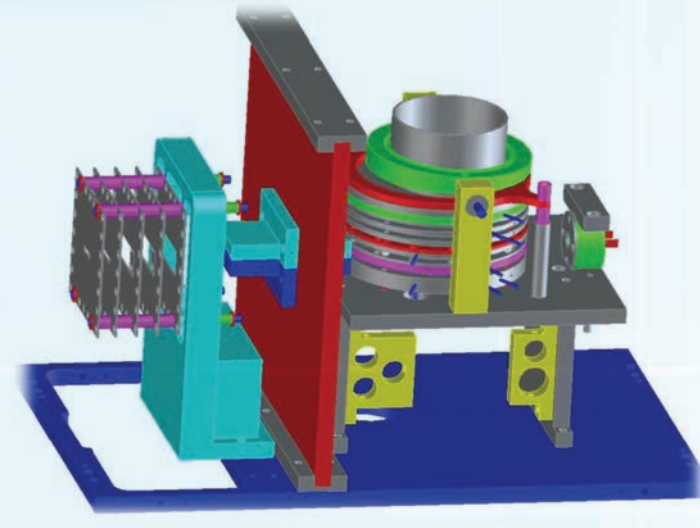
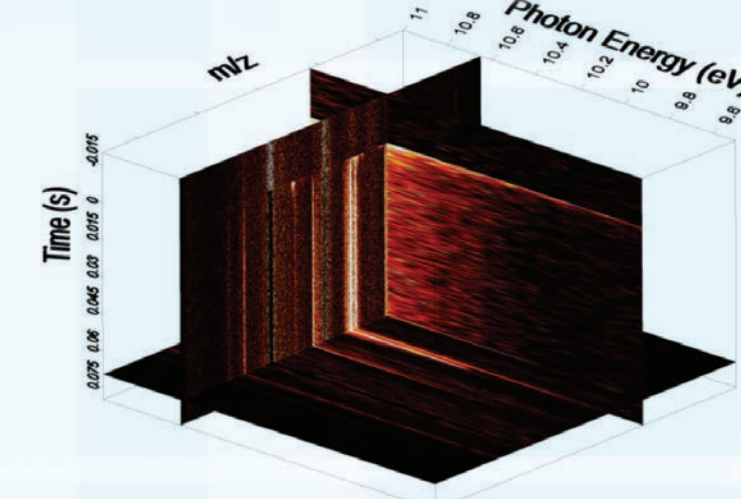


# Breakthrough Tools for Chemical Discovery



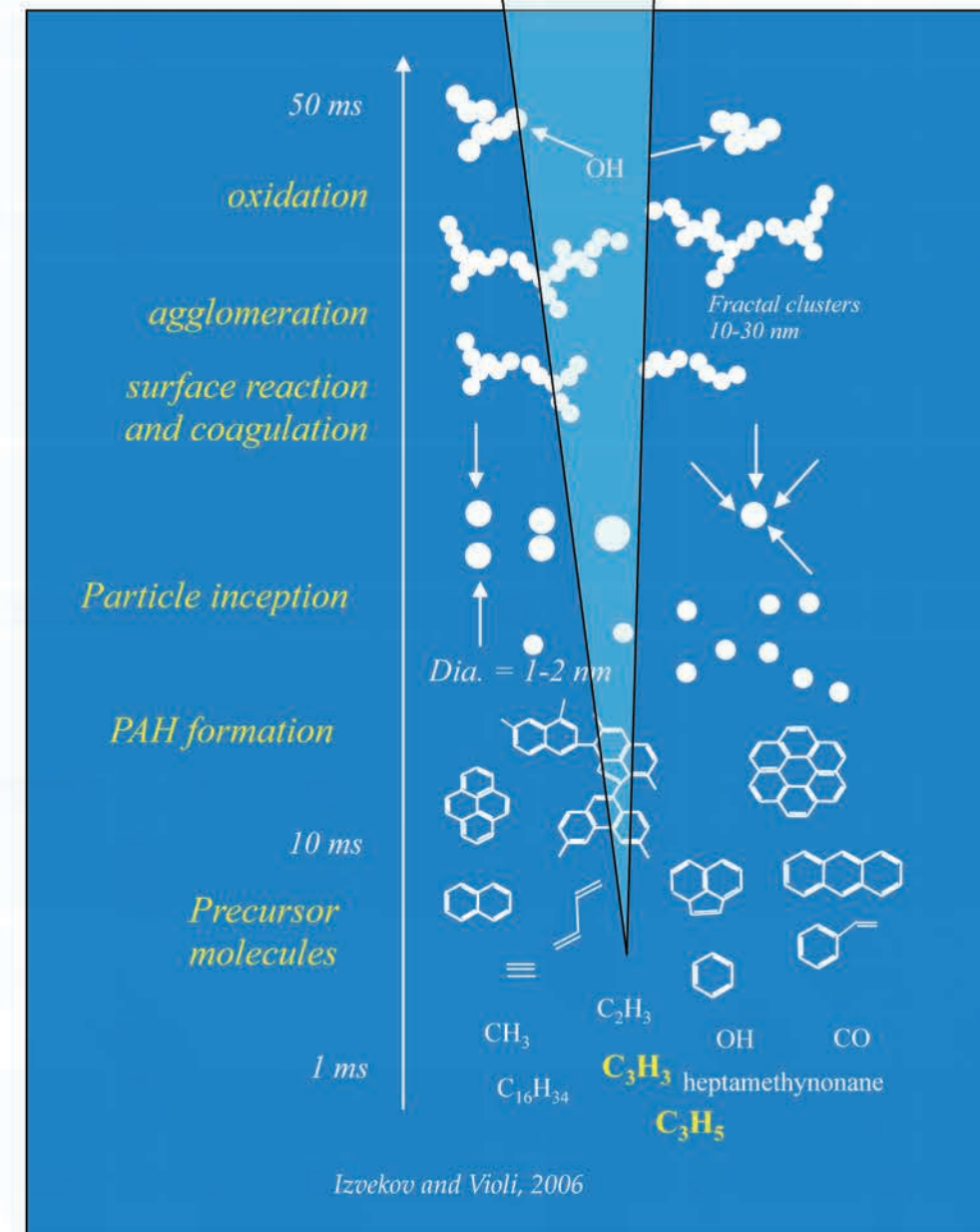
Talitha Selby, Arkke Eskola, Haifeng Huang,  
Howard Johnsen, David Osborn, John Savee, Lenny Sheps,  
Max Sloss, Craig Taatjes, Subith Vasu, Oliver Welz, Judit Zádor



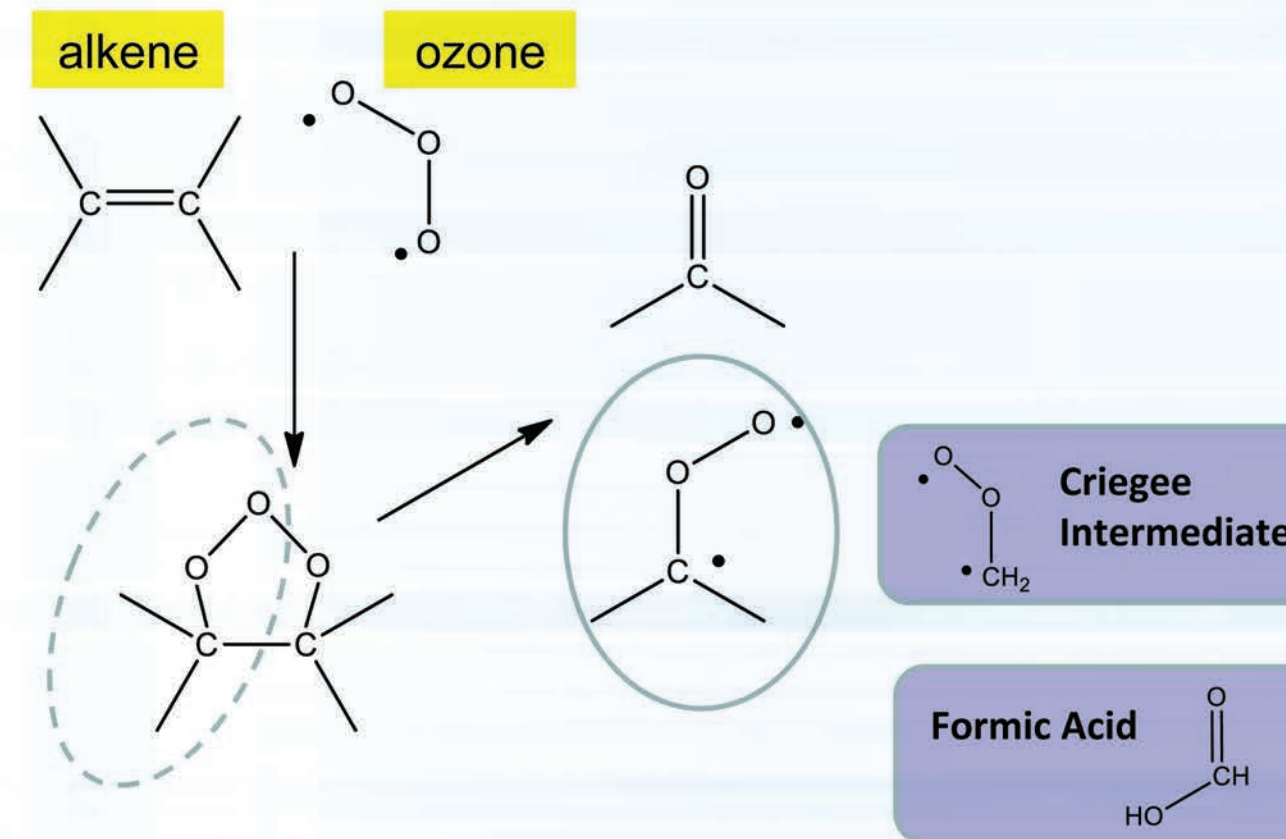
## Direct observation of chemical intermediates answers longstanding questions

- Understanding the first steps of soot formation is critical to pollutant reduction
- Shape matters – which isomers are formed?

Soot is carcinogenic  
Soot formation reduces efficiency  
Soot deposits may accelerate global warming



Tropospheric and engine oxidation processes both depend on elusive isomeric intermediates



Alkenes are both biogenic and man-made. How they react in the atmosphere affects our climate, but the affects are not well understood

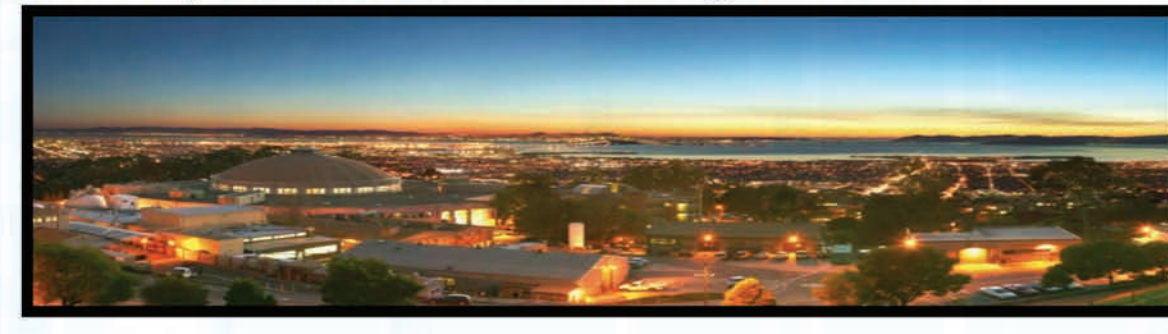
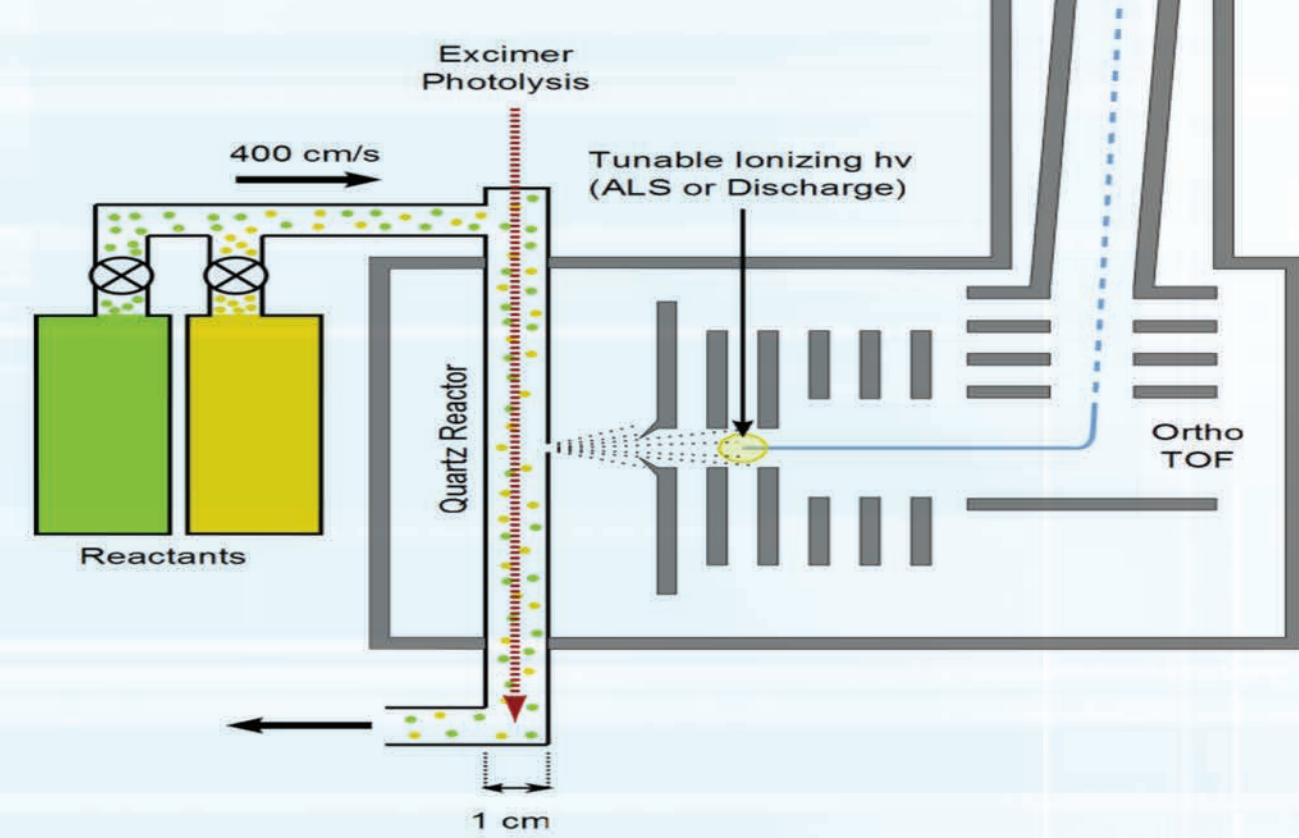
Criegee intermediates are *isomers* of more stable products, organic acids or esters

No one ~~has~~ directly measured a Criegee reaction

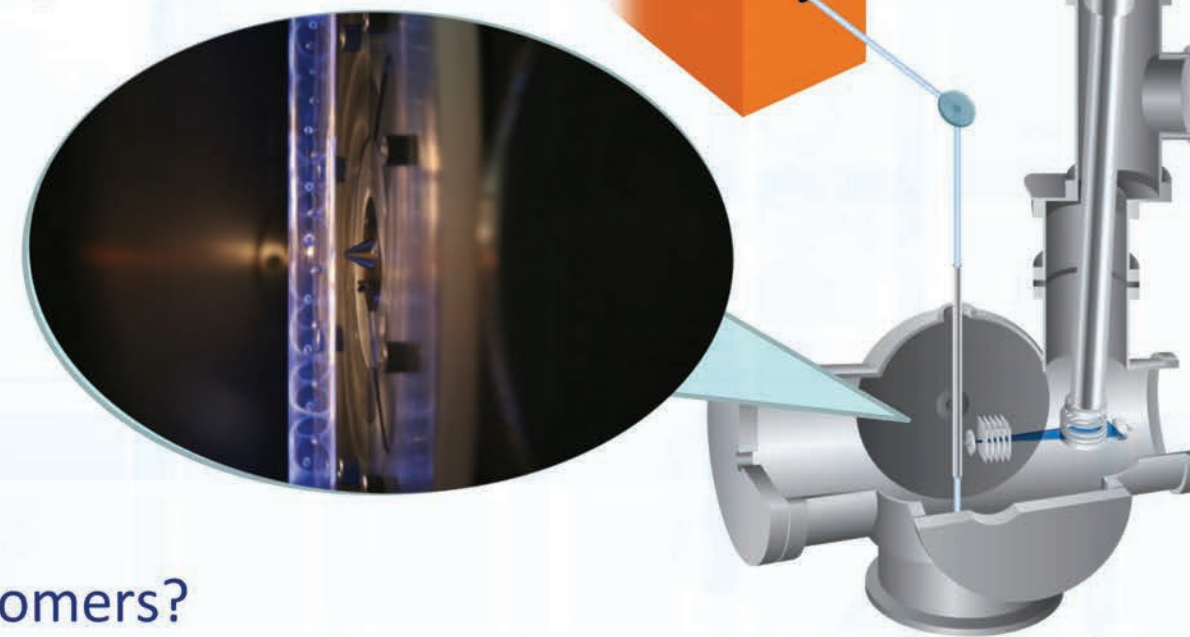
## How do we learn about intermediates?

Multiplexed Photoionization Mass Spectrometry at the Advanced Light Source

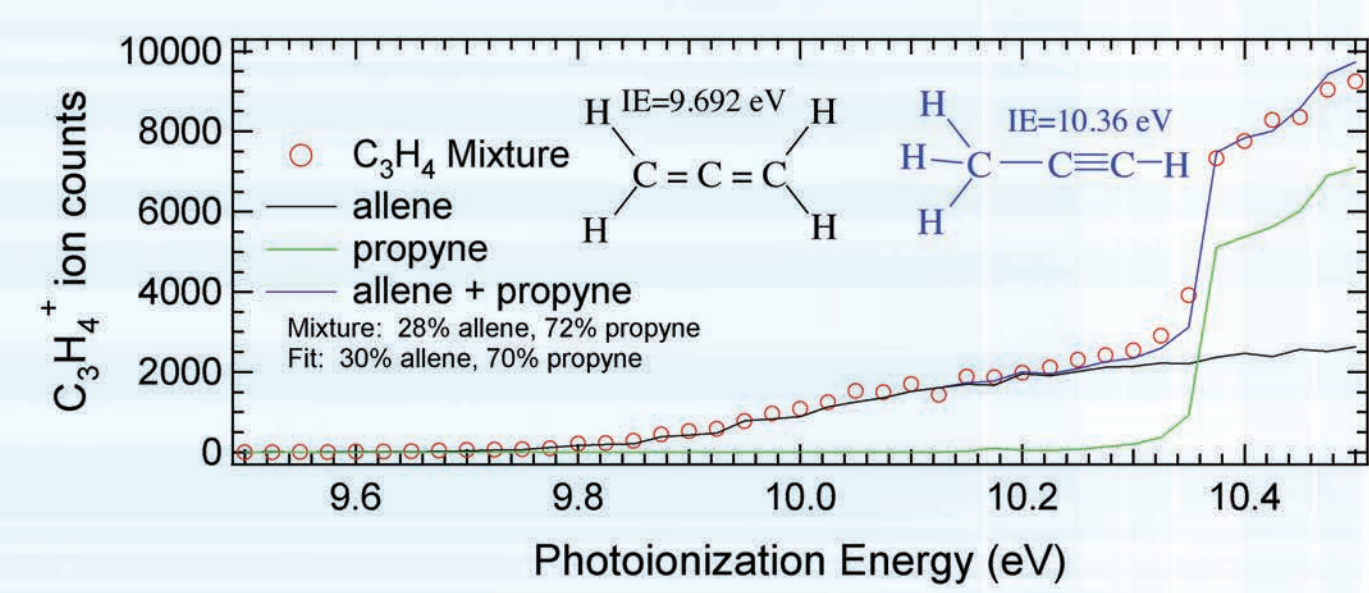
Pressure: 1 – 10 torr  
Temperature: 300 – 1000 K  
Temporal Resolution: ~40 μs  
Mass Resolution: ~1600



Our Sandia-designed apparatus can sensitively detect specific isomers!

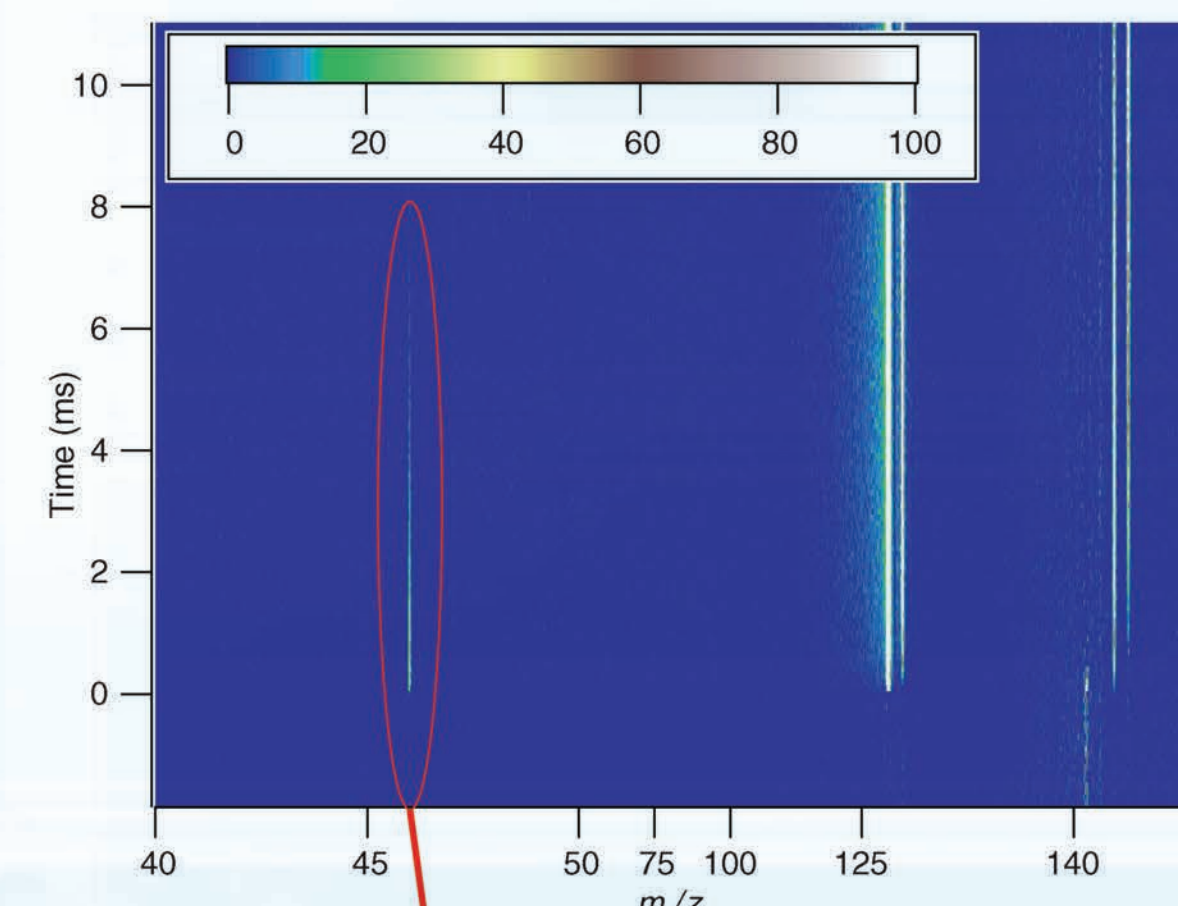


How do we measure the contribution of different isomers?  
Photoionization spectra provide fingerprints



- Kinetic data acquired as a function of time, mass, and photoionization energy
- Photoionization spectra can distinguish among isomers

## Tunable synchrotron photoionization enables the first Criegee kinetics measurement



The Criegee intermediate is a biradical (having two unpaired electrons).

But how reactive is it really?

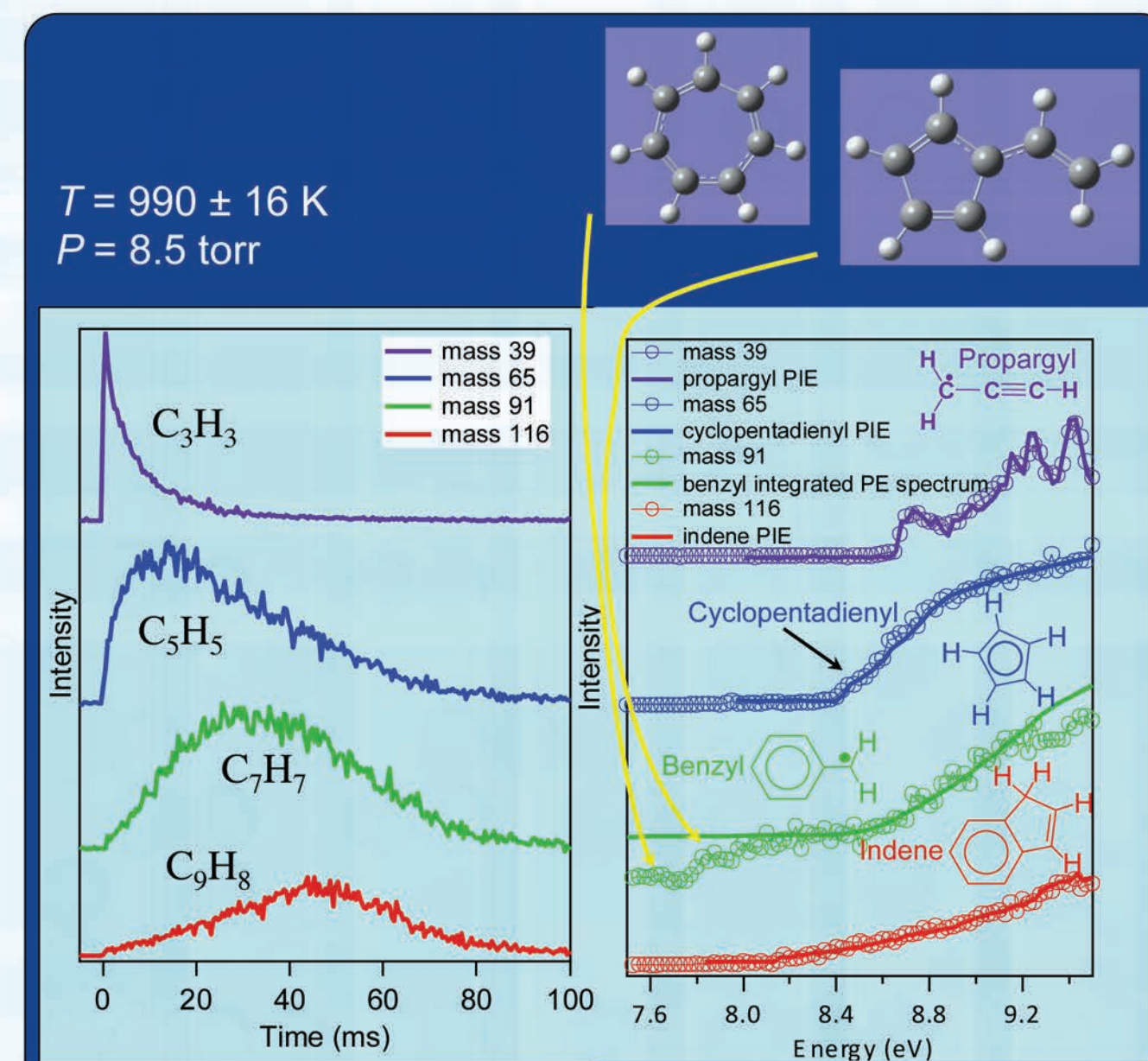
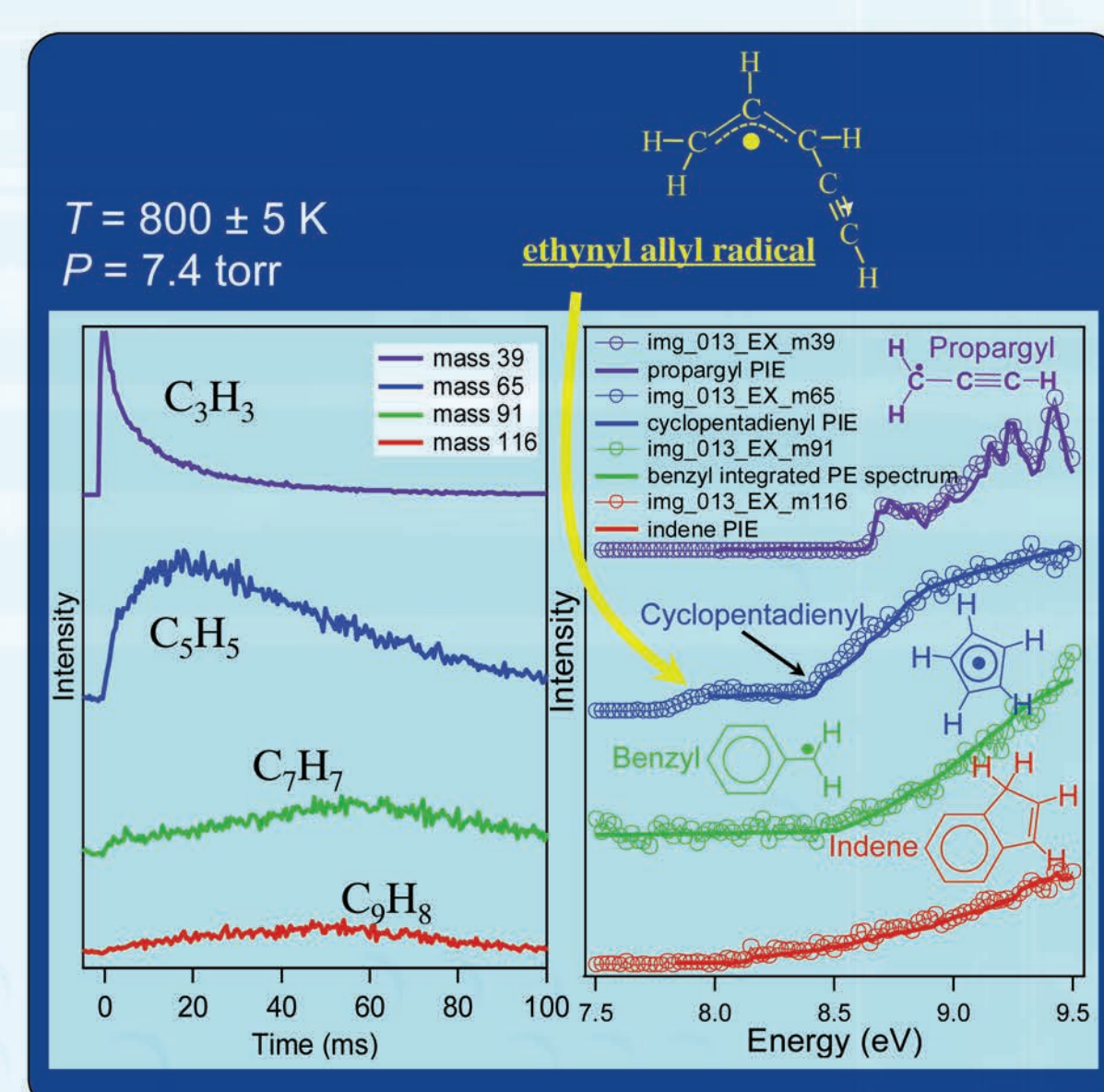
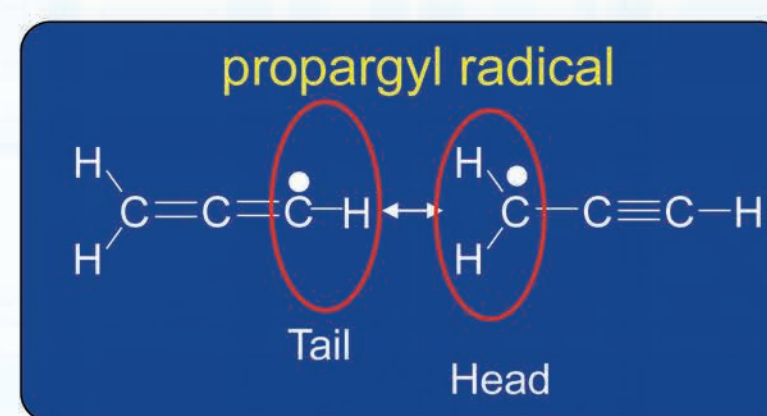
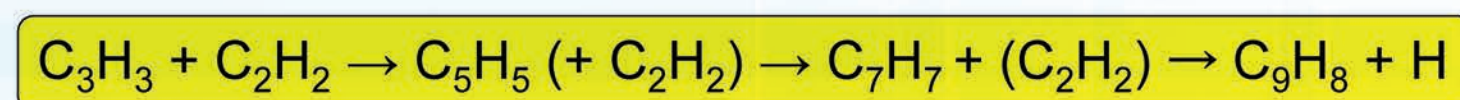
Model predictions vary widely: direct measurements are needed



## Isomers are a sensitive function of temperature

The reaction of propargyl with acetylene has been proposed as a key pathway to soot.

- Can we uncover the chemical mechanism?
- Each step's chemistry depends on the previous step.

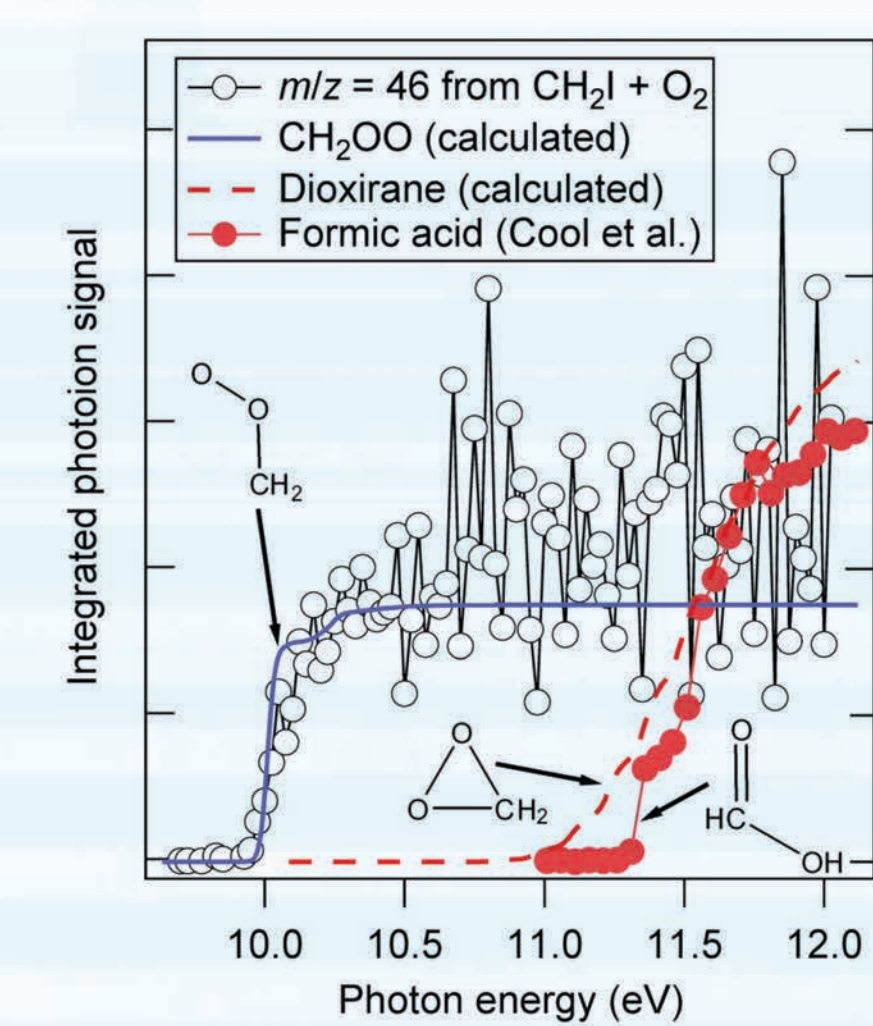


These isomer-resolved product measurements will provide a benchmark for predictive simulation of this pathway in soot formation chemistry.

Direct monitoring of Criegee intermediates opens the door to all these studies

- Arkke Eskola et al. *Phys. Chem. Chem. Phys.* 8, 1416 (2006) found that  $CH_2I$  reaction with  $O_2$  made I atom – turns out that what's left is Criegee intermediate!
- Can make lots of Criegee this way, measuring reactions with important tropospheric species

With Dudley Shallcross (Bristol) and Carl Percival (Manchester) Welz, Savee, et al., *Science* 335, 204 (2012)



Reaction of  $CH_2OO$  with  $NO_2$  is 50 times what is used in models  
If other Criegee intermediates react similarly, Criegee reactions are significant  $NO_3$  source  
Reaction of  $CH_2OO$  with  $SO_2$  is up to 10 000 times models  
If other Criegee intermediates react similarly, Criegee reactions are major  $SO_2$  oxidant

