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Multiplexed Photoionization Mass Spectroscopy at Synchrotrons: Past Accomplishments and Future Challenges

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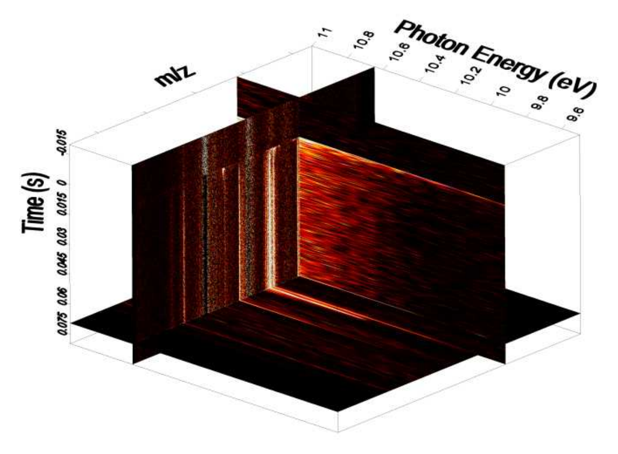


Swiss Light Source, Febuary, 2013

Outline

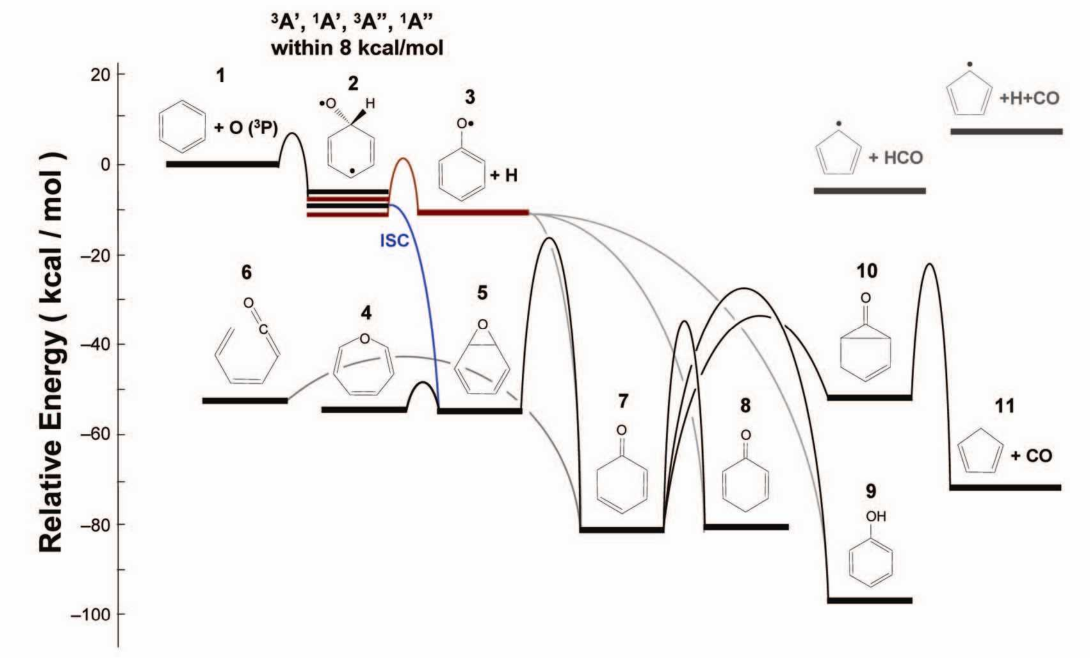
- Exploring chemical reactions
- Time-resolved photoionization mass spectrometry
- Complications
- Entering the 4th dimension?
- Conclusions

How do we explore chemical reactions?

$O(^3P) + C_6H_6 \rightarrow$ products

Good questions to ask:

- What are the reaction products?
- What is the reaction rate?
- How do temperature and collisions (pressure) affect the reaction?
- How is energy disposed in the reaction (vibration, rotation, translation)?
- What shape is the potential energy surface?



What should we measure and how?

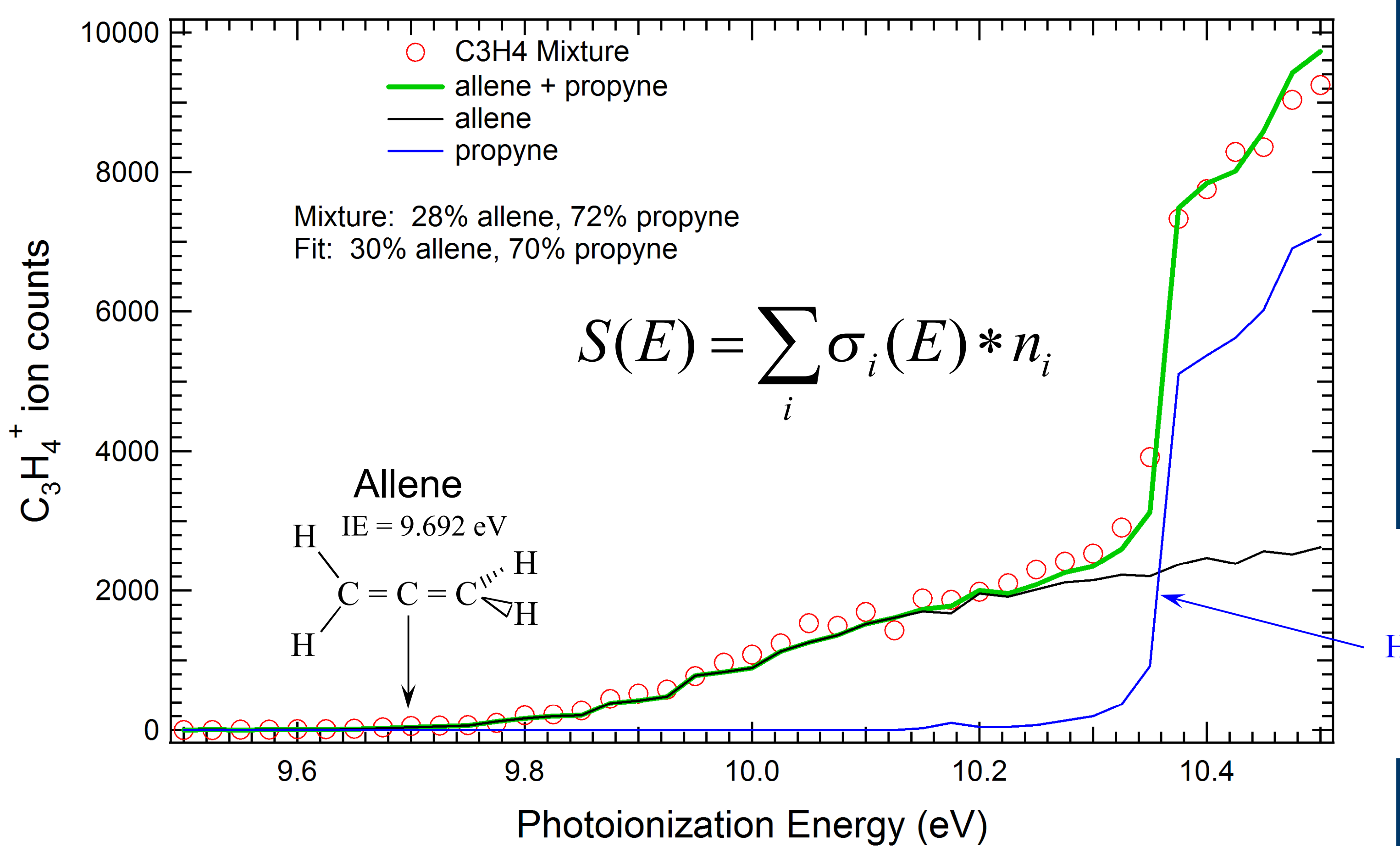
- Goals in studying chemical reactions of neutral molecules
  - Universal detection (mass spectrometry)
    - separation of molecules (mass / charge ratio)
  - High sensitivity (detect ions -- single ion counting)
  - Good selectivity at each m/z ratio
    - Can you tell HCN from HNC? (tunable photoionization, synchrotron)
  - Simultaneous detection (*multiplexed* mass spectrometry)
  - Dependence of signals on:
    - Temperature & pressure (when collisions are allowed)
    - Initial & final quantum state selection (single collisions conditions)

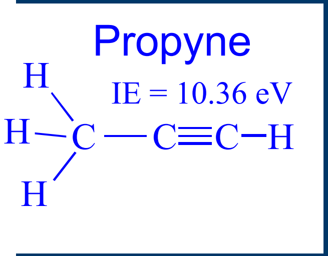
Photoionization Source

The Advanced Light Source
Lawrence Berkeley National Laboratory

- Chemical Dynamics Beamline
- VUV tunability 7.3 - 15 eV
- Resolution 10-50 meV

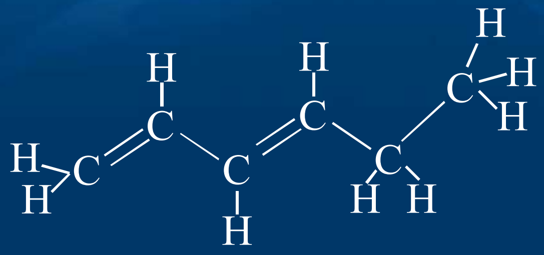
Quantitative branching ratios from photoionization spectra



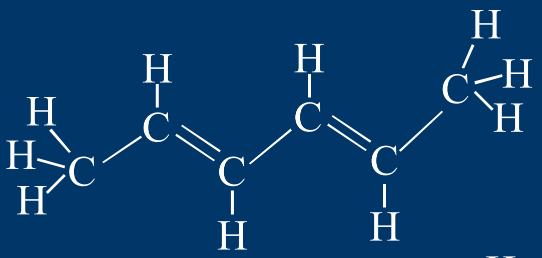


- From photo-ionization spectra we can extract the proportion of each isomer present

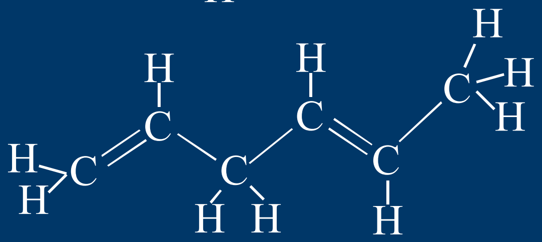
C_6H_{10} Isomers: high selectivity is possible



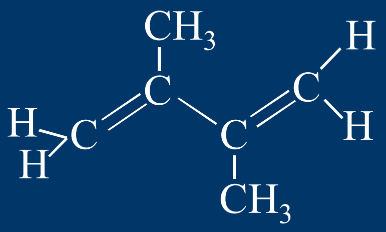
🟥 1,3-hexadiene



● 2,4-hexadiene

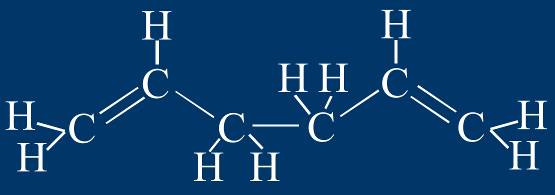


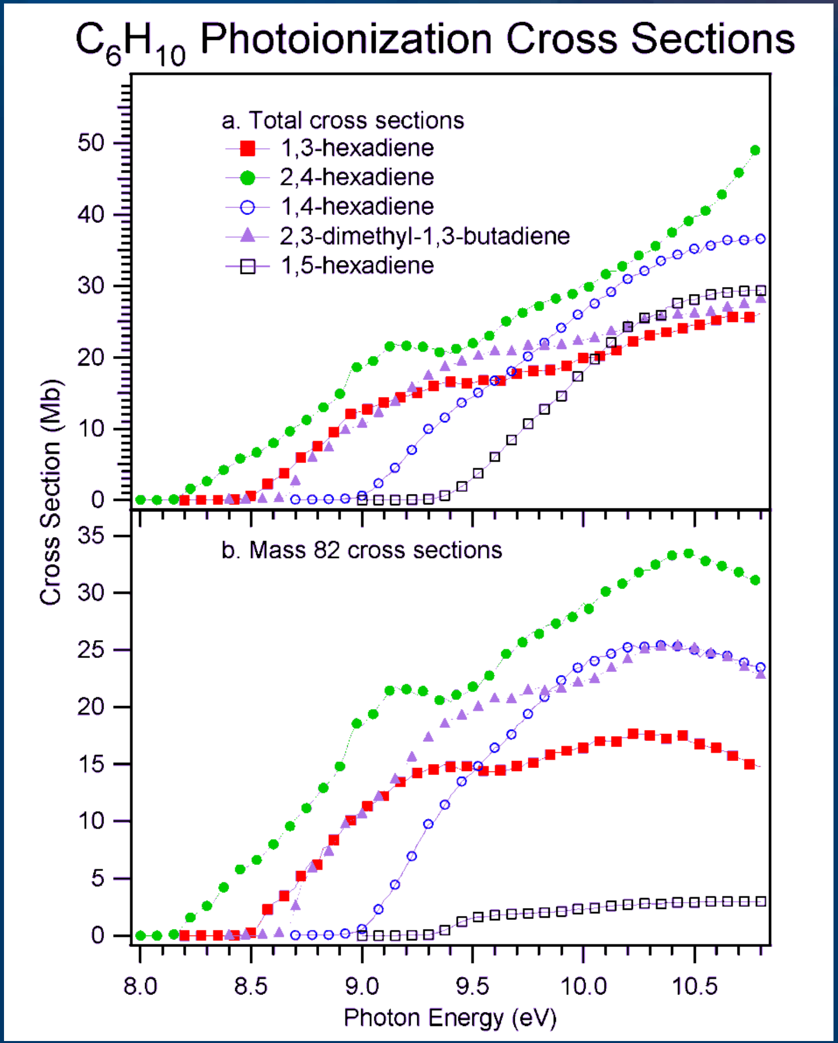
○ 1,4-hexadiene



△ 2,3-dimethyl-1,3-butadiene

☐ 1,5-hexadiene





Studying reactions through 3-D imaging

Techniques for multidimensional studies of chemical reactions

Three dimensions:

1) Mass
2) time (distance or velocity)
3) photoionization energy

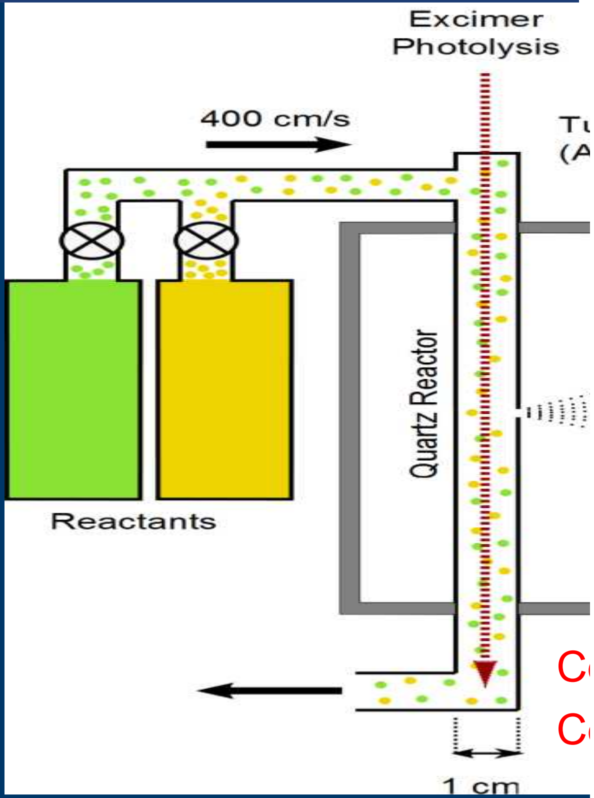
- Low pressure flame studies with molecular beam mass spectrometry (Nils Hansen)

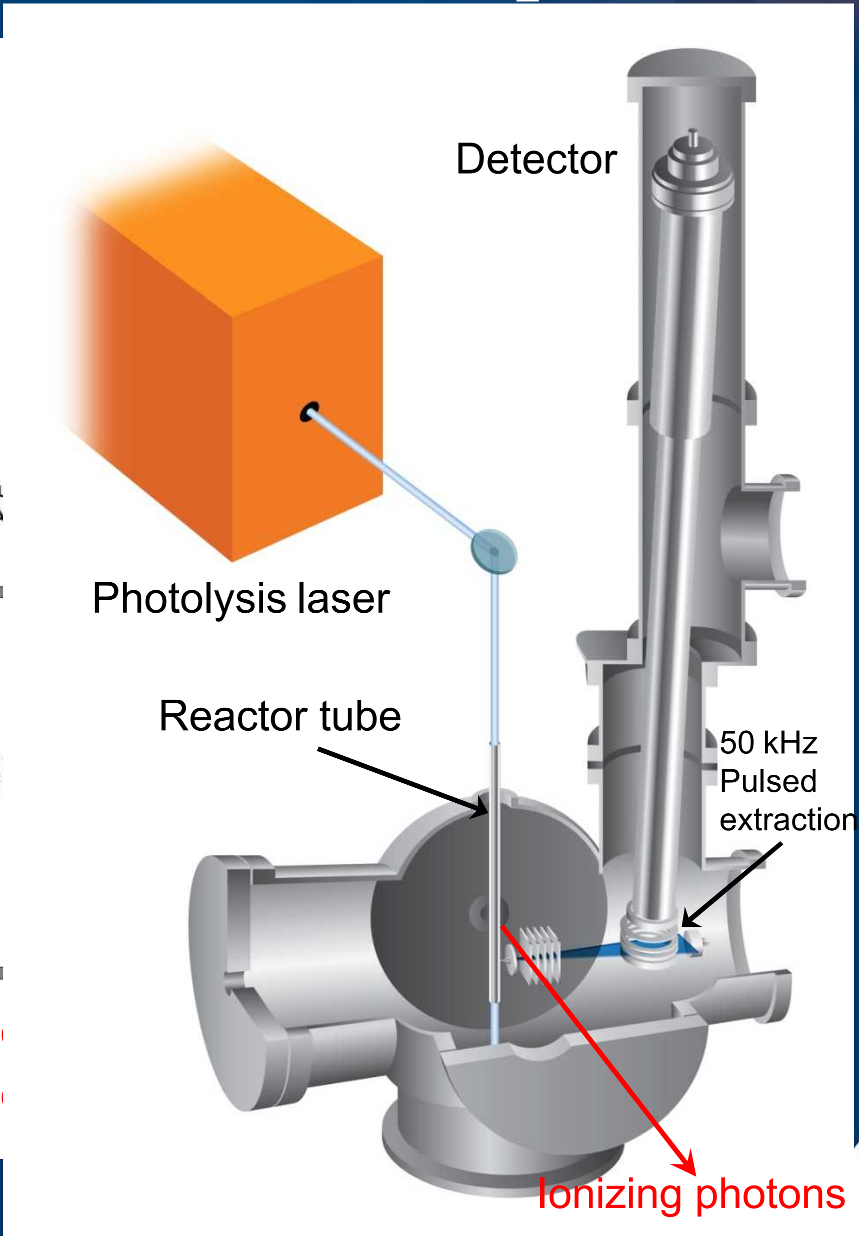
- Isolated elementary reactions with photoionization crossed molecular beams (Jim Lin)

- Reaction kinetics with time-resolved photoionization mass spectrometry (Osborn, Taatjes)

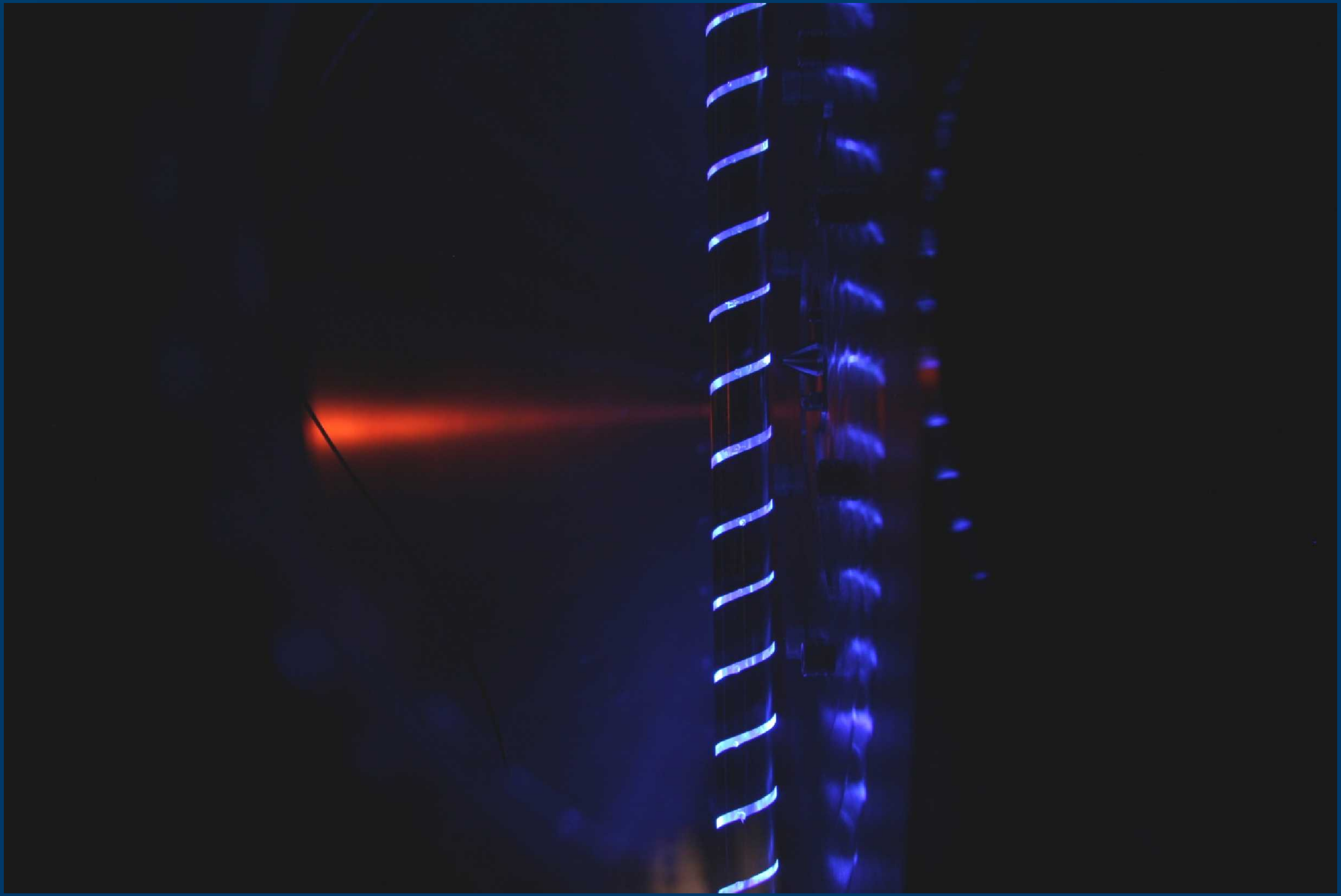
Multiplexed Photoionization Mass Spectrometer

Dimension	Use
Mass / charge ratio	Identify / quantify species
Reaction Time	Observe reaction kinetics
Photoionization Spectra	Identify / quantify species





Reactor, pinhole, and skimmer



Three-Dimensional Data: *S*(*m*, *t*, *hν*)

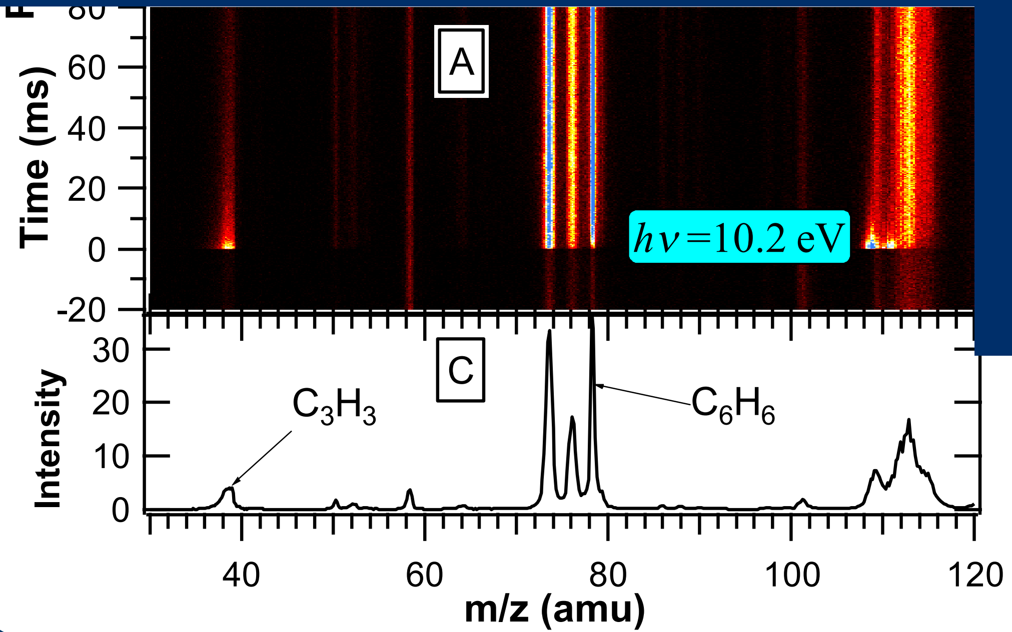
$$C_3H_3Cl \xrightarrow{193\text{ nm}} C_3H_3 + Cl$$

$$C_3H_3 + C_3H_3 \rightarrow C_6H_6$$

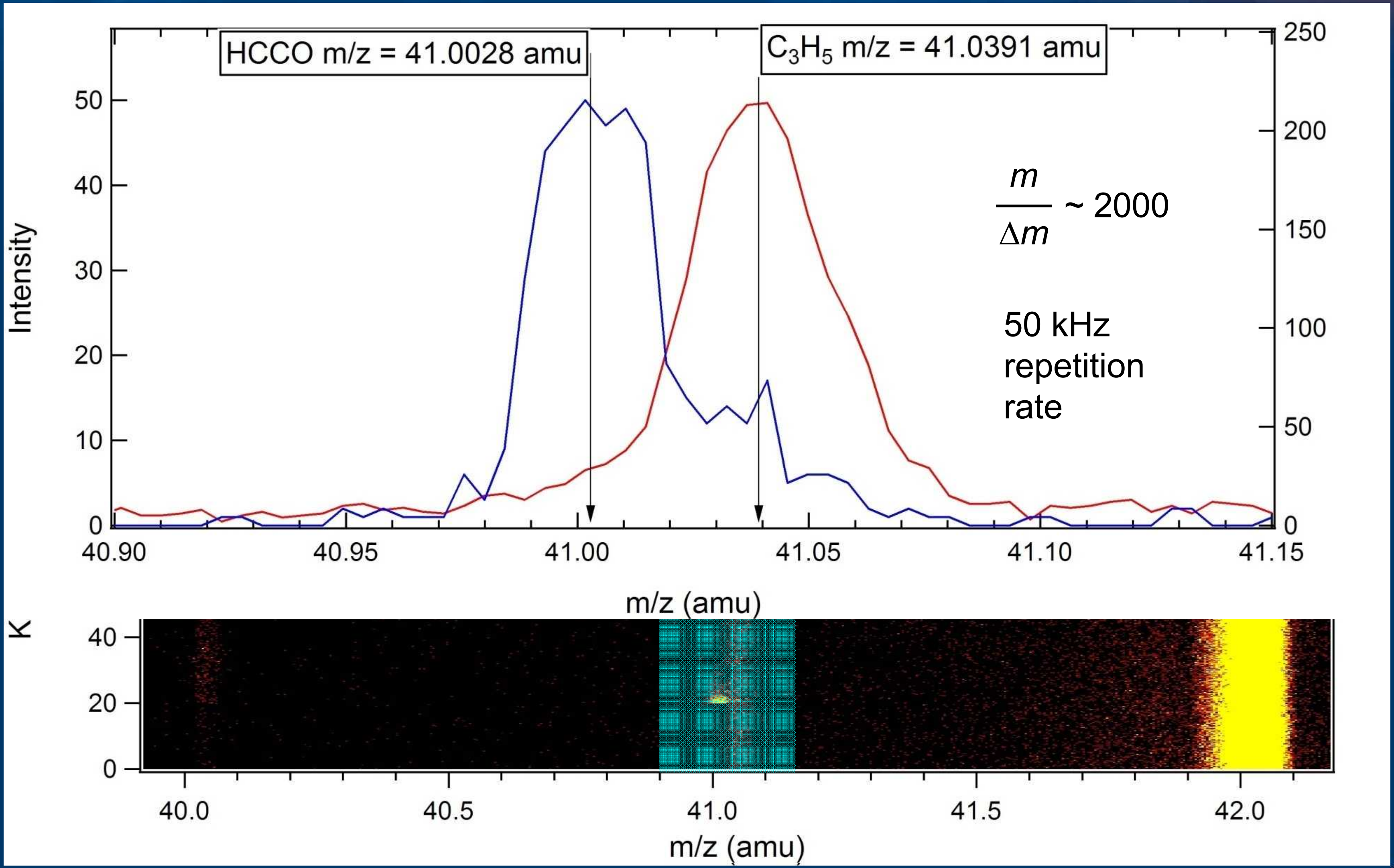
$[C_3H_3] \sim 4 \times 10^{12}$ molec/cm^3

$P = 4$ Torr

$T = 305$ K



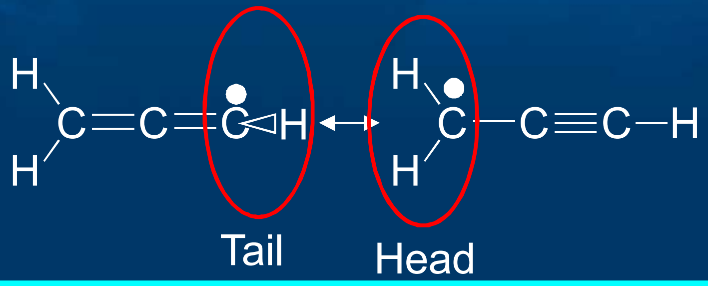
Upgrade to Orthogonal Acceleration TOF



$$\frac{m}{\Delta m} \sim 2000$$

50 kHz repetition rate

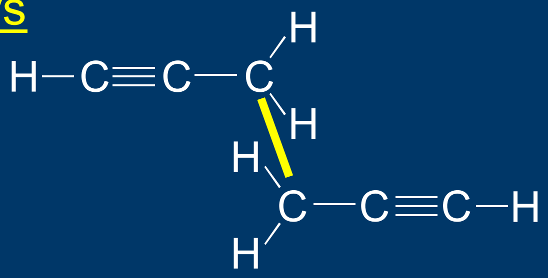
Propargyl Radical Addition Pathways



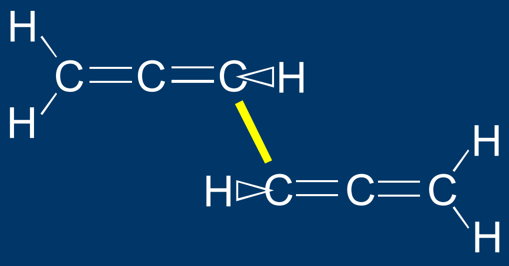
Propargyl Radical

<u>Three addition pathways</u>

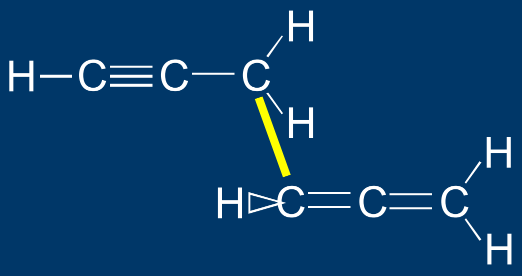
1) Head-to-Head



2) Tail-to-Tail



3) Head-to-Tail



(x2)

Radical-Radical Potential Surfaces

Chemical Reaction →

Multiple-well “Master Equation” describes chemical reactions AND energy transfer

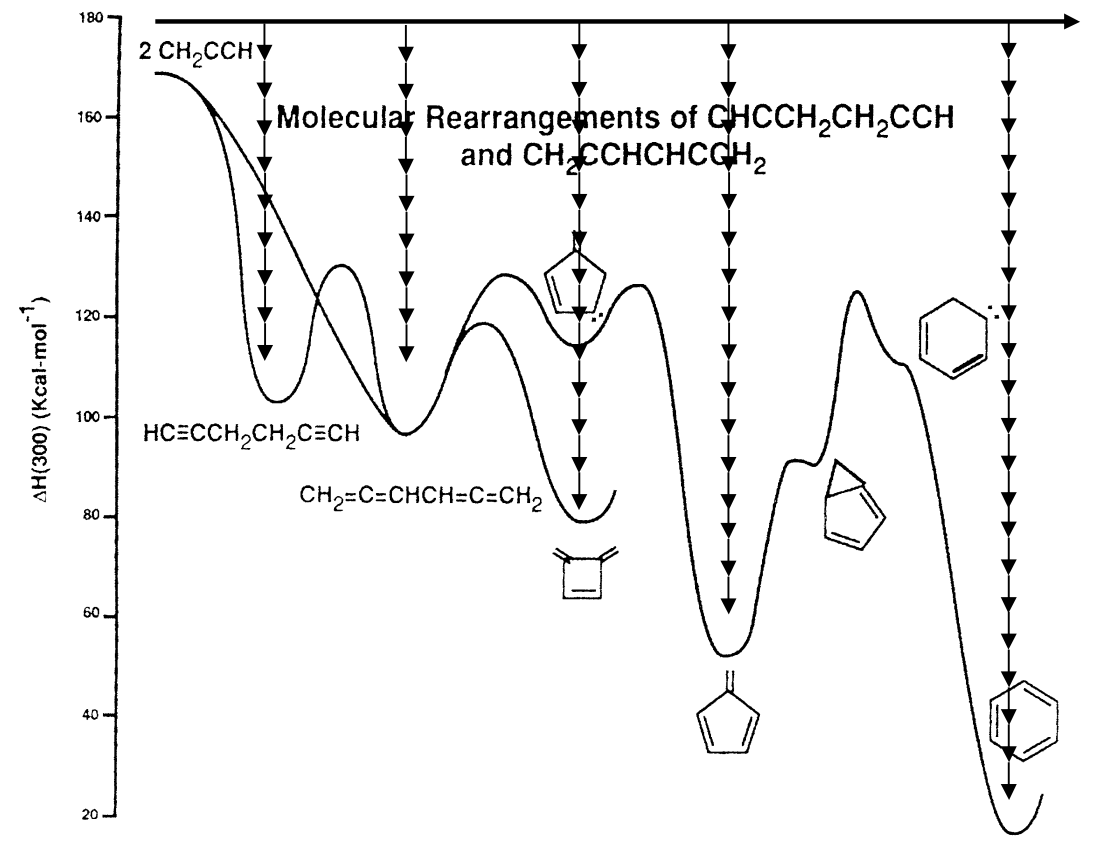


Fig. 11. Reaction coordinate diagram for head-to-head and tail-to-tail recombination of propargyl (C_3H_3) radicals (Miller and Melius [77]).

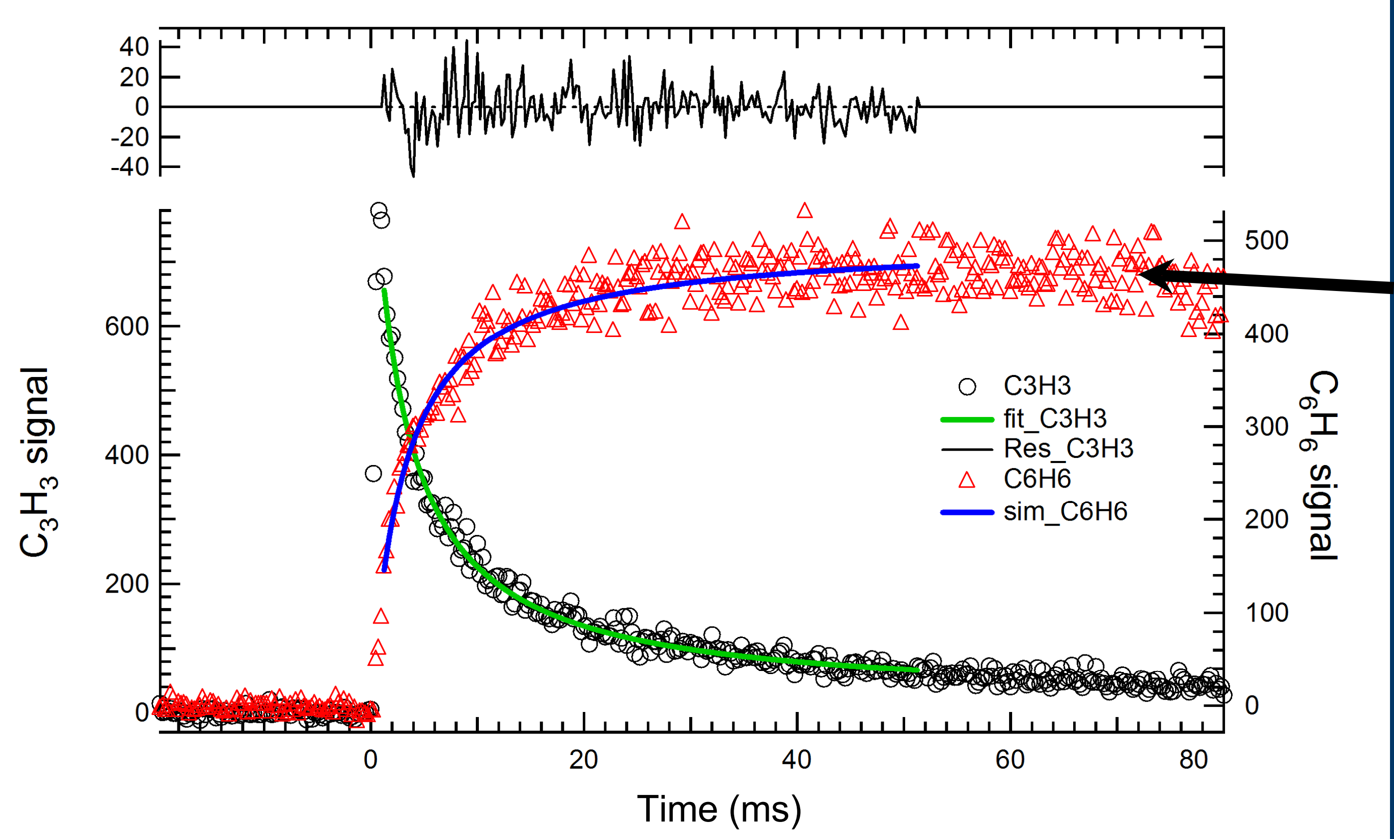
←Energy Transfer (→)

Combust Flame 1992;91:21–39.

C_3H_3 kinetics

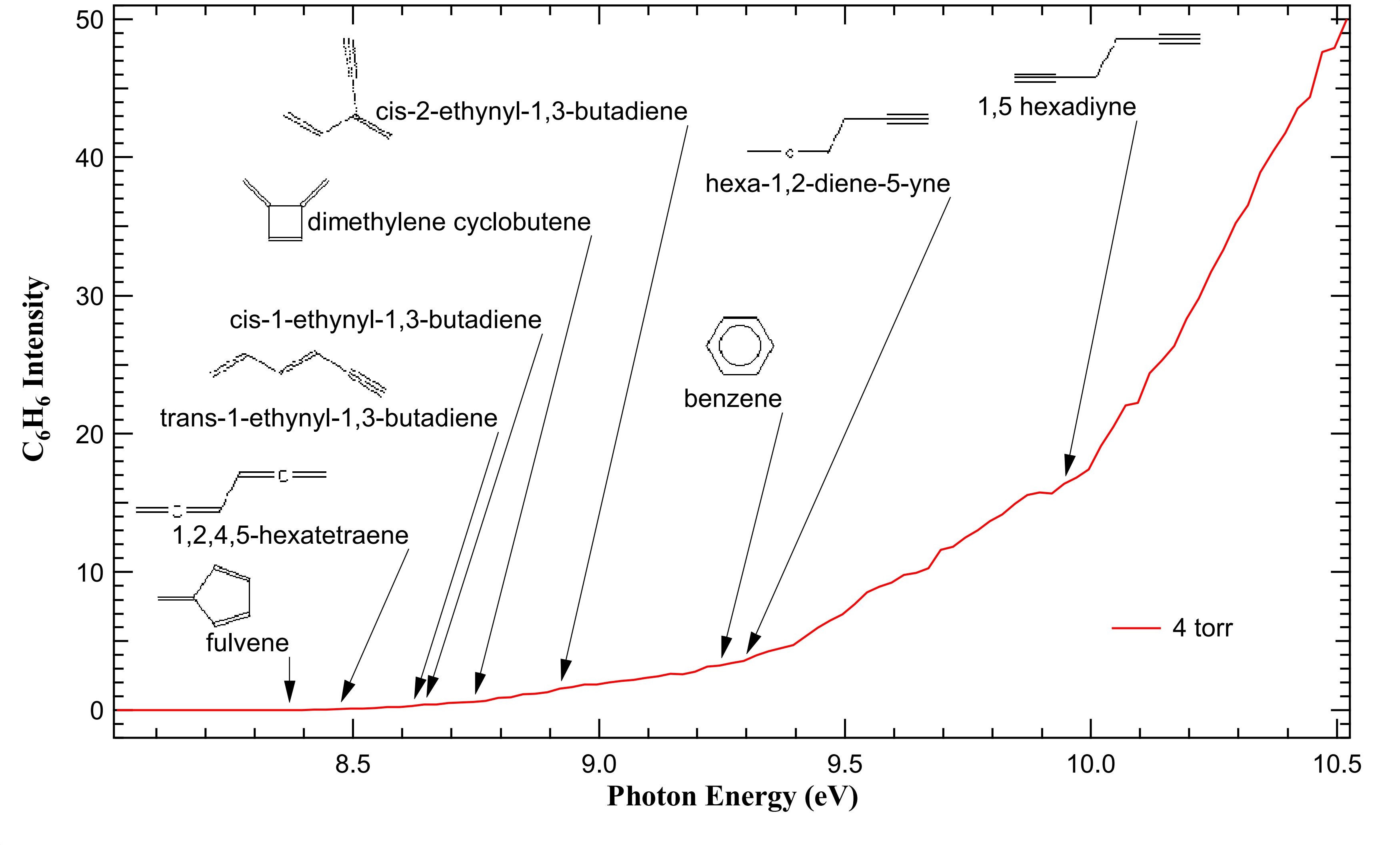
$[C_3H_3] \sim 4 \times 10^{12}$ molec/cm^3
P = 4 Torr
T = 305 K
$h\nu$ = 10.2 eV

$C_3H_3 + C_3H_3 \rightarrow C_6H_6$

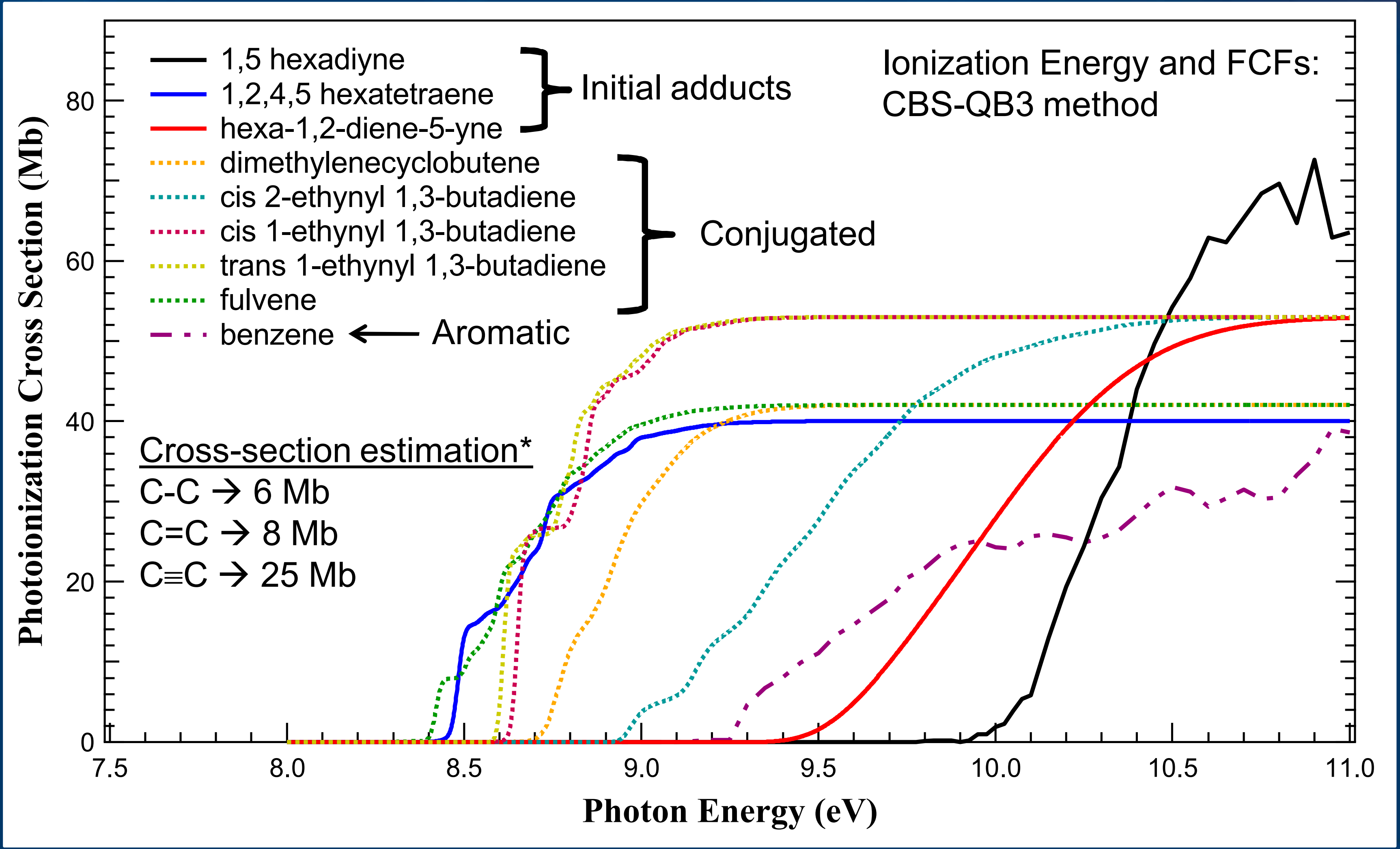


Is C_6H_6 benzene?
or a mixture of isomers

$C_3H_3 + C_3H_3$ photoionization efficiency



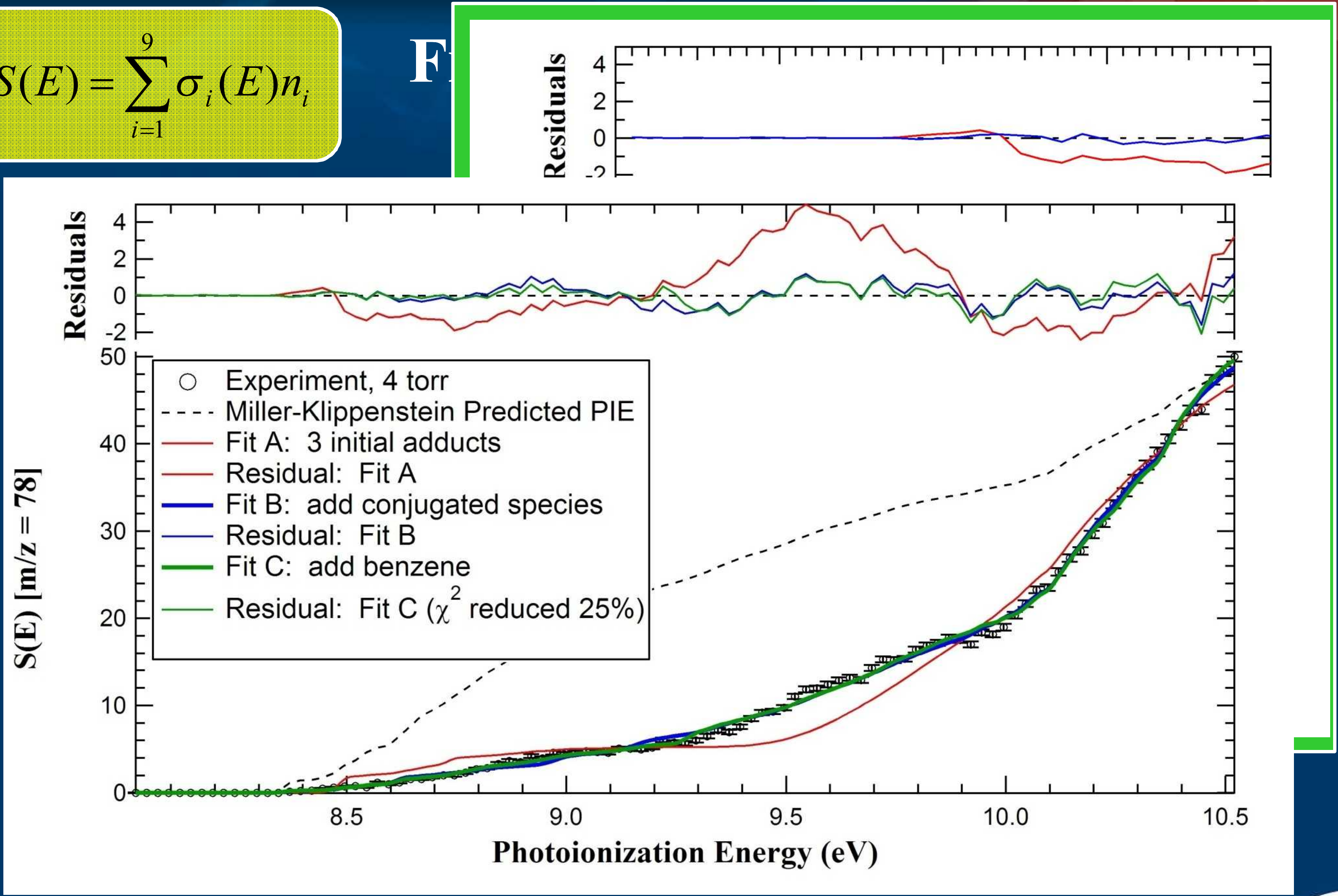
Basis Functions



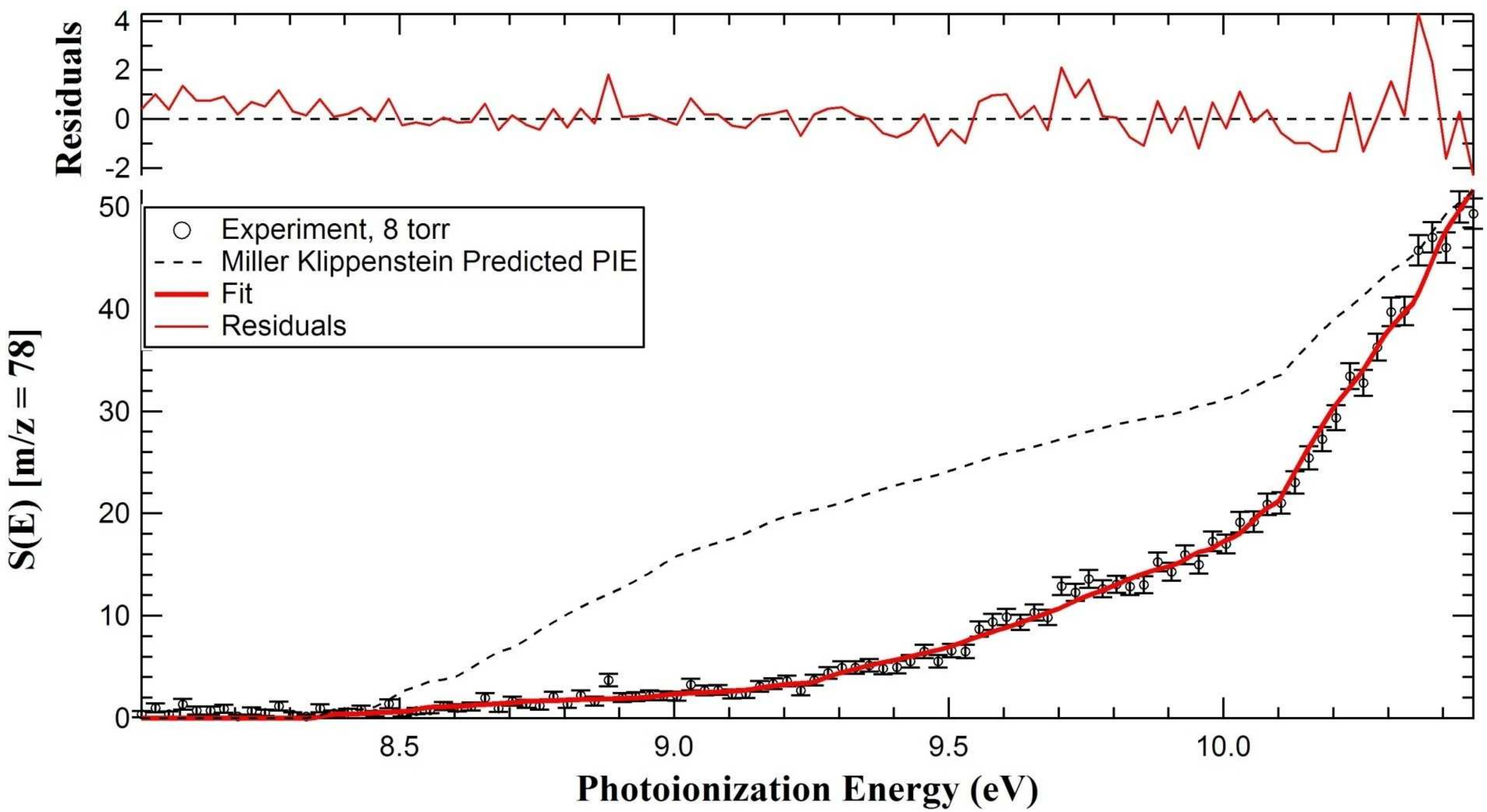
*M. Bobeldijk, W. J. van der Zande, and P. G. Kistemaker, Chem. Phys. **179**, 125 (1994).

$$S(E)=\sum_{i=1}^{9}\sigma_i(E)n_i$$

Fi

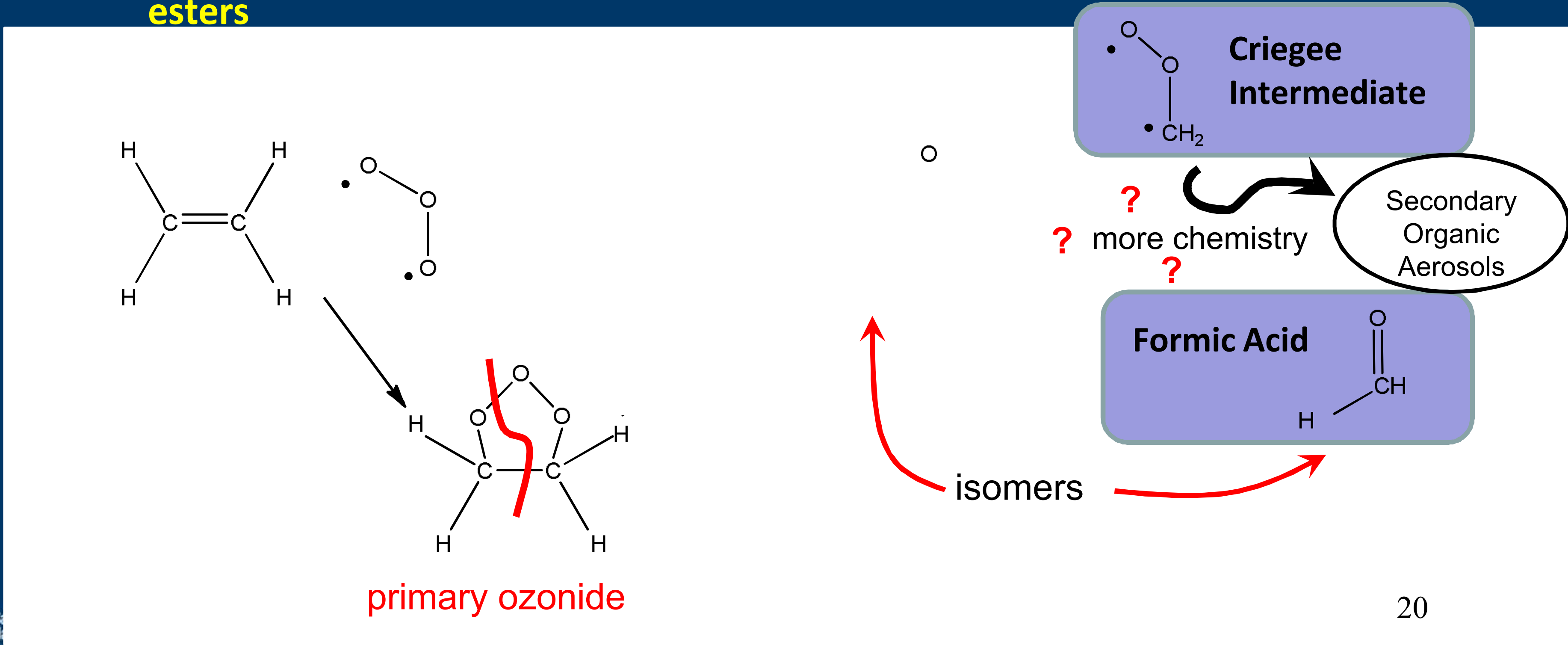


Fit to the data: 8 torr



Criegee’s hypothesis and his “intermediate”

- In 1949, Rudolf Criegee proposed a mechanism for degradation of alkenes in the presence of ozone
- Many indirect studies support Criegee’s hypothesis that ozonolysis is a major component in tropospheric removal of hydrocarbons – makes Criegee biradicals
- Criegee intermediates are *isomers* of more stable products, organic acids or esters



Criegee Intermediate

more chemistry

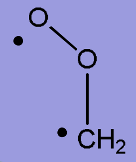
Secondary Organic Aerosols

Formic Acid

isomers

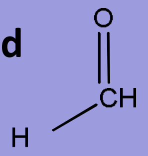
primary ozonide

Example: $O_3 + C_2H_4$



Criegee Intermediate

Formic Acid

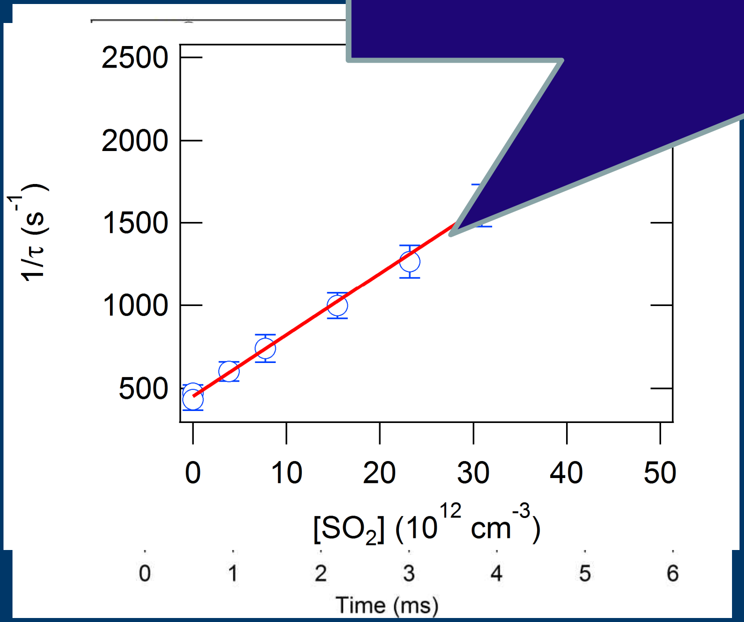


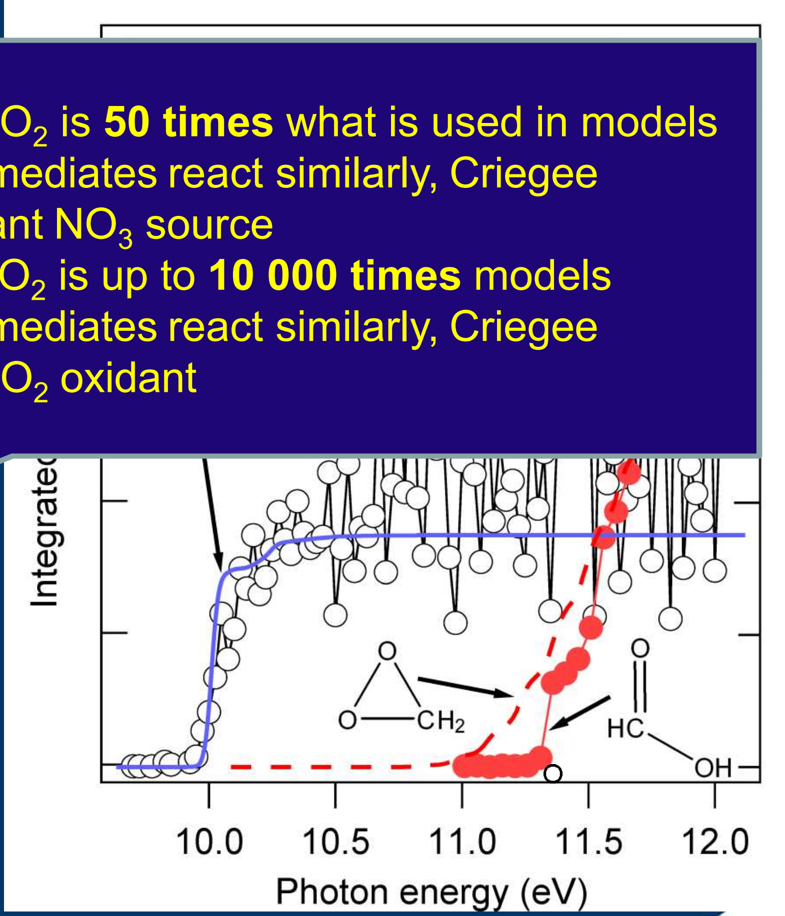
Reaction of CH_2OO with NO_2 is **50 times** what is used in models

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





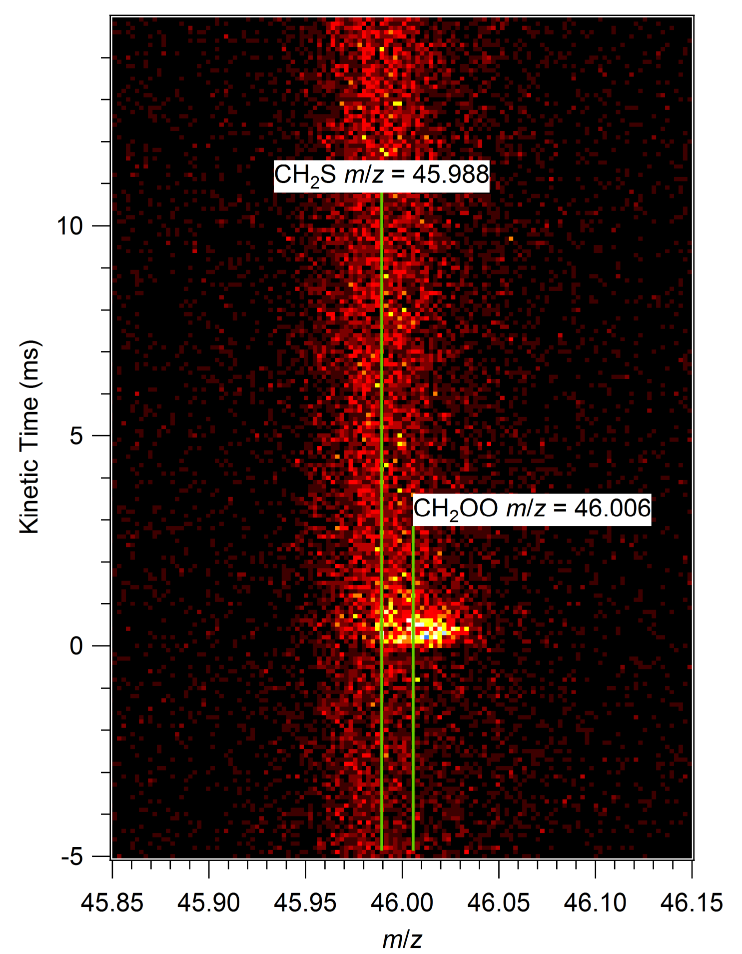
Welz, Savee, et al., *Science* **335**, 204 (2012)

Our Needs / Wants in a Light Source

- Needs
  - Repetition Rate 50 kHz or greater
  - High average power (> 10^{13} photons / s at 0.1% bandwidth)
  - Continuous, rapid tunability (7.3 – 16 eV)
  - Light with no harmonics (at least 1 part in 10^4)
  - High brightness (spot size ~ 1 x 1 mm)
- Wants
  - Much higher average power (10^{17} photons / s at 0.1% bandwidth)
  - Tunability from 6.0 – 16 eV
  - Only moderate peak power (to avoid multiphoton processes)

High mass resolution is valuable

- Cumulative evidence for •CH_2OO•
  - Correct mass
  - Ionization energy agrees with calculations
  - CH_3SO co-product observed
- Can we study reactions of CH_2OO?



Could we add a 4th dimension?

- It is hard to distinguish isomers when:
  - Two isomers have similar ionization energies
  - More than 4 isomers are present at one m/z ratio

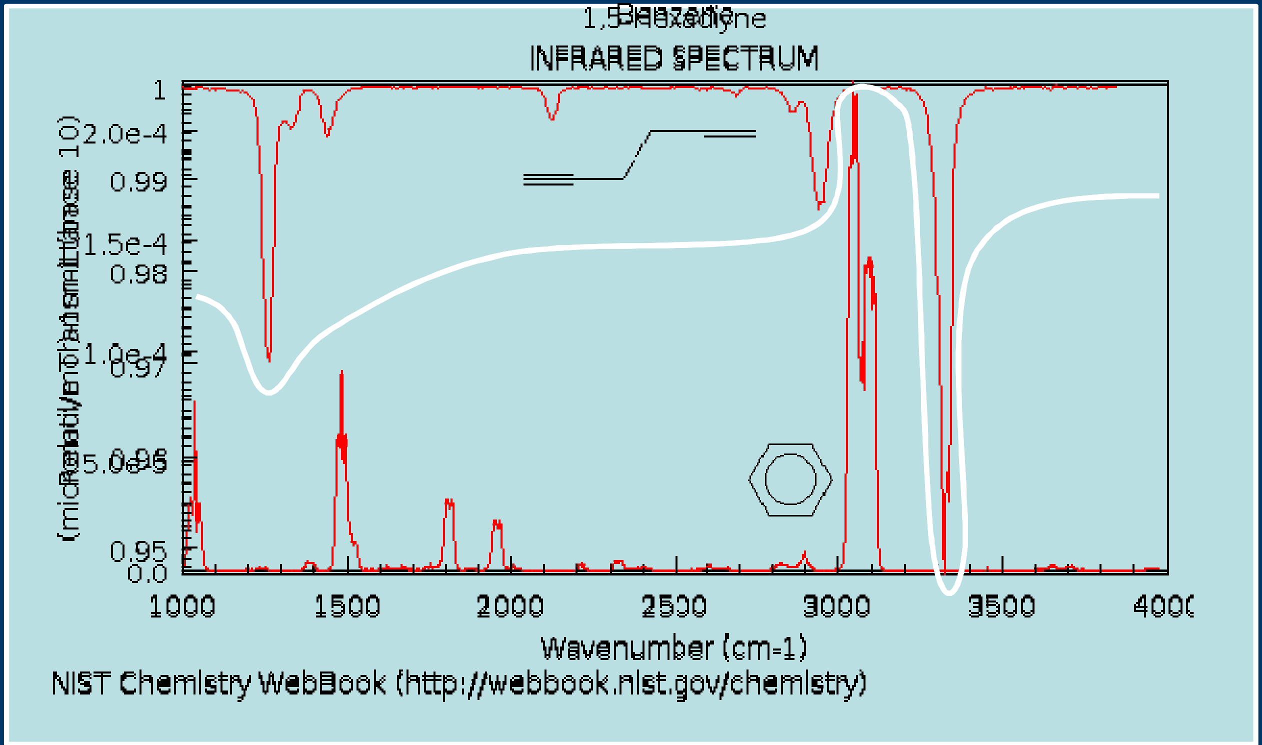
- Rydberg Field Ionization Techniques
  - ZEKE: Provides a threshold photoelectron spectrum for each ion
  - MATI: Provides a mass-selected threshold cation spectrum

- Measure photoelectron – photoions in coincidence? (PEPICO)
  - Provides a true photoelectron spectrum for each cation

- Double resonance (IR + VUV)
  - Sort isomers by infrared spectra

It will be challenging to stay highly multiplexed

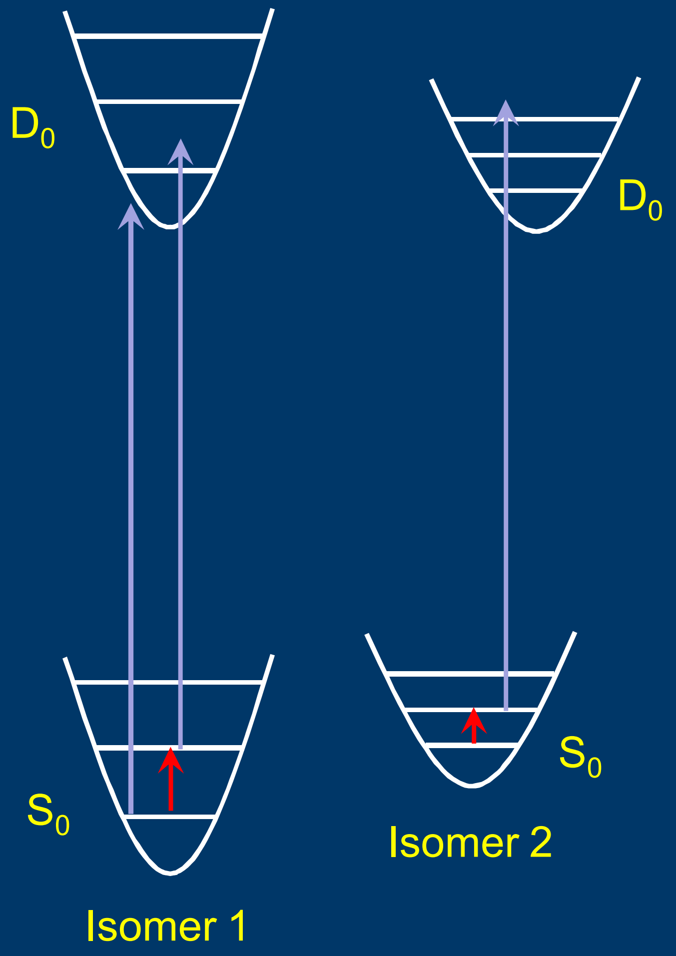
Infrared Spectra: Benzene vs. 1,5-hexadiyne



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

It is hard to beat the selectivity of infrared spectroscopy.
If only it were mass-selected!

IR-UV Double Resonance



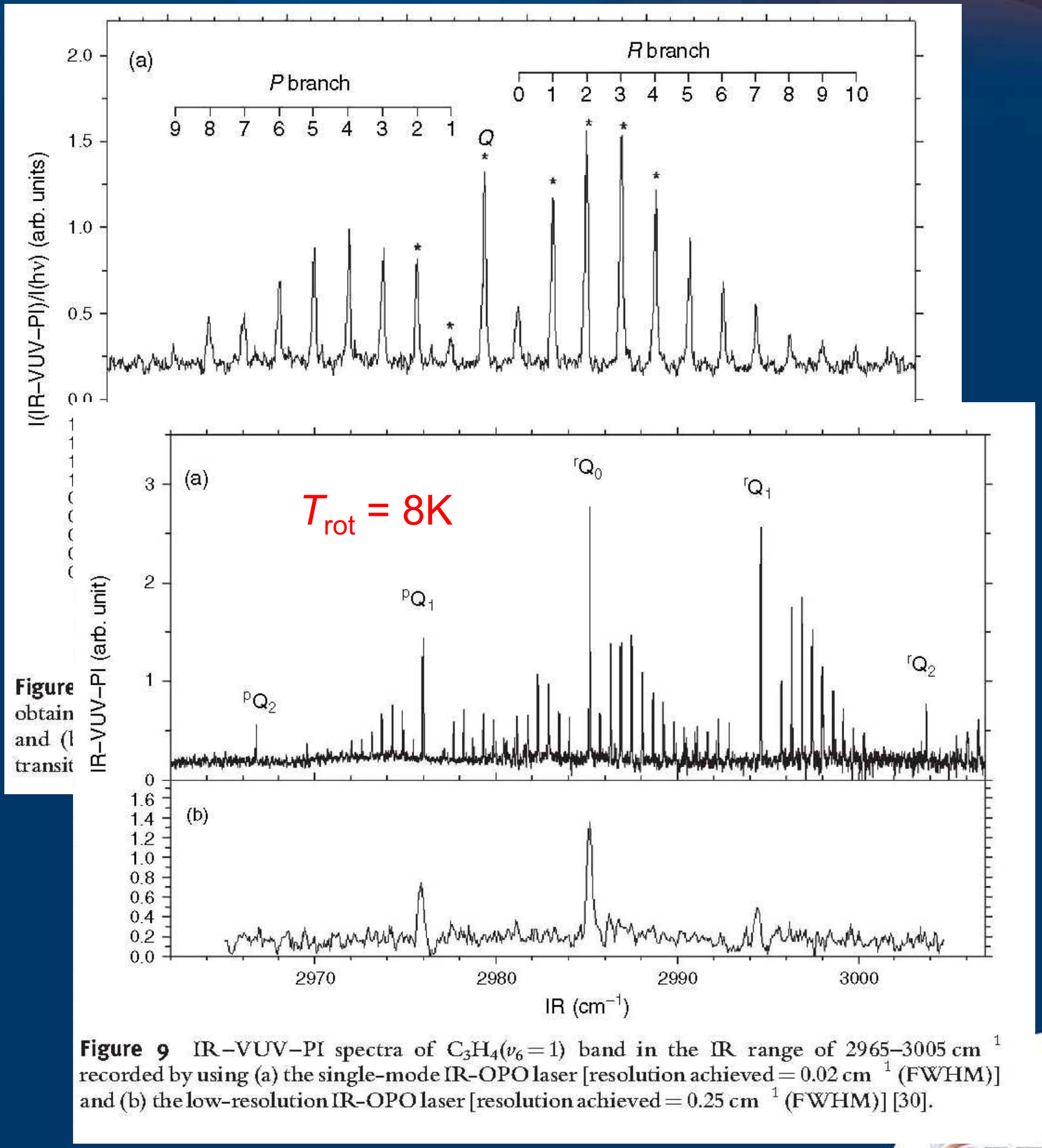


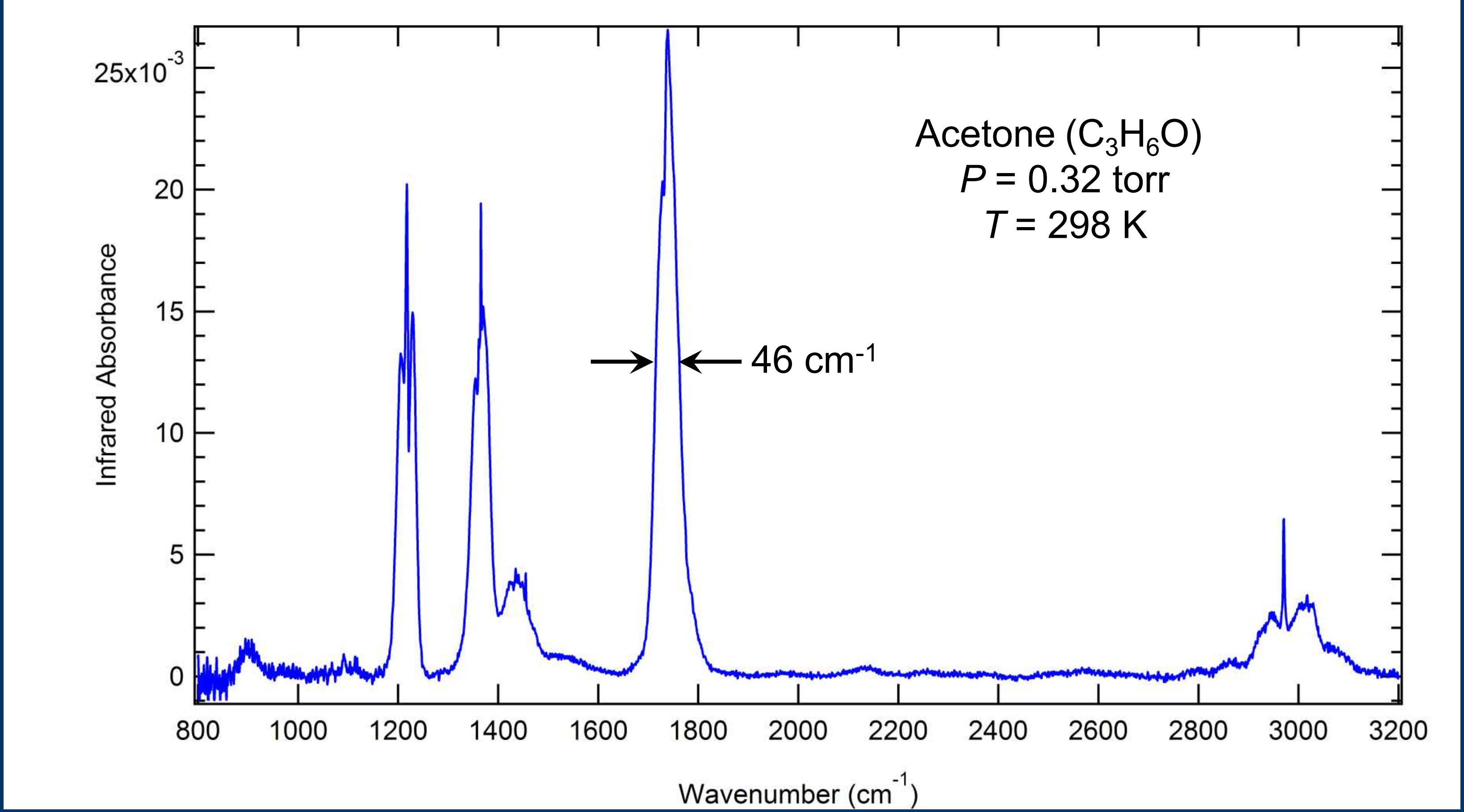
Figure
obtain
and (l
transit

Figure 9 IR–VUV–PI spectra of $C_3H_4(\nu_6 = 1)$ band in the IR range of 2965–3005 cm ^{1} recorded by using (a) the single-mode IR-OPO laser [resolution achieved = 0.02 cm ^{1} (FWHM)] and (b) the low-resolution IR-OPO laser [resolution achieved = 0.25 cm ^{1} (FWHM)] [30].

Spectra Courtesy of Cheuk Ng, UC Davis

Spectral Widths

High resolution is neither needed nor desired. 1 - 5 cm^{-1} is plenty



σ= 1 x 10^{-18} cm^2, 1 mm x 1 mm spot size, 6.6 x 10^{-20} J/photon $\Rightarrow$
0.66 mW cw power required @ 3300 cm^{-1}

Photoelectron – Photoion Coincidence

- For each ionization
  - Collect electron
  - Collect its coincident cation
  - Sensitivity decrease of 2-3x (η_e ~ 33 – 50%)
- Photoelectron spectrum (0 – 800 meV) at each m/z ratio gives better fingerprint
- Could be time-stamped to provide kinetic information
- But, spectroscopy is of cation!

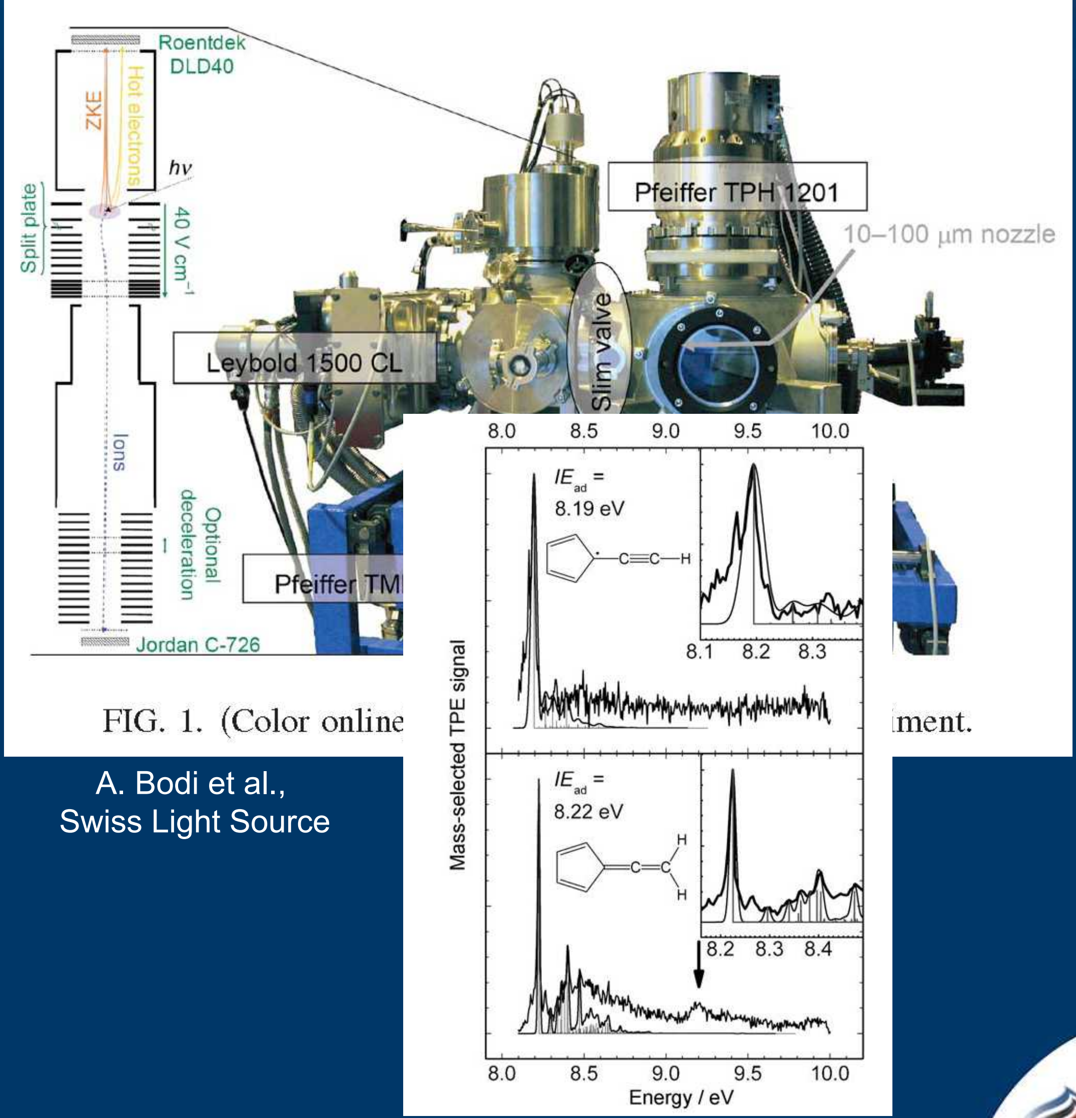


FIG. 1. (Color online ... ment.

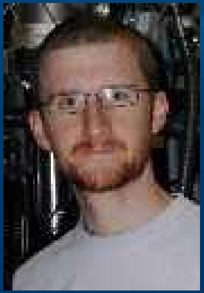
A. Bodi et al.,
Swiss Light Source

M. Steinbauer et al., ChemPhysChem,

Conclusions

- Multi-dimensional experiments using valence photoionization are powerful tools to study gas phase chemical reactions.
  - Mass-to-charge sorting of species
  - Time / distance / velocity information
  - Photoionization spectra to sort species
- Valence orbitals cover the whole molecule → isomer specific
- High repetition rate, low peak power VUV sources needed
- Challenges for the future
  - Greater sensitivity (high pressure chemistry)
  - More selective probes (PEPICO, MATI, double resonance)
  - Maintaining a highly multiplexed experiment

Acknowledgements

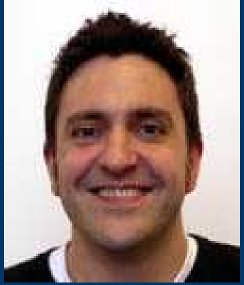

Adam Trevitt


Fabien Goulay

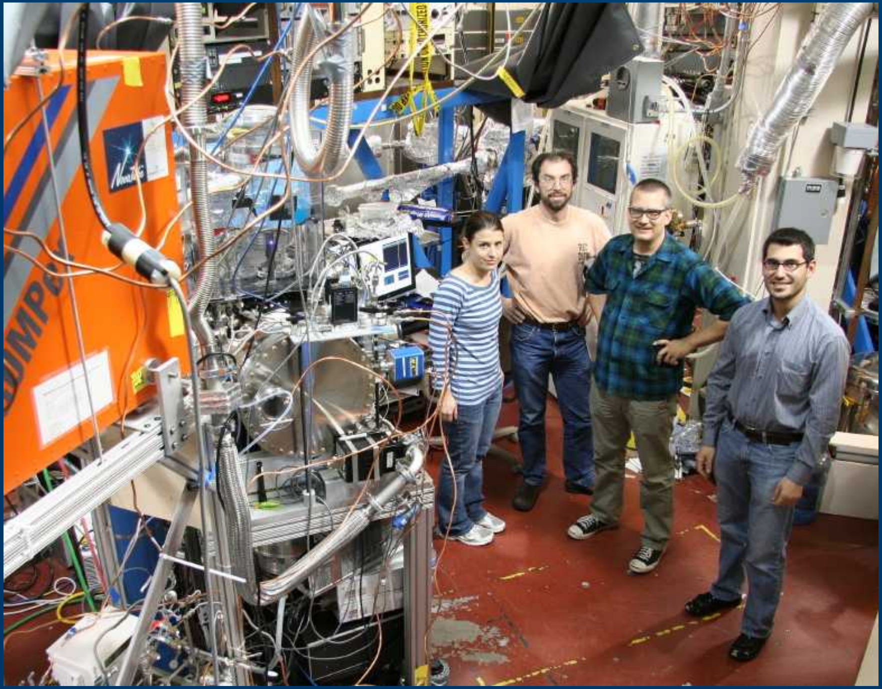

Musa Ahmed


Stephen Klippenstein


Howard Johnsen


Carl Percival


Dudley Shallcross



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Adam Scheer

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Challenges of High Pressure

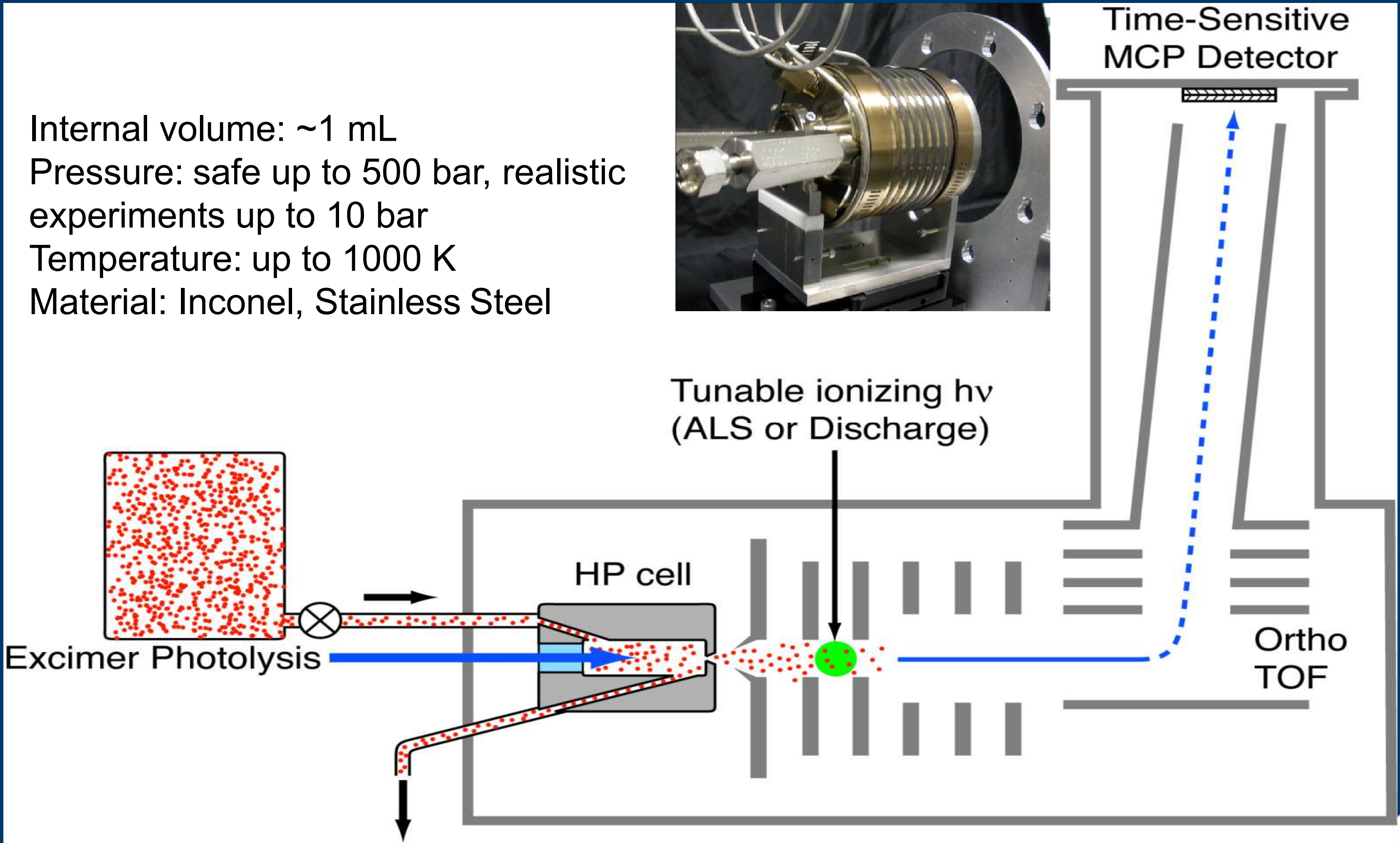
- Future engine designs will critically depend on our understanding of chemistry at:
  - Pressure: 50 – 150 atmospheres
  - Temperatures: 600 – 1100 K
- Extrapolations to these regimes require solid science
- Pseudo-first order conditions
  - $C_2H_3 + O_2 \rightarrow CH_2O + HCO$ (in great excess of helium)
  - Rate $= -d/dt\,[C_2H_3] = \{k[O_2]\}\,[C_2H_3] \approx k'[C_2H_3]$

molecules cm^{-3}

- 0.01 atm → 100 atm increased dilution by 10^4.
- Best solution is increase of VUV photon flux by 10^4.

Photoionization experiments for high-pressure chemical kinetics

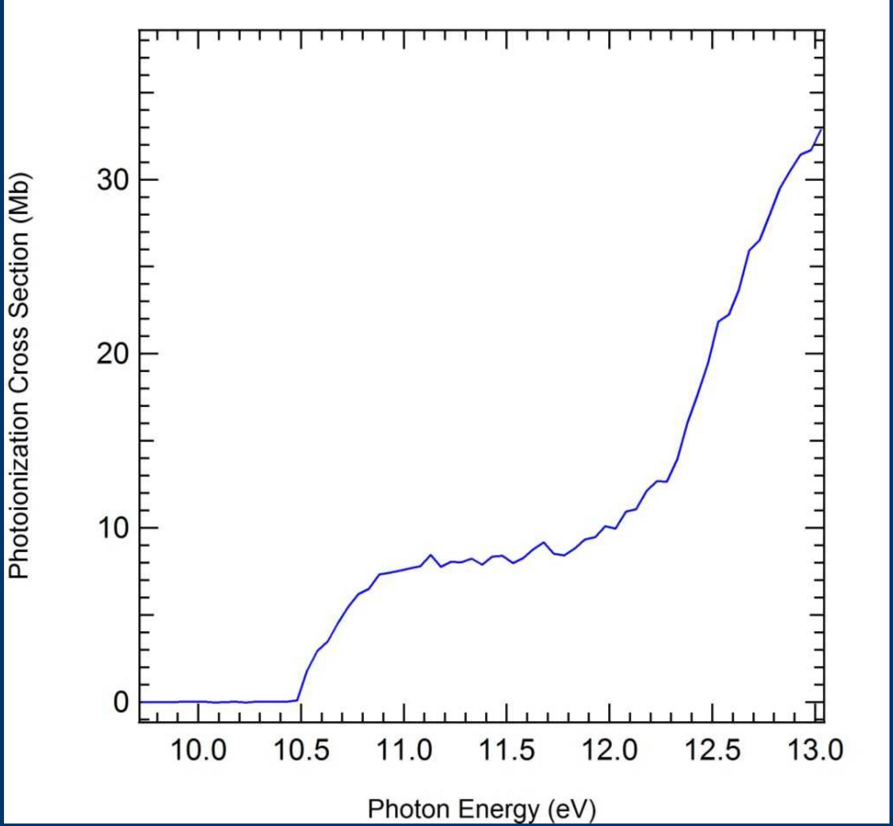
Internal volume: ~1 mL
Pressure: safe up to 500 bar, realistic experiments up to 10 bar
Temperature: up to 1000 K
Material: Inconel, Stainless Steel



Valence photoionization cross sections are large

Ethene ($CH_2=CH_2$), mass = 28 amu

Valence Photoionization



Core Photoionization

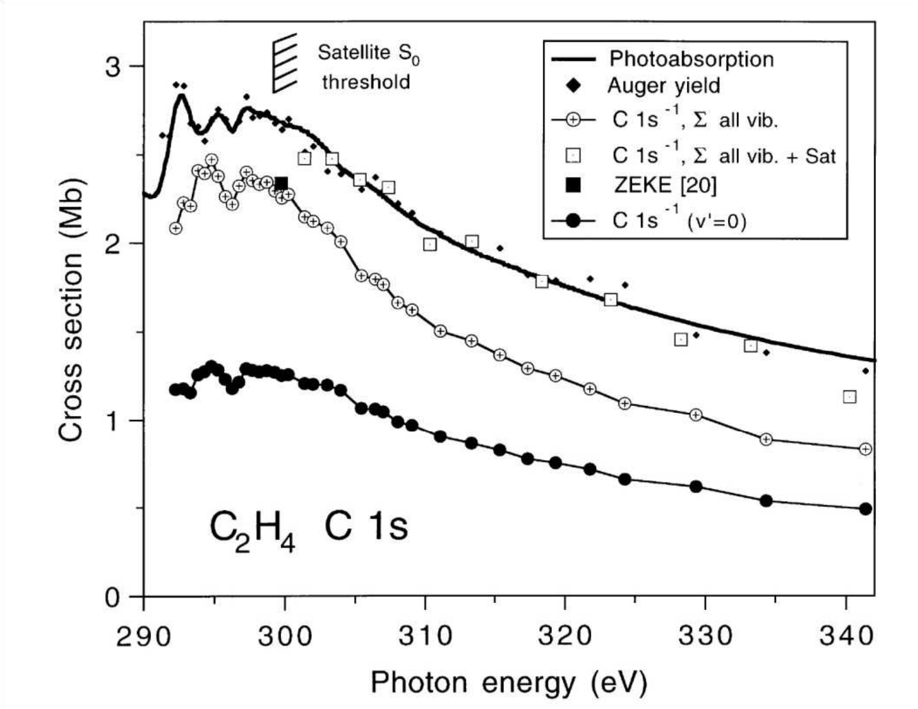


Fig. 4. The C 1s photoionisation cross-section of C_2H_4; the bold solid line represents the photoabsorption cross-section after subtraction of the valence ionisation contribution.

B. Kempgens et al., J. Elec. Spec. Relat. Phenom. 93 (1998) 39

Our Needs / Wants in a Light Source

- Needs
  - Repetition Rate 50 kHz or greater
  - High average power (> 10^{13} photons / s at 0.1% bandwidth)
  - Continuous, rapid tunability (7.3 – 16 eV)
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  - High brightness (spot size ~ 1 x 1 mm)
- Wants
  - Much higher average power (10^{17} photons / s at 0.1% bandwidth)
  - Tunability from 6.0 – 16 eV
  - Only moderate peak power (to avoid multiphoton processes)
  - Tabletop source ?

Balancing information with understanding

- Too much overlapping information ⇒ obscures interpretation
- Too little information ⇒ doesn't allow definitive results

Multi-dimensional data can provide rich information without obscuring understanding

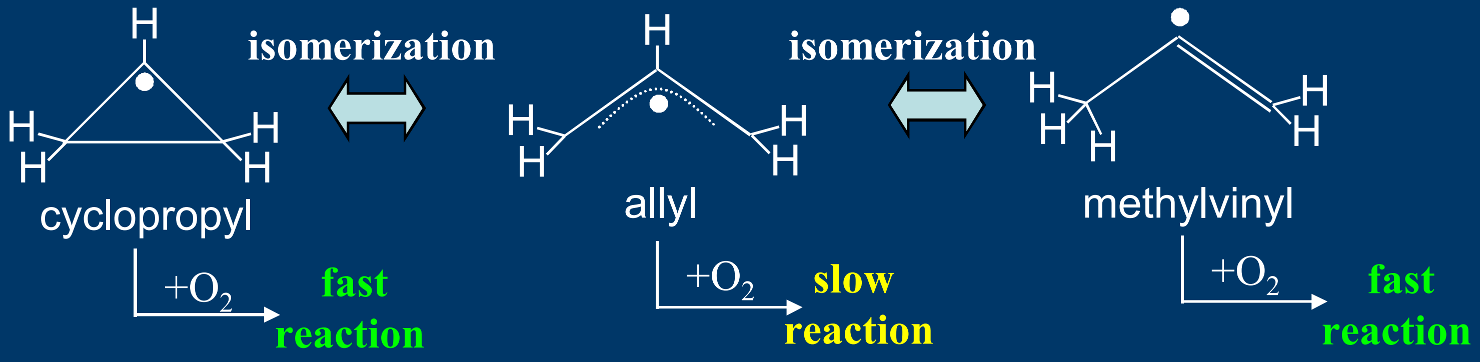
⇓

Valence photoionization detecting positive ions

Isomer distributions are a sensitive probe of reaction mechanisms

- Isomers often show different reactivity, steering downstream chemistry in new directions.

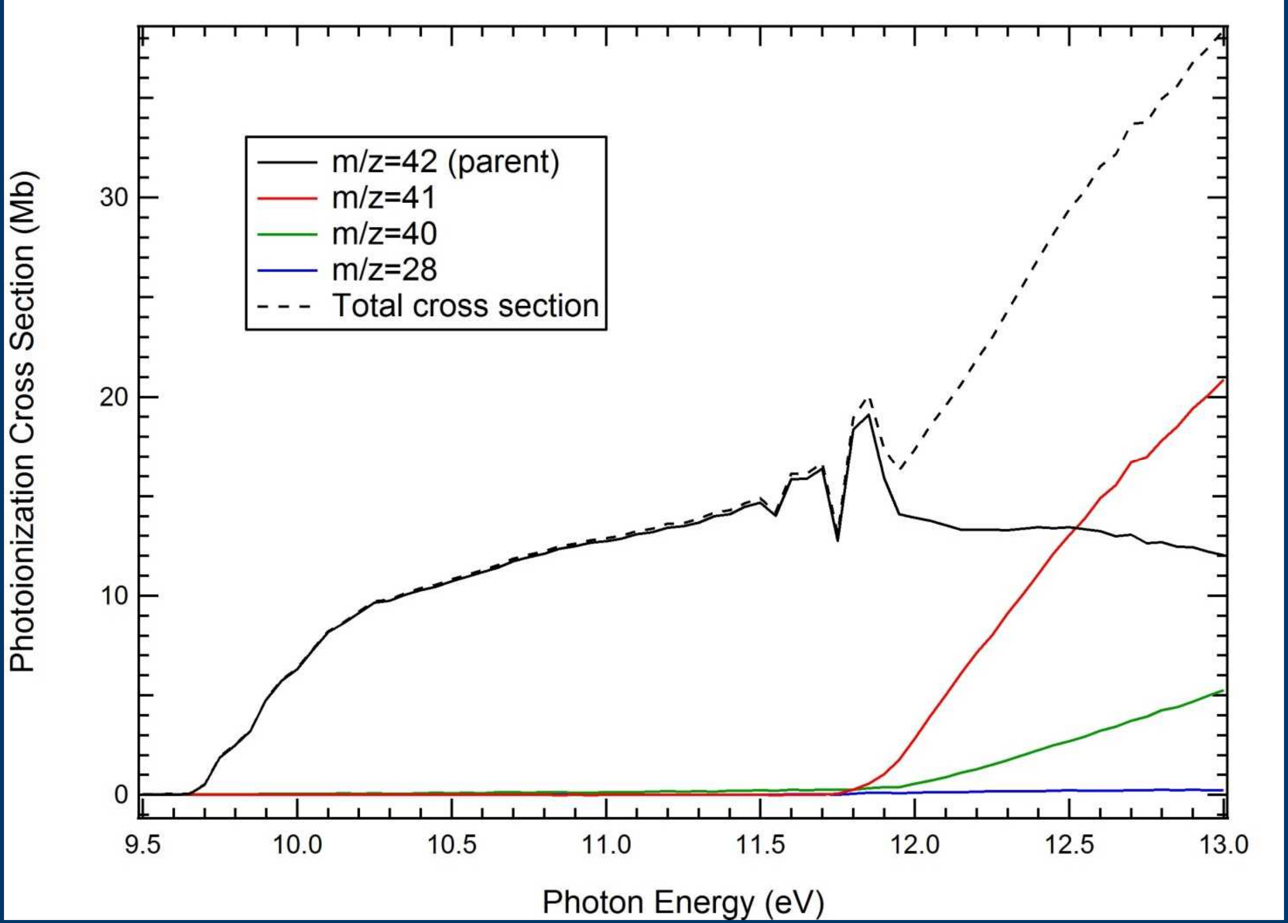
$C_3H_5 + O_2 \rightarrow$ products



Valence photoionization examples

Propene (CH_3-$CH=CH_2$), mass = 42 amu

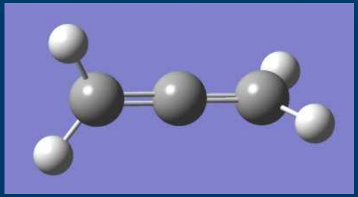
1 Mb = 10^{-18} cm^2



Static gas sample of a stable molecule

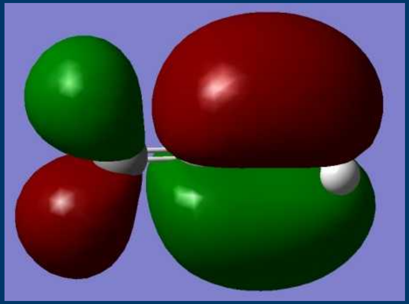
Valence compared to core ionization

allene

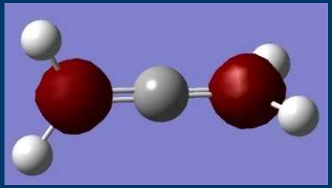


Energy (eV)

-10.32



-305.78



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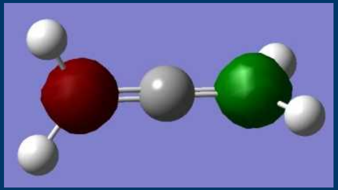

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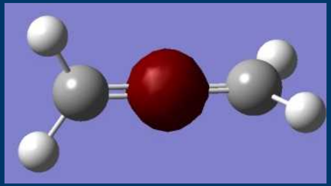
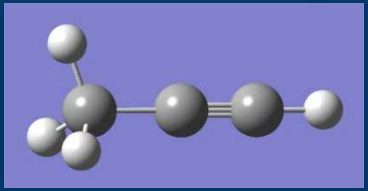
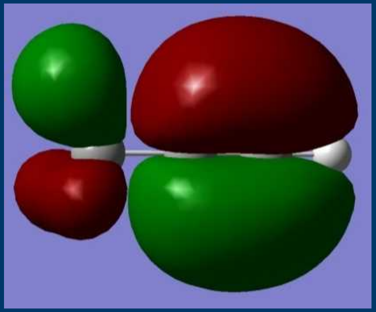


propyne



Energy (eV)

-10.49



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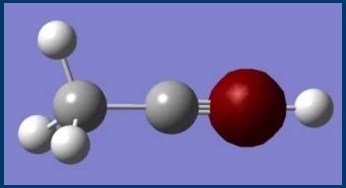
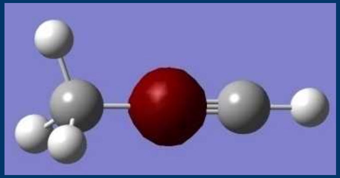
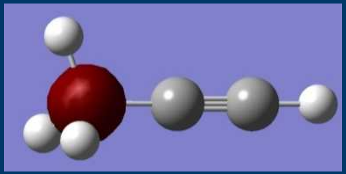


-305.73



-306.17



Structure

Valence Orbitals
- Whole molecule
- e- + cation only
- Sensitive to molecular structure

Core Orbitals
- Tightly localized
- Significant fragmentation
- Limited sensitivity to structure

CCSD(T)/aug-cc-pVTZ // B3LYP/6-311G**

What photon characteristics do we need?

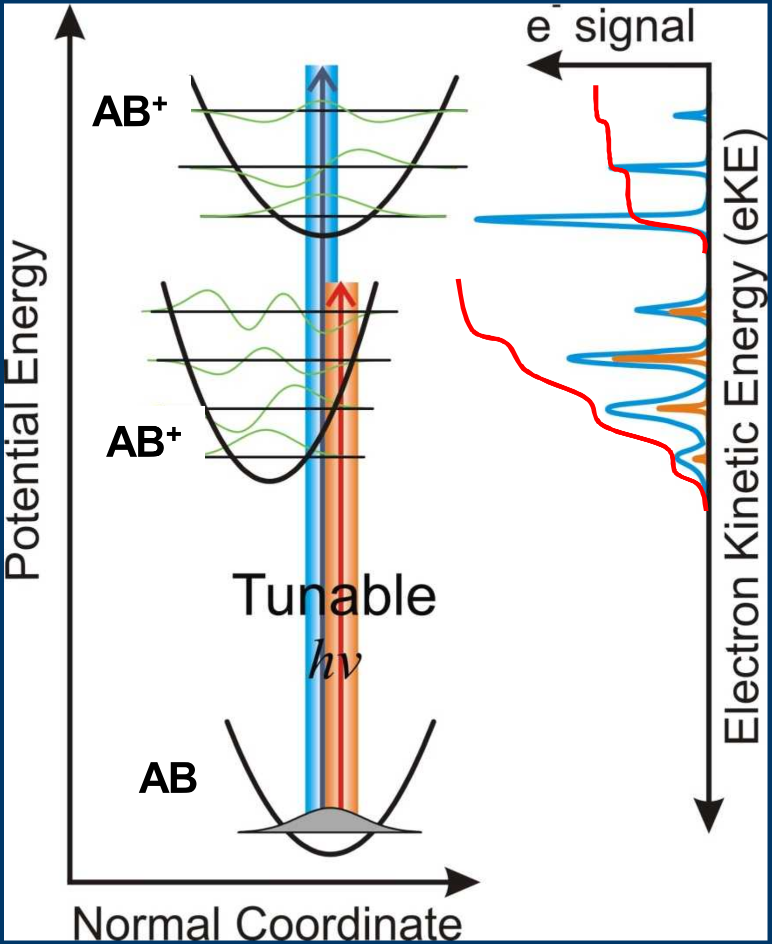
Desired characteristics	Example: Advanced Light Source, Lawrence Berkeley Lab, Beamline 9.0.2		
Linear spectroscopy (high average power, low peak power, high repetition rate)	500 MHz repetition rate	<u>Low resolution mode</u>	<u>Medium resolution mode</u>
		10^{16} photons / s (16 mW @ 10 eV)	5 x 10^{13} photons / s (80 μW @ 10 eV)
Small photon beam cross section (needed for high mass resolution)	1 mm x 1 mm		
Tuning range, tuning rate, resolution	7.3 – 24 eV; seconds per step;	$\Delta E / E \sim 4\%$	$\Delta E/E \sim 0.2\%$
Fractional light absorption (σ_{abs} = 1 x 10^{-17} cm^2) (N = 3.2 x 10^{13} cm^{-3}) (L = 1 cm)	$I/I_0 = e^{-(\sigma NL)}$	10% of light absorbed	0.03% of light absorbed
Fraction of sample ionized (σ_{ioniz} = 1 x 10^{-17} cm^2) (spot size = 0.01 cm^2)	σ*Fluence	~ 100%	~ 5%

Every silver lining must have a cloud

Problems with tunable valence photoionization techniques

- Photoionization spectra can change when the molecule is internally excited
- Spectral overlap can prevent isomer identification when many isomers are present

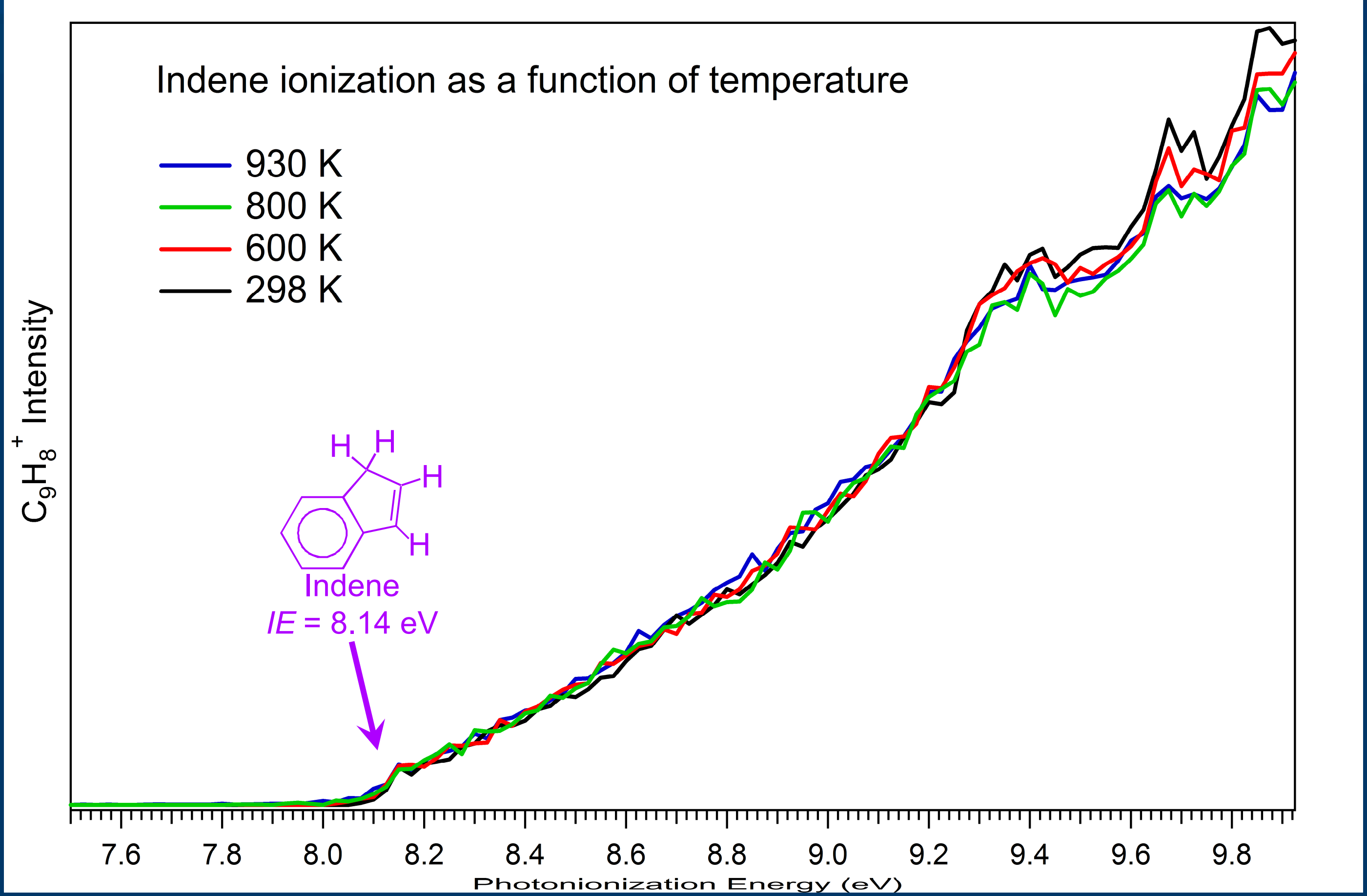
Franck-Condon factors determine spectral shape



Vertical transition
(not much temperature dependence)

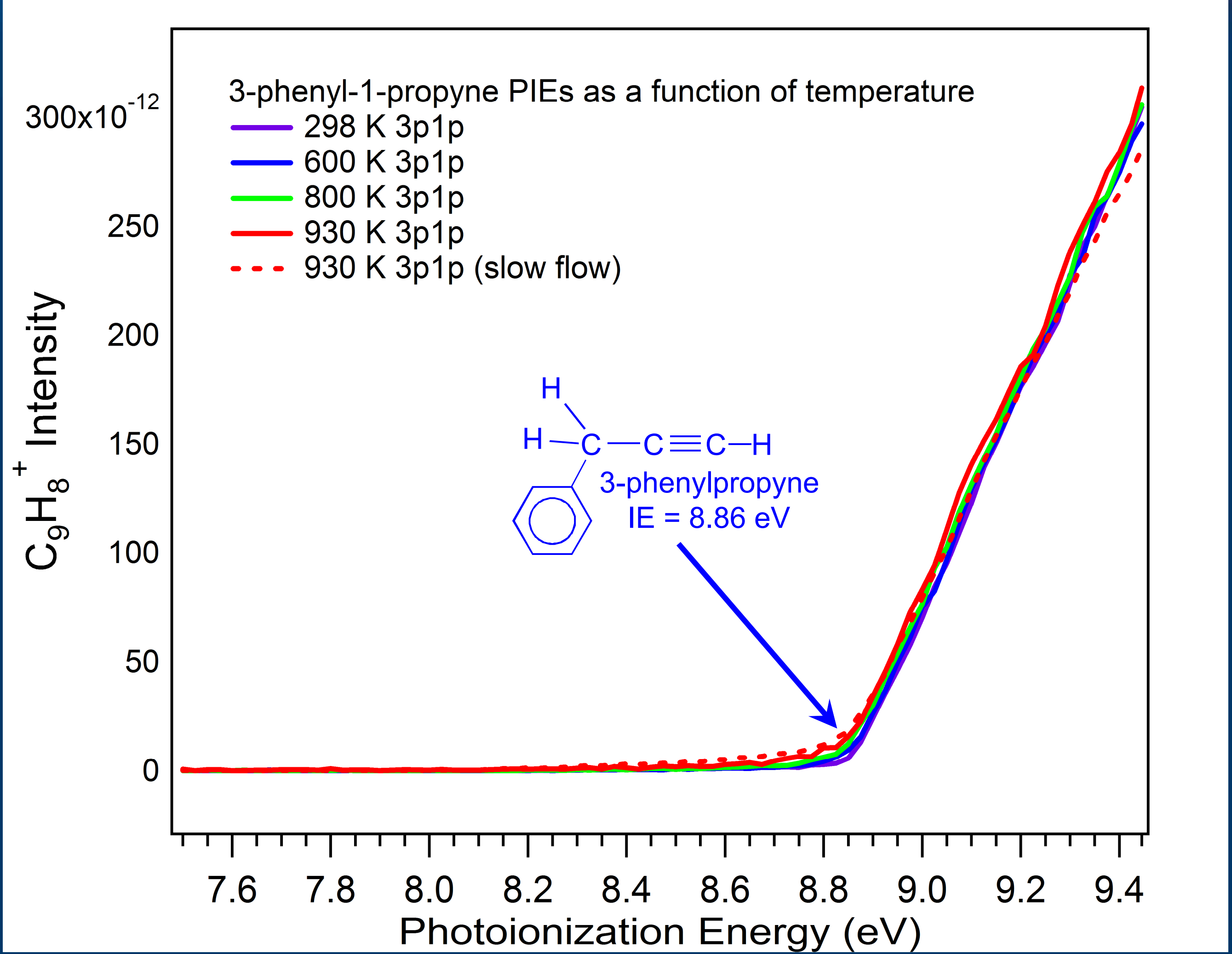
Non-vertical transition
(significant temperature dependence)

Photoionization Energy Dependence



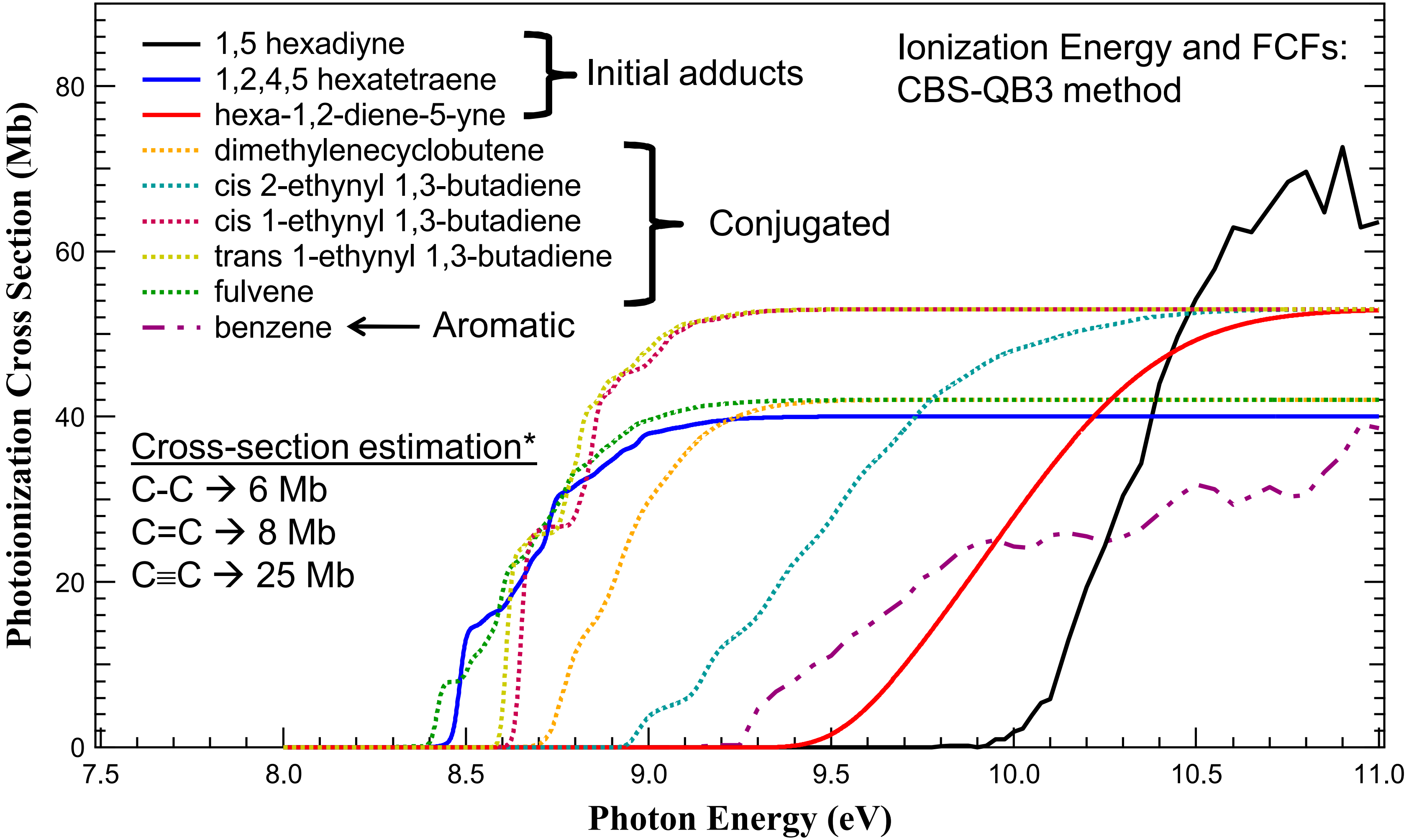
Indene photoionization is essentially temperature independent

Photoionization Energy Dependence



3-phenyl propyne photoionization has a mild temperature dependence

Spectral overlap can be severe (e.g., C_6H_6)

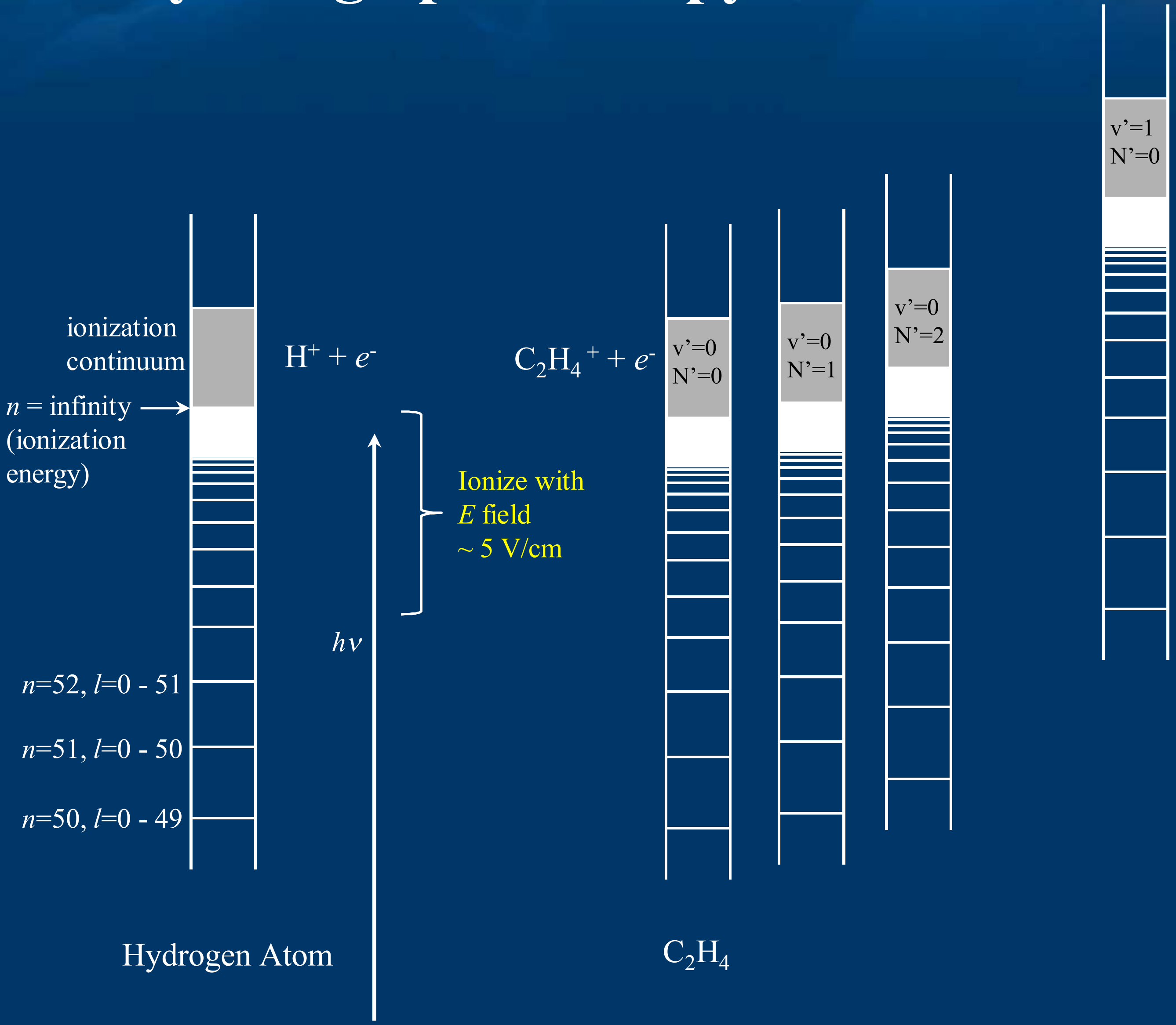


Ionization Energy and FCFs:
CBS-QB3 method

Cross-section estimation*
C-C → 6 Mb
C=C → 8 Mb
C≡C → 25 Mb

*M. Bobeldijk, W. J. van der Zande, and P. G. Kistemaker, Chem. Phys. **179**, 125 (1994).

Rydberg Spectroscopy: Pulsed Field Ionization

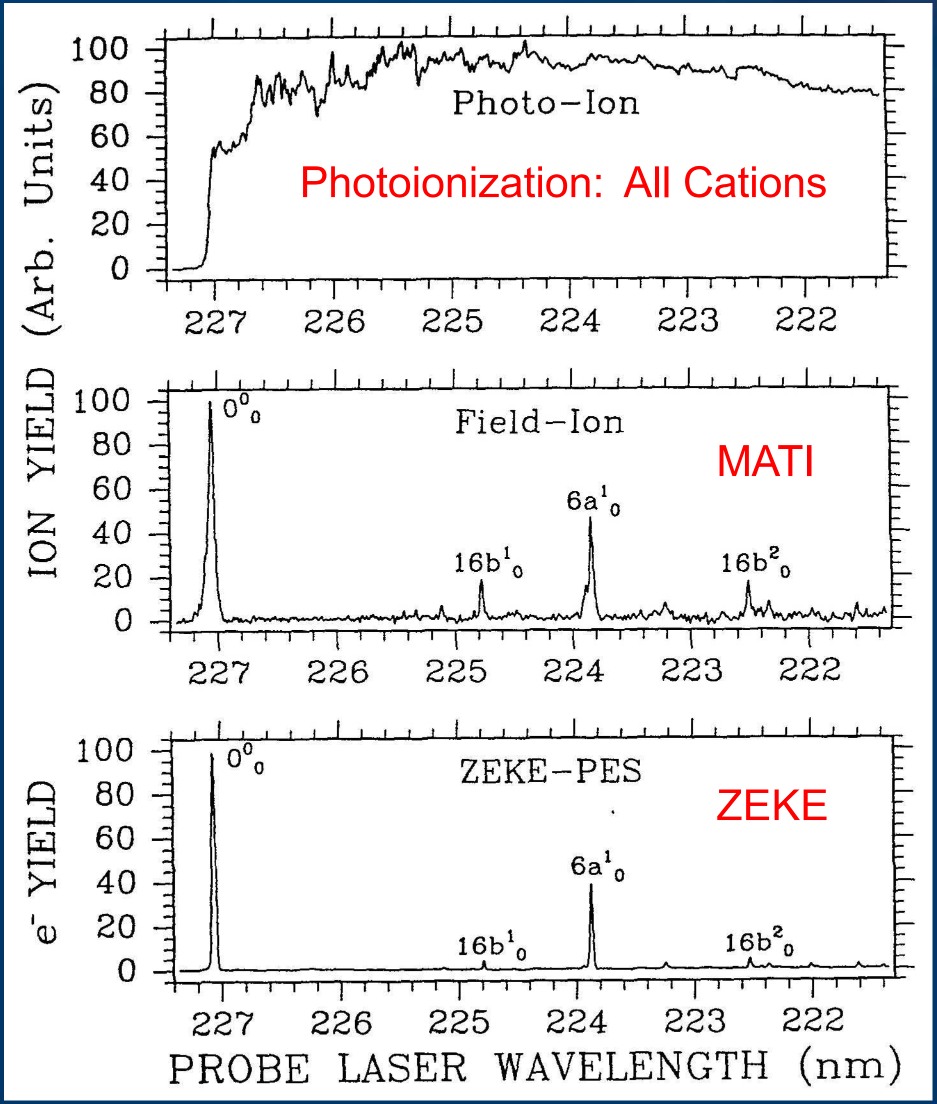


Field ionization produces an electron and an ion with near zero kinetic energy (threshold)

We can detect either one to locate
electronic
vibrational
rotational
levels

ZEKE vs. MATI spectroscopy

- Zero Electron Kinetic Energy Spectroscopy
  - Detects the nearly zero kinetic energy electron ejected near a threshold
  - All electrons identical: no information on the cation produced
- Mass Analzyed Threshold Ionization Spectroscopy
  - Detects the cation that just lost a nearly zero energy electron
  - This information is mass analyzed – useful for mixtures, clusters, etc.
  - Sensitivity 100 – 1000x lower than direct ionization



Zhu and Johnson, JCP **94**, 5769 (1991)