initiated oxidation of dimethyl sulfoxide (DMSO); the reaction of $CH_2S(O)CH_3$ with O_2 is calculated to produce CH_2OO with little excess energy (Asatryan, R.; Bozzelli, J. W. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1769)



← The *m*/*z* = 46 signal from the reaction (open circles) shows CH_2S (solid circles) and an additional contribution. The difference → gives the photoionization spectrum of the Criegee intermediate CH_2OO.



The team: David Osborn, Peng Zou, Giovanni Meloni, Talitha Selby, Judit Zádor, Howard Johnsen (Sandia); Fabien Goulay, Adam Trevitt, Steve Leone (UC Berkeley); Carl Percival (Manchester); Dudley Shallcross (Bristol)

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