INTERMEDIATES IN THE COMBUSTION OF ALTERNATIVE FUELS

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Low-temperature combustion and alternative fuels increase the importance of poorly characterized species and reactions

- Many advanced engine designs call for low temperature and high pressure
- Under these conditions, new species and reactions can become important
- Oxygenated intermediates, such as peroxyalkyl radicals (ROO•) and QOOH species can become important
- In addition, many potential biofuels are oxygenated (ethanol, butanol, methyl esters, dimethyl ether, etc.)

Our Goal

Use complementary experimental approaches at the University of Chicago and Argonne National Laboratory to develop the means to characterize these radicals and their reactivity

Importance of C_2H_4OH and the reaction C_2H_4 + OH

- Reactions of OH with fuel molecules are important in Combustion Chemistry
- In fuel-rich flames, reaction with OH is usually the first step in the oxidation of olefins
- Reactions with OH are the primary degradation path of ethylene in the troposphere
- Mechanistically, the reaction proceeds via a molecular adduct
- H loss from this adduct is the dominant source of ethenol (vinyl alcohol) in many flames, including ethanol flames
- Alternatively, C_2H_4OH is a radical formed by hydrogen abstraction from ethanol, C_2H_5OH, currently one of the most important biofuels

Produce C_2H_4OH in a well-characterized manner, and determine its decomposition pathways as a function of internal energy

Preparation of C_2H_4OH via the photodissociation of the halogenated ethanols, BrC_2H_4OH and IC_2H_4OH

The photodissociation of halogenated ethanols in the near uv results in two sets of products. For IC_2H_4OH these are:

$$IC_2H_4OH + h\nu \rightarrow I(^2P_{3/2}) + C_2H_4OH \qquad (1)$$
$$IC_2H_4OH + h\nu \rightarrow I^*(^2P_{1/2}) + C_2H_4OH \qquad (2)$$

The threshold for reaction 1 is 21.7 kcal/mol lower than for reaction 2

★ We want to know the branching ratio between the two reactions, and how the excess energy is distributed between internal energy of the C_2H_4OH and translational energy of the two fragments

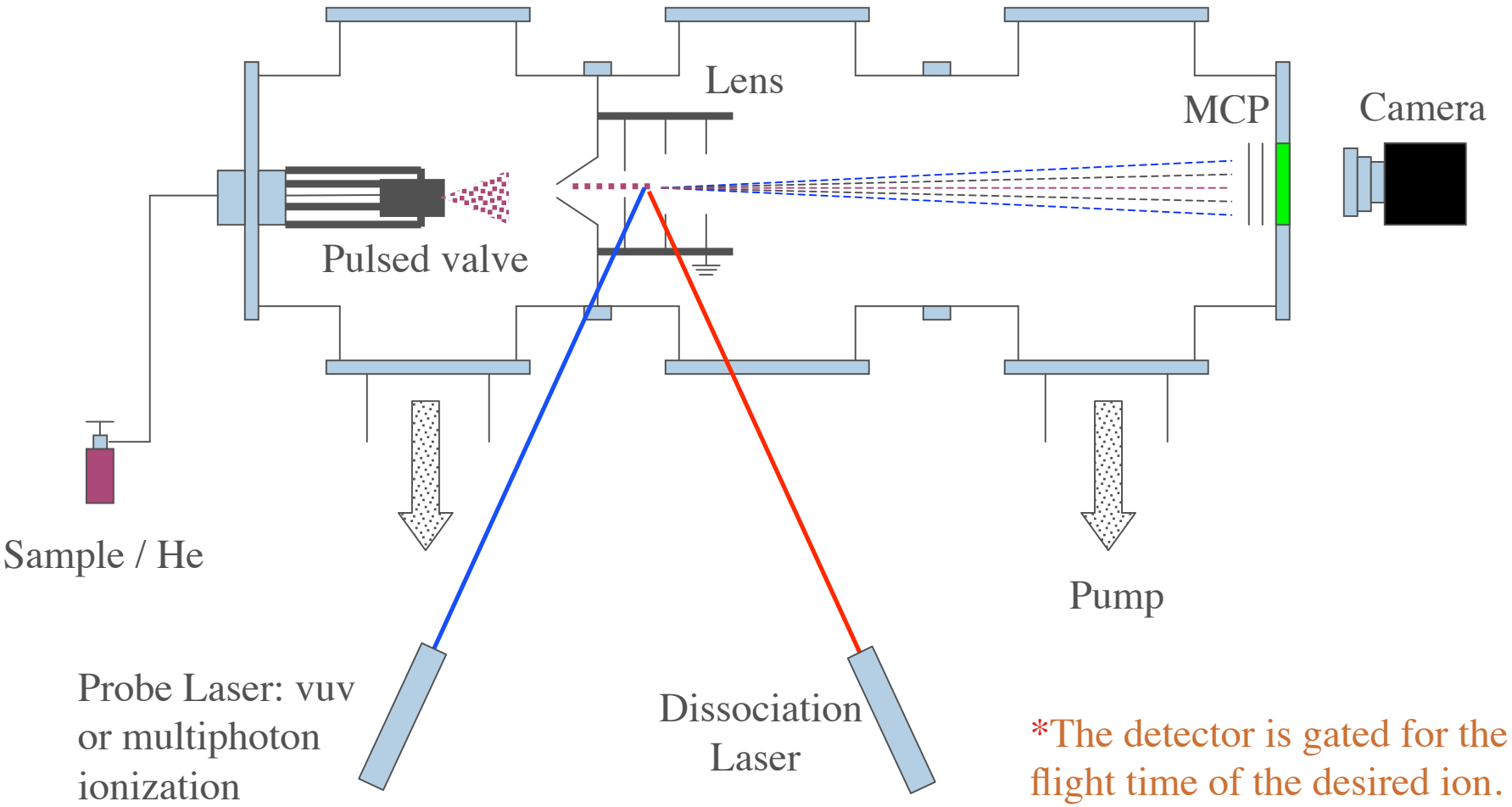
★ We also want to know if there is sufficient internal energy in the C_2H_4OH for it to undergo secondary fragmentation via

$$C_2H_4OH \rightarrow C_2H_4 + OH \qquad (3)$$
$$C_2H_4OH \rightarrow C_2H_4O + H \qquad (4)$$

★ And we want to know the identity of the C_2H_4O: acetaldehyde or ethenol?

Ion imaging dissociation fragments

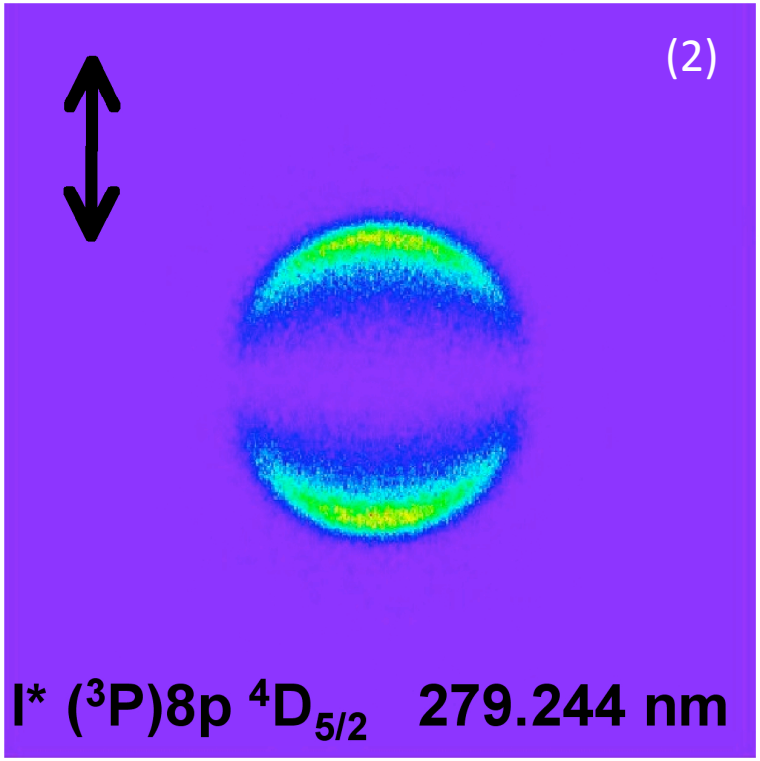
vuv = universal detection; multiphoton = state selective detection

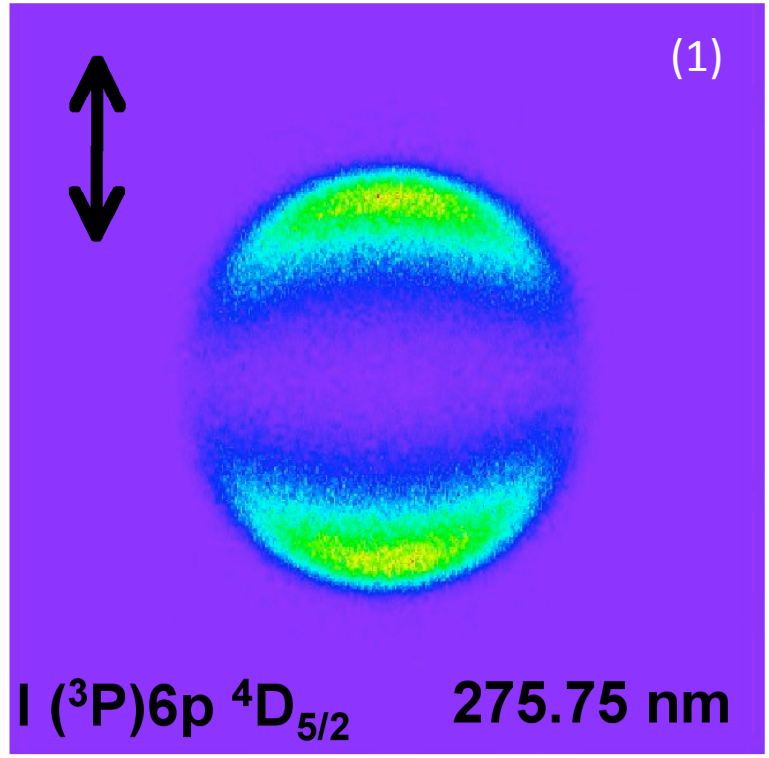


*The detector is gated for the flight time of the desired ion.

vuv ionization = universal detection; multiphoton ionization = state selective detection

$$h\nu - D_o(X\text{-}C) = E_{el}(I) + E_{trans} + E_{int}(C_2H_4OH)$$





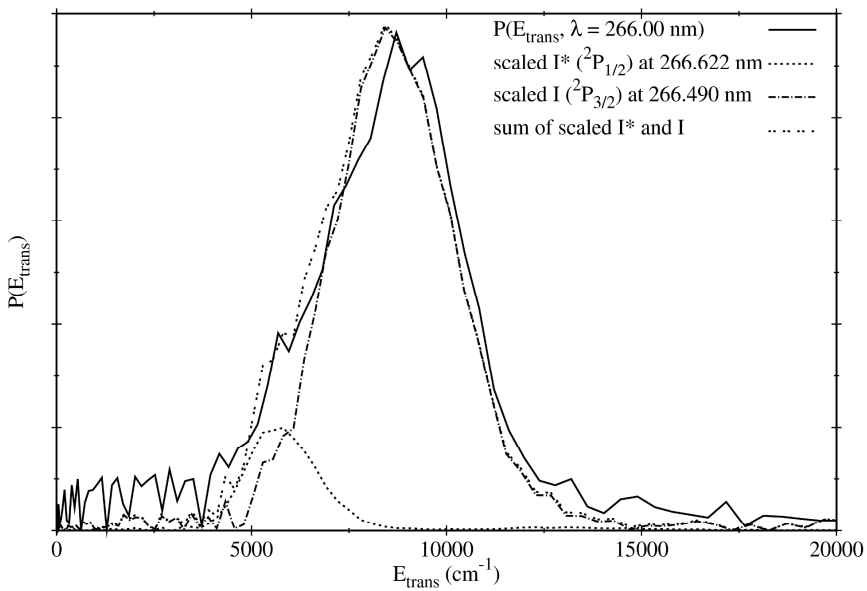
$$IC_2H_4OH + h\nu(266\text{ nm}) \rightarrow I(^2P_{3/2}) + C_2H_4OH \qquad (1)$$
$$IC_2H_4OH + h\nu(266\text{ nm}) \rightarrow I^*(^2P_{1/2}) + C_2H_4OH \qquad (2)$$

The I* image is smaller because there is less excess energy in the reaction

There is a distribution of translational energy in both channels

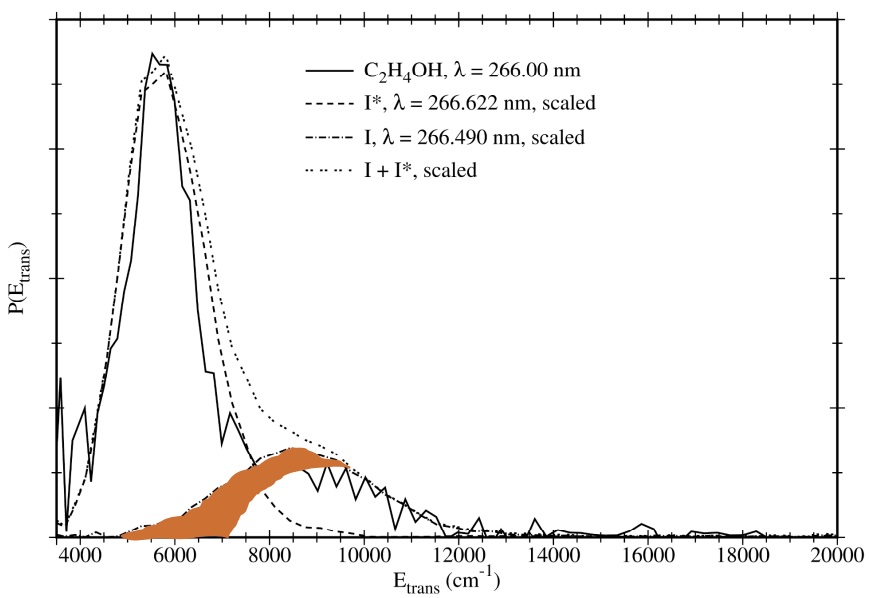
This translates to a distribution of internal energy in the C_2H_4OH

Determining Branching Ratios



- Separately image I and I* by using resonant multiphoton ionization
- Image both I + I* by using single-photon ionization with vuv light
- Reconstruct the images to obtain the translational energy distributions
- Using the known cross vuv cross sections for I and I*, fit the separate I and I* distributions to the summed distribution

This gives the I/I* branching ratio

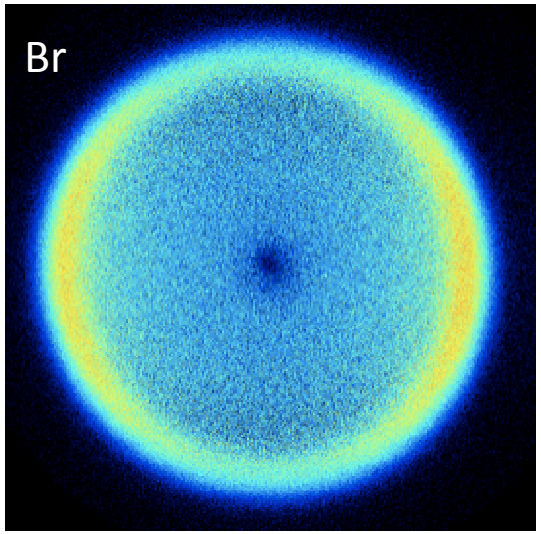


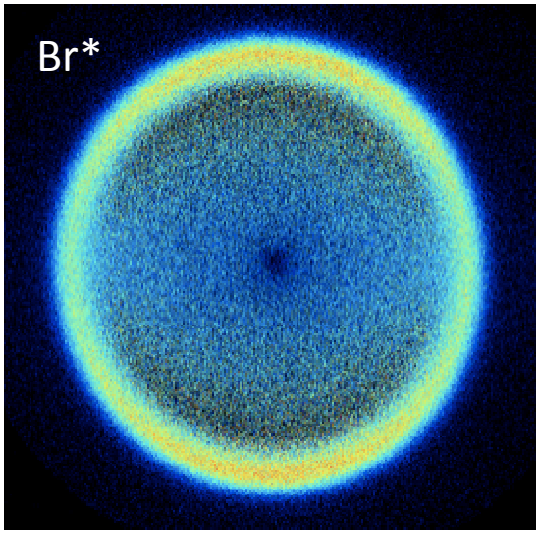
- Image the CH_2CH_2OH radical by using single-photon ionization
- Scale the I and I* distributions by the I/I* branching ratio to prepare a synthetic radical distribution
- Compare the radical and I + I* distributions

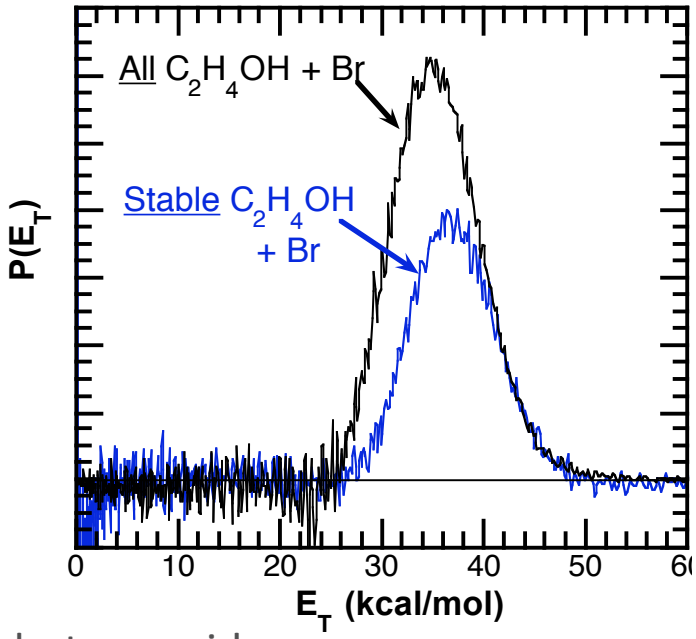
This comparison indicates that radicals formed with E_{trans} < ~9,500 cm^{-1} may undergo secondary decomposition

Photodissociation of BrC_2H_4OH

Detection of $Br(^2P_{3/2})$, $Br^*(^2P_{1/2})$, and C_2H_4OH

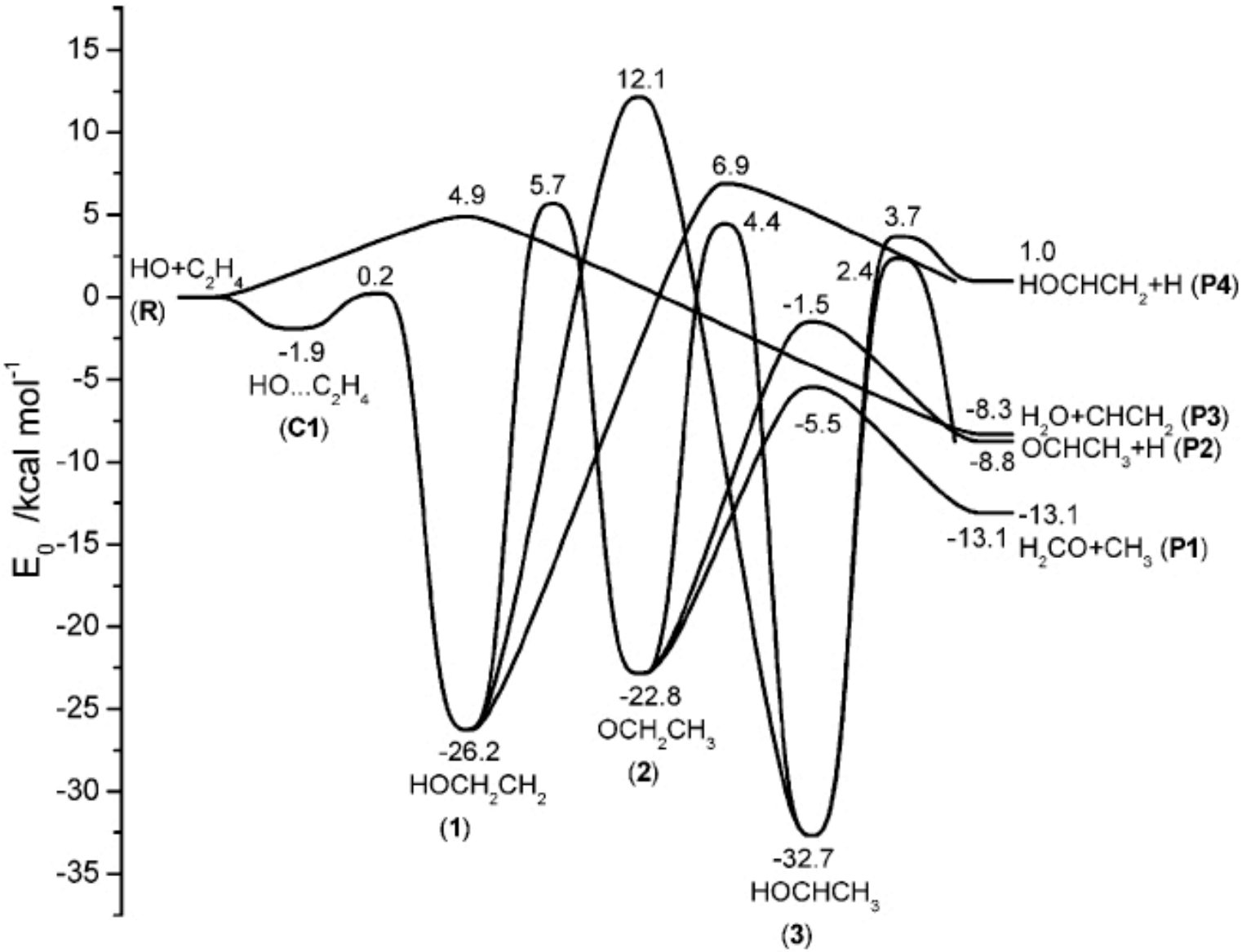






- Somewhat different methodology than for IC_2H_4OH, but same idea
- State-selected Br and Br* distributions used to make full distribution
- VUV ionization of C_2H_4OH used to determine "stable" C_2H_4OH distribution
- Difference shows decomposition of C_2H_4OH
- Unusual stability explained in terms of rotational excitation and dissociation dynamics
- Significantly improved modeling of rotational distributions

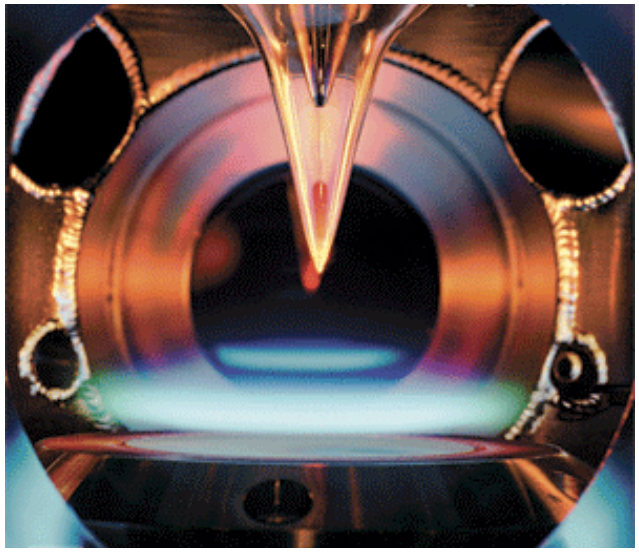
Energetics and decay paths of C_2H_4OH



Identification of products with tunable vuv light

$C_2H_4OH \rightarrow H + CH_3CHO$ (acetaldehyde, IP = 10.229 eV)

$C_2H_4OH \rightarrow H + CH_2CHOH$ (ethenol/vinyl alcohol, IP = 9.33 eV)



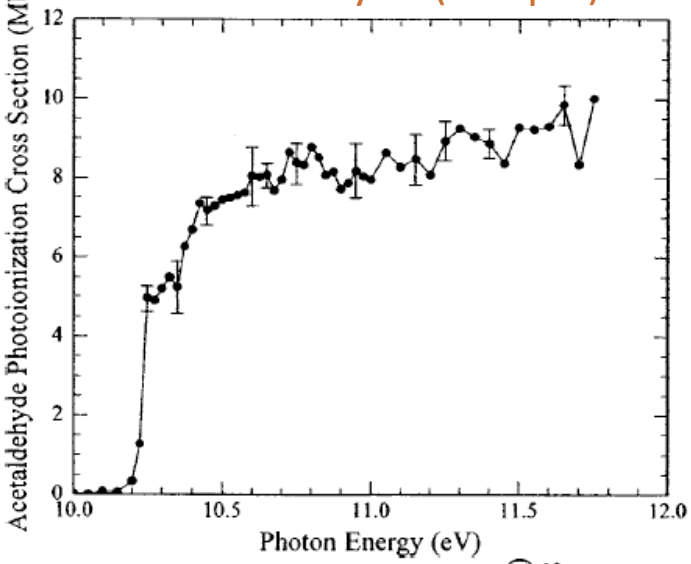
Ethenol has been identified in recent flame experiments for a wide range of fuels

By using vuv photoionization of the C_2H_4O fragment at several energies between 9.0 and 10.5 eV, these isomers can be distinguished

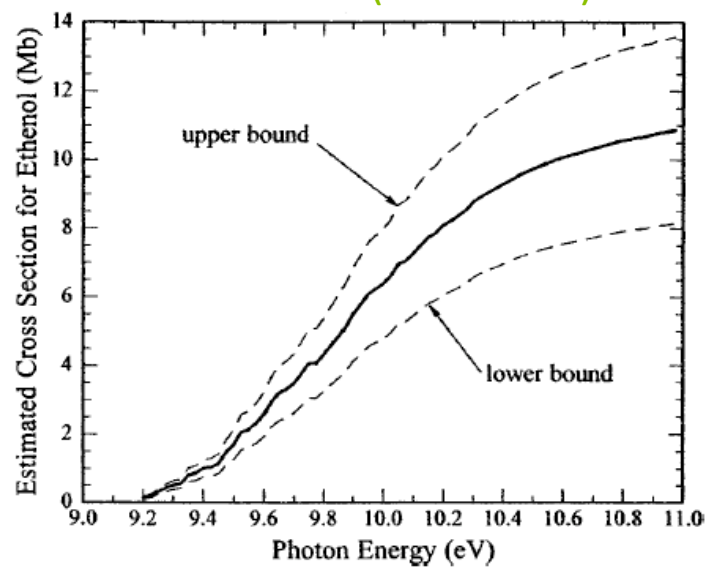
Photoionization of acetaldehyde and ethenol

results from T. A. Cool et al., J. Chem. Phys. **119**, 8356 (2003)

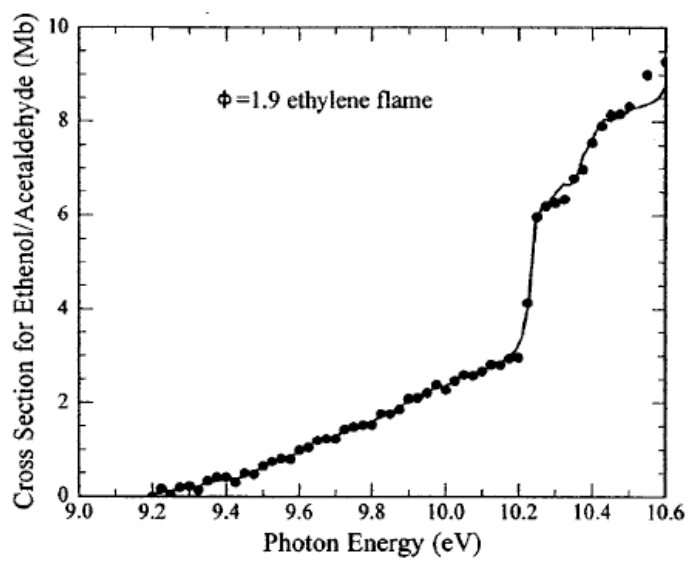
Acetaldehyde (sample)



Ethenol (estimated)



Absolute photoionization cross sections are required to extract concentrations



Ethylene Flame estimated concentrations

~37% Ethenol

~63% Acetaldehyde

Progress

- Graduate student Britni Ratliff was to have worked Argonne beginning in January to work on this project using tunable vuv light
- Laurie was granted beamtime at the NSRRC in Taiwan to use their synchrotron source for this work*
- Britni went to Taiwan to perform the experiments
- Britni is currently analyzing the data
- Her visit to Argonne has been postponed

using a vuv beamline

Continuing Efforts

Complete the halogenated ethanol studies

Produce C_2H_4OH via alternative approaches

- Photodissociation of ethylene glycol vinyl ether, $C_2H_3OCH_2CH_2OH$
- Form cold C_2H_4OH by photodissociation in the expansion, and photodissociate the radical directly
- A new apparatus at Argonne allows such sample preparation

Characterization of alkyl peroxy radicals

- These radicals can be formed by photodissociation of appropriate precursors in supersonic expansions in the presence of O_2
- These radicals are thought to be very important in low-temperature combustion
- Imaging techniques and vuv photoionization will be essential to detect these species and their decay products

Publications:

V. A. Shubert, M. Rednic, and S. T. Pratt, J. Phys. Chem. A **113**, 9057-9064 (2009).

B. J. Ratliff, C. C. Womack, X. N. Tang, W. M. Landau, L. J. Butler, and D. E. Szpunar, J. Phys. Chem. A **114**, 4934-4945 (2010).

Future Funding Opportunities

DOE is considering significant new programs in Combustion

$20M is in the President's FY2011 budget for DOE-SC-BES-CSGSBS Gas-Phase Chemical Physics Program:

> "High-fidelity models of combustion processes will be critical to enabling the transition from hardware-intensive, experience-based engine design to simulation-intensive, science-based design, accommodating new fuel types and engine combustion systems."

This Program will include funding for new experiments for validation and verification.

This increase may be a jump-start for an ASCI-scale program (~$200M/year) in Combustion Modeling that is being considered by Steven Koonin for FY2012 and beyond.

The End

Thank you for your attention