Valence Photoionizatoin: a Whole-Molecule Approach to Sensitive and Selective Chemical Detection

SAND2011-7548C

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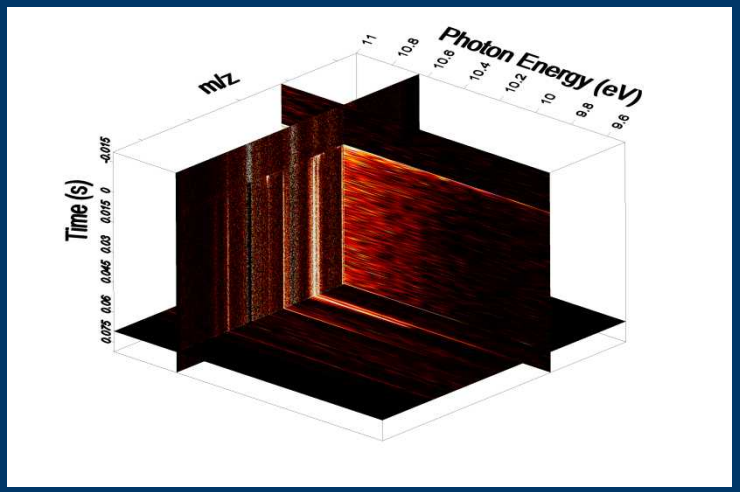

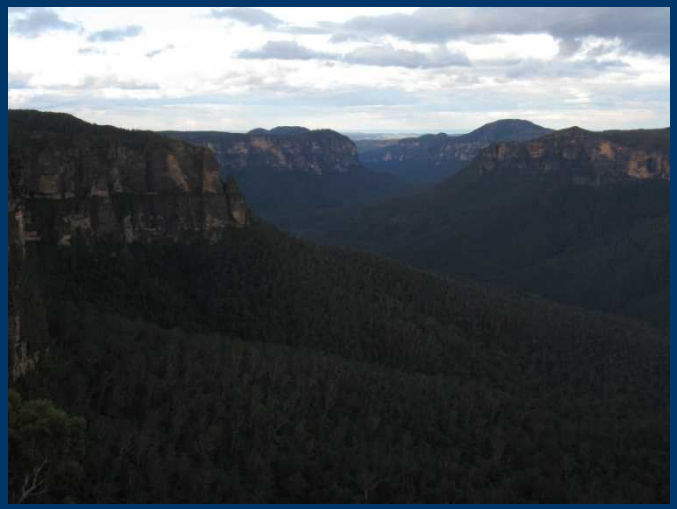

665th Meeting of the Sydney Chemical Society
August 17, 2011

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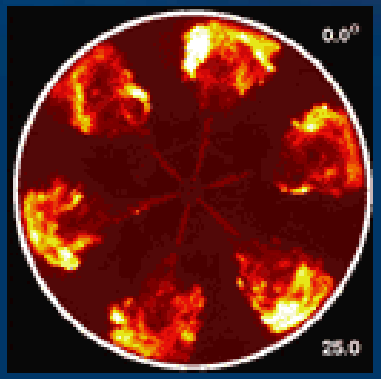
Outline

- Exploring chemical reactions
- Overview of valence ionization
- Overview of techniques
- Complications
- Future goals and needed innovations
- Conclusions

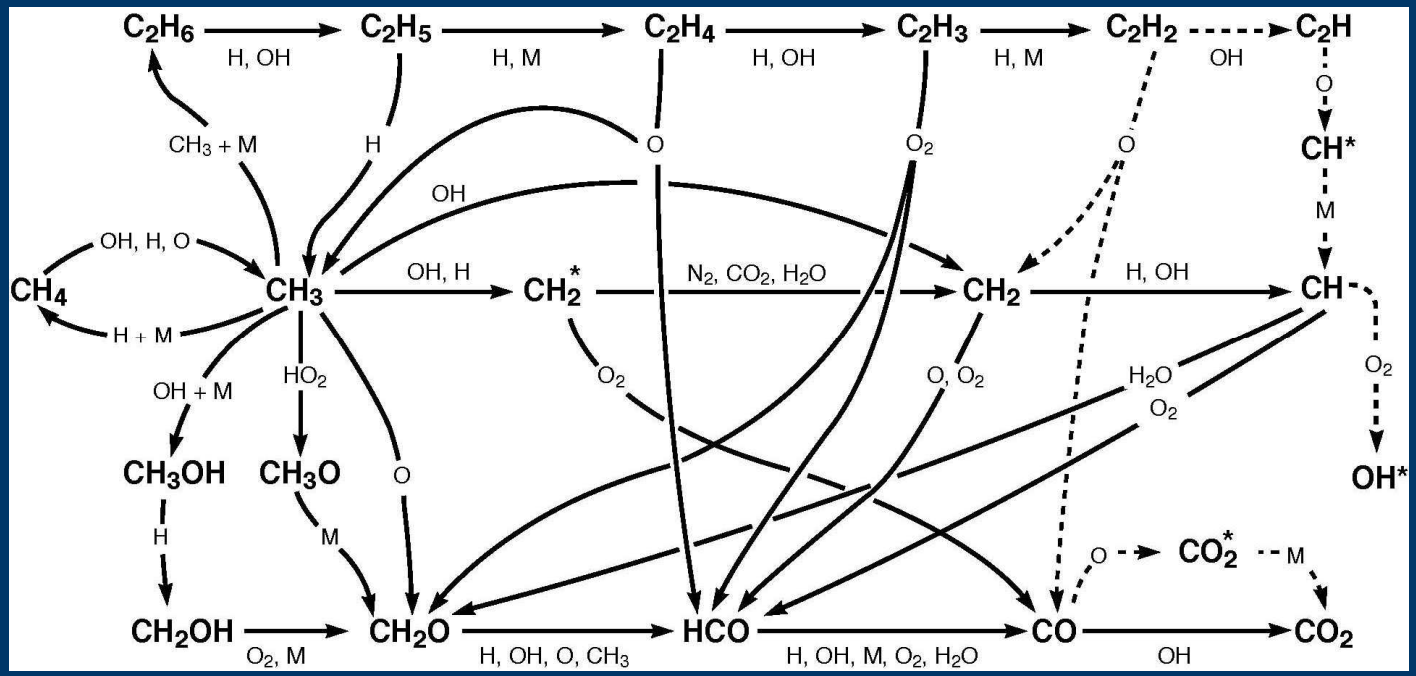
Combustion (and atmospheric chemistry) are

- A dense web of coupled reaction sequences
- Predictive chemical models rely on
  - Rate determinations of elementary reaction steps
  - Product branching ratios (isomer-resolved)
  - An accurate potential energy surface

Fuels Research Lab (C.J. Mueller, Sandia)



Turbulence ↔ Chemistry



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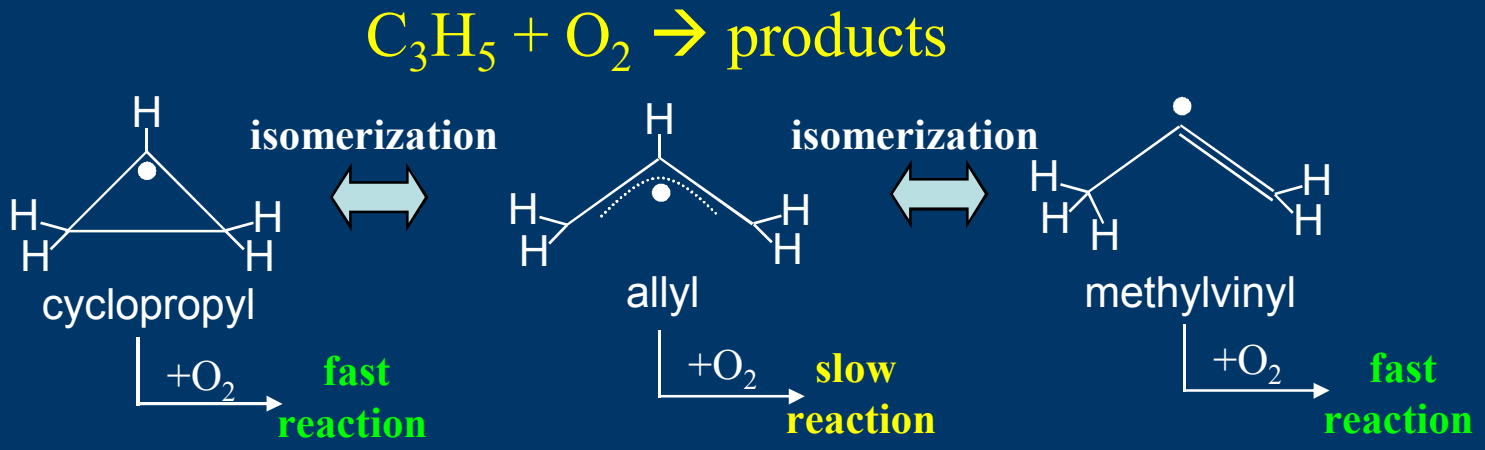
Exploring chemical reactions

Isomer distributions are a sensitive probe of reaction mechanisms

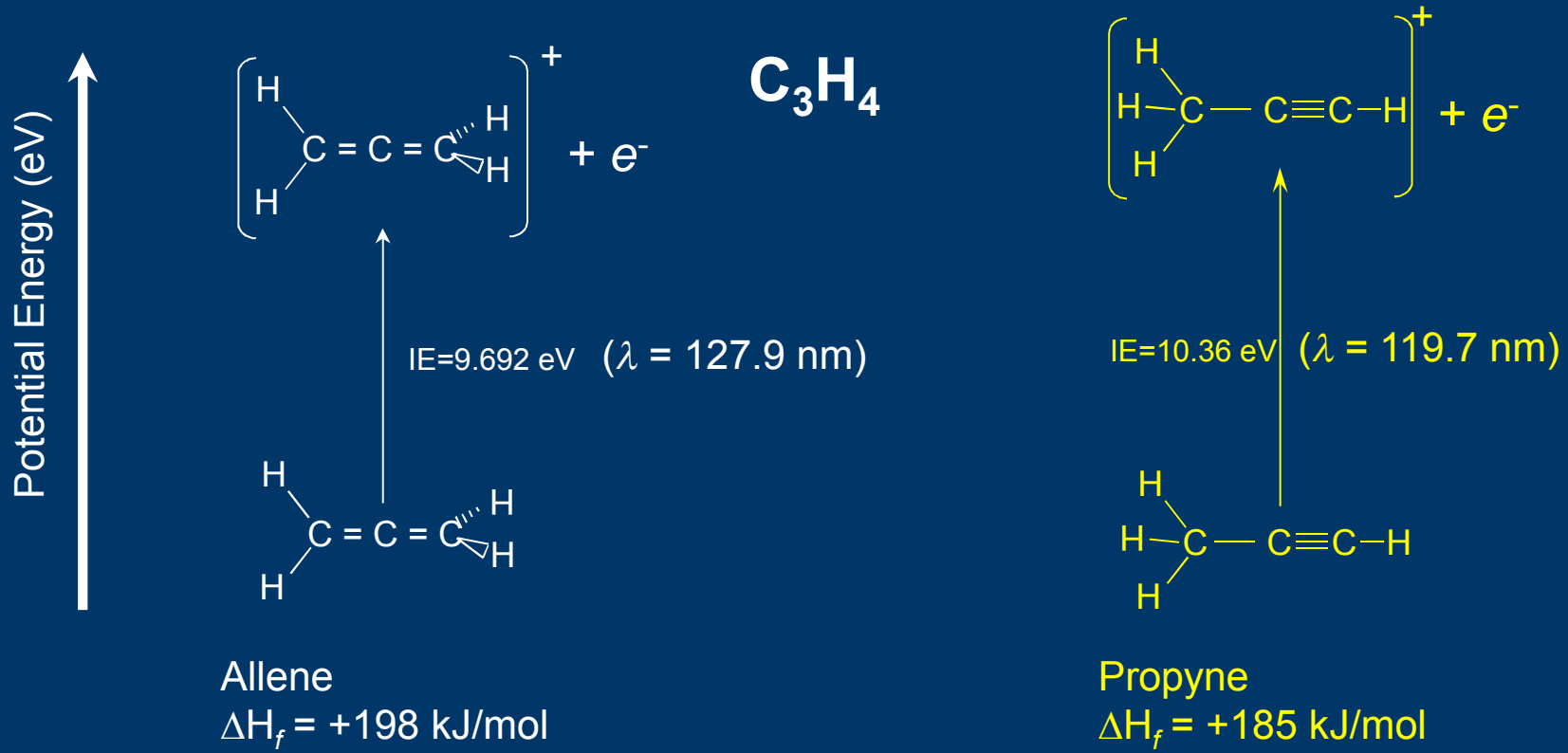
- Isomers often show different reactivity, steering downstream chemistry in new directions.



Distinguishing Isomers

Infrared spectroscopy: selective, but not sensitive
Microwave spectroscopy: ultra-selective, but…

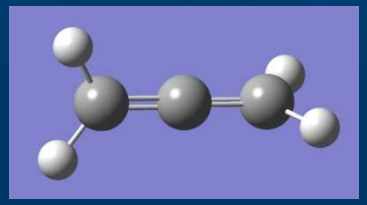
Each isomer of a chemical usually has a distinct ionization energy, and a characteristic shape of its photoionization curve (Franck-Condon).

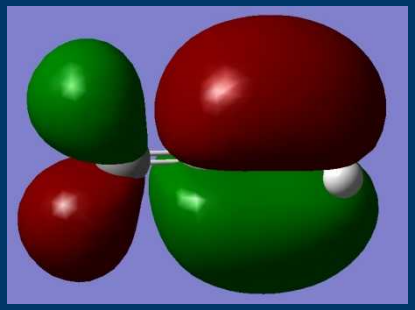


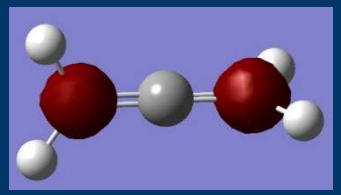
Allene
ΔH_f = +198 kJ/mol

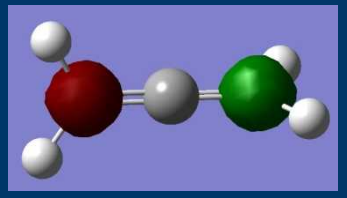
Propyne
ΔH_f = +185 kJ/mol

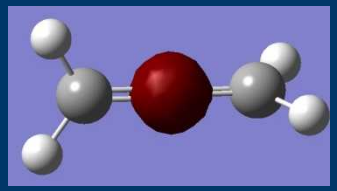
Valence compared to core ionization





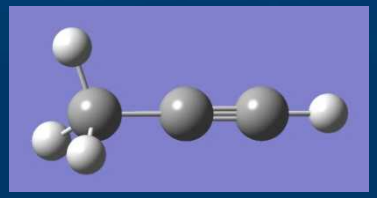


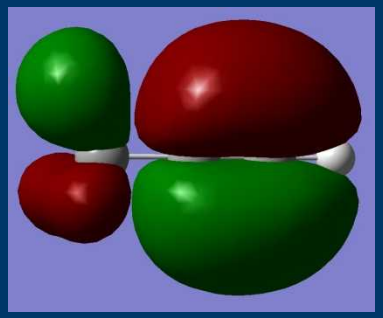


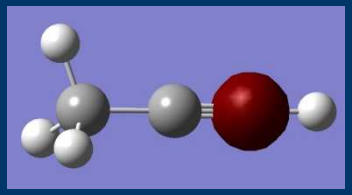


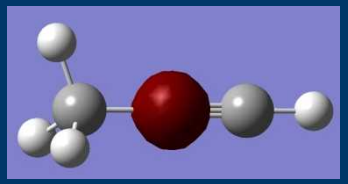
I'd like to put in orbital energies, but why don't they add up to the total energy?

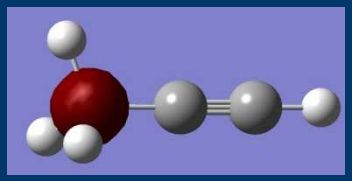
Can I use these energies to represent orbital detachment energies?











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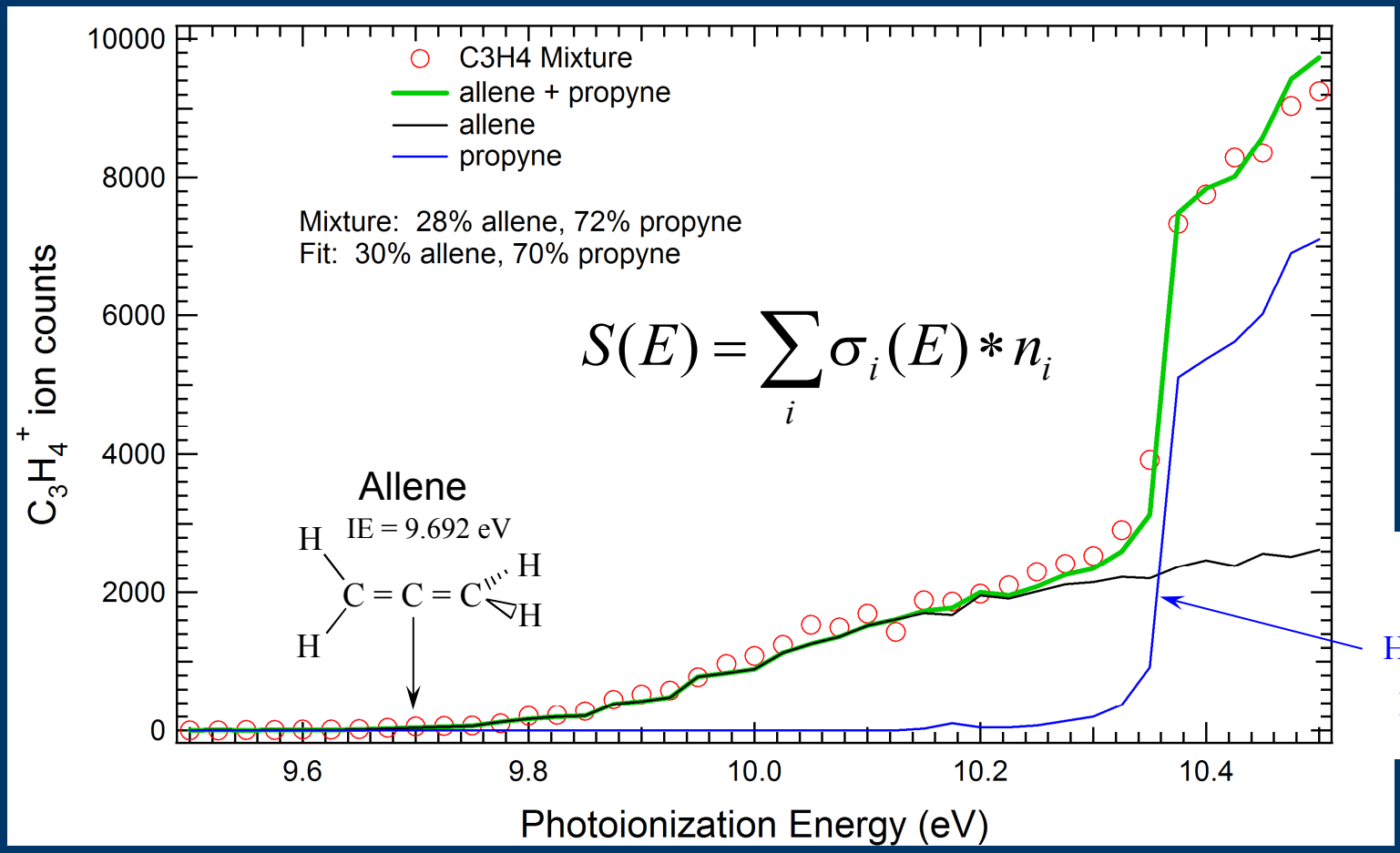
Quantitative branching ratios from photoionization spectra



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

Photoionization Source

The Advanced Light Source
Lawrence Berkeley National Laboratory

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

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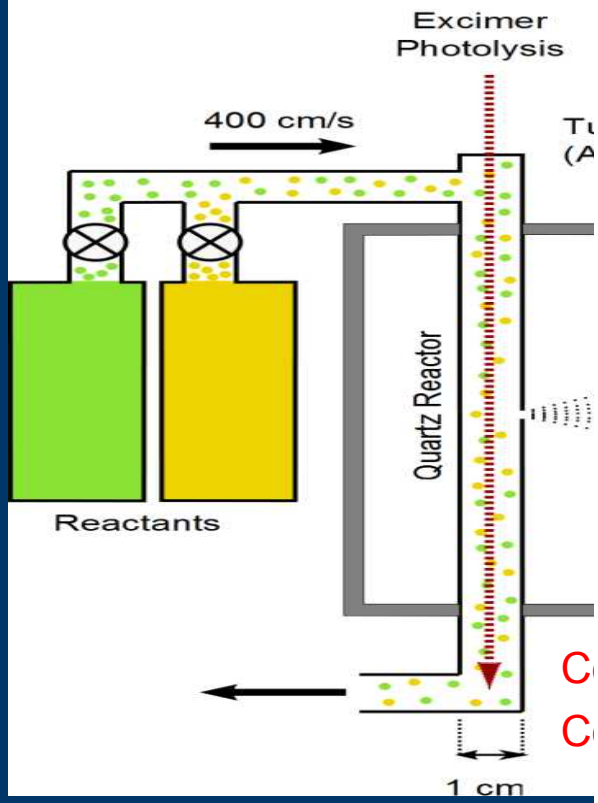
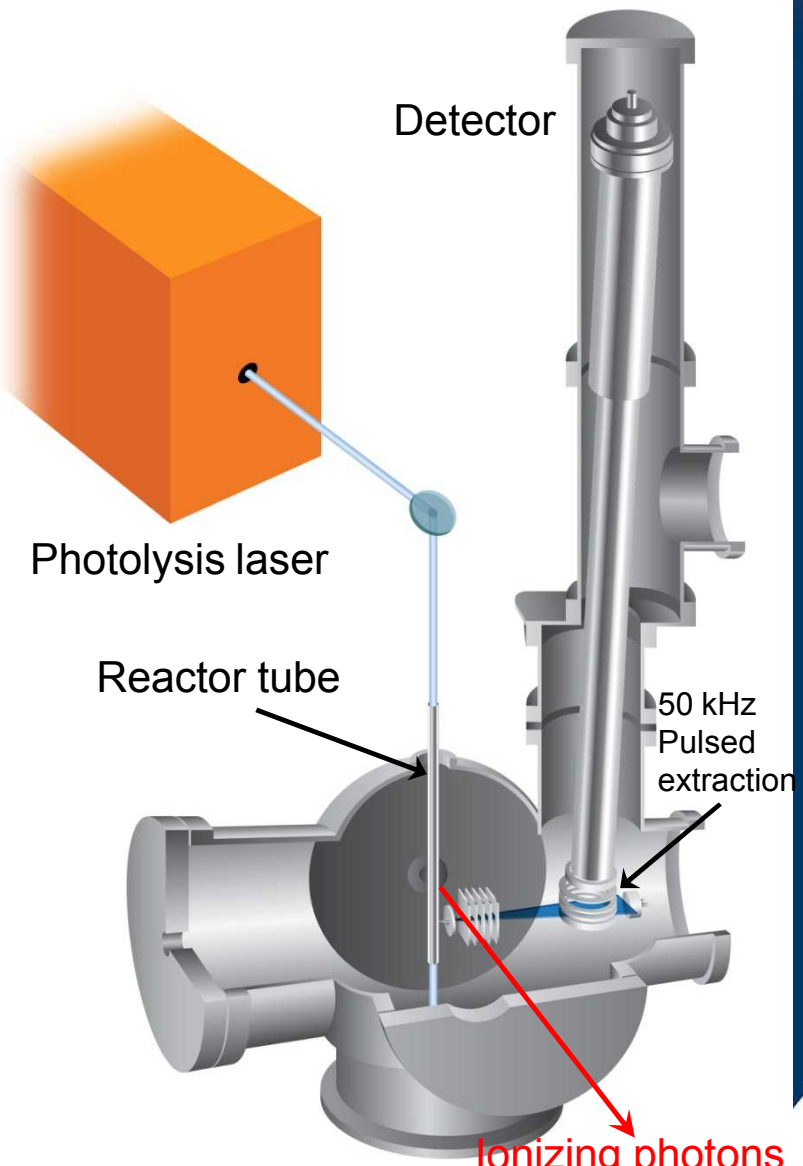
How do we study reactions with isomeric selectivity?

- Multiplexed photoionization mass spectrometry (MPIMS)
  - Universal detection (mass spectrometry)
  - Simultaneous detection (*multiplexed* mass spectrometry)
  - Isomer-resolved detection (tunable VUV, ALS synchrotron)
  - High sensitivity (synchrotron radiation + single ion counting)

Multiplexed Photoionization Mass Spectrometer

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



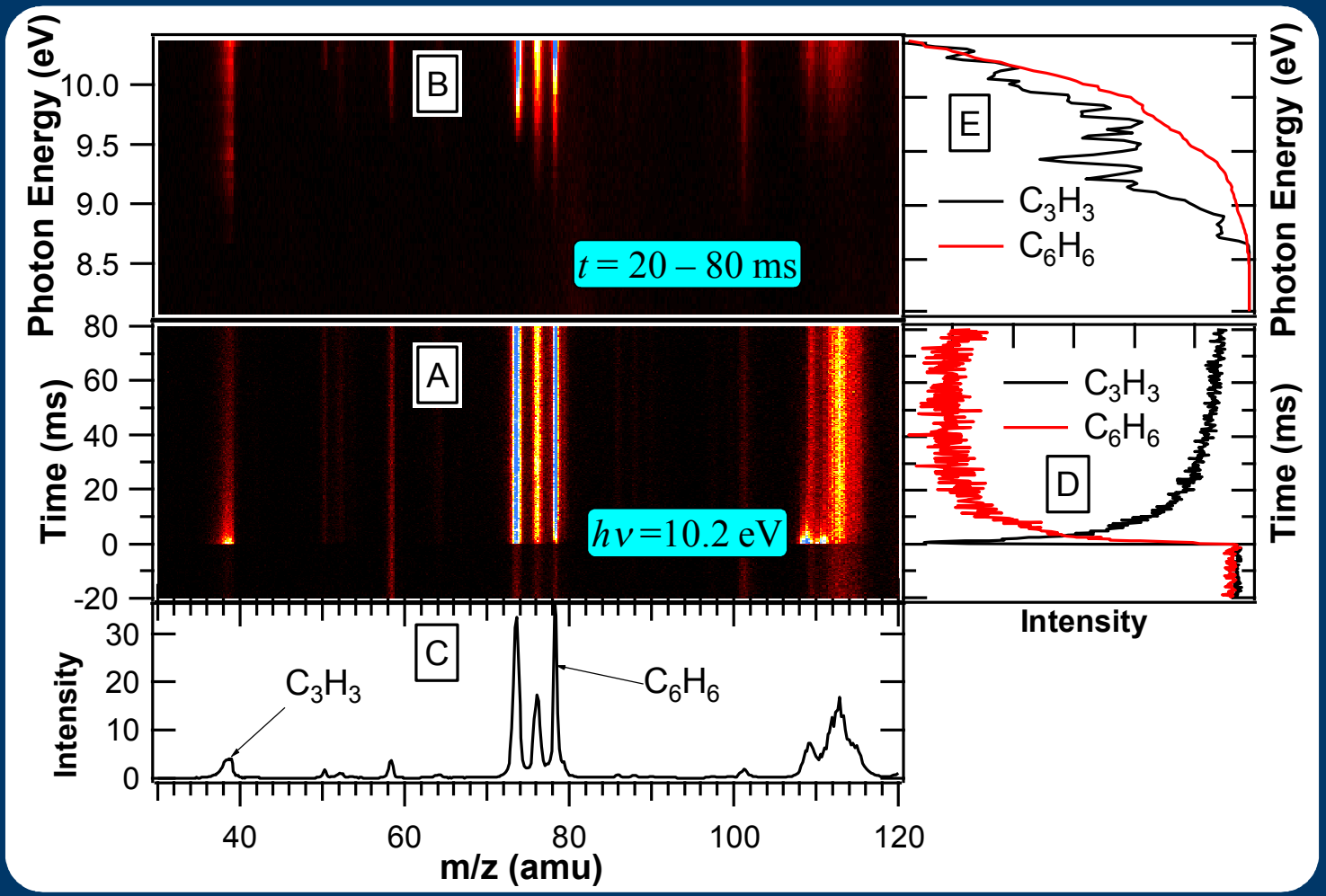


Three-Dimensional Data: $S(m, t, h\nu)$

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

$$C_3H_3 + C_3H_3 \rightarrow C_6H_6$$

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



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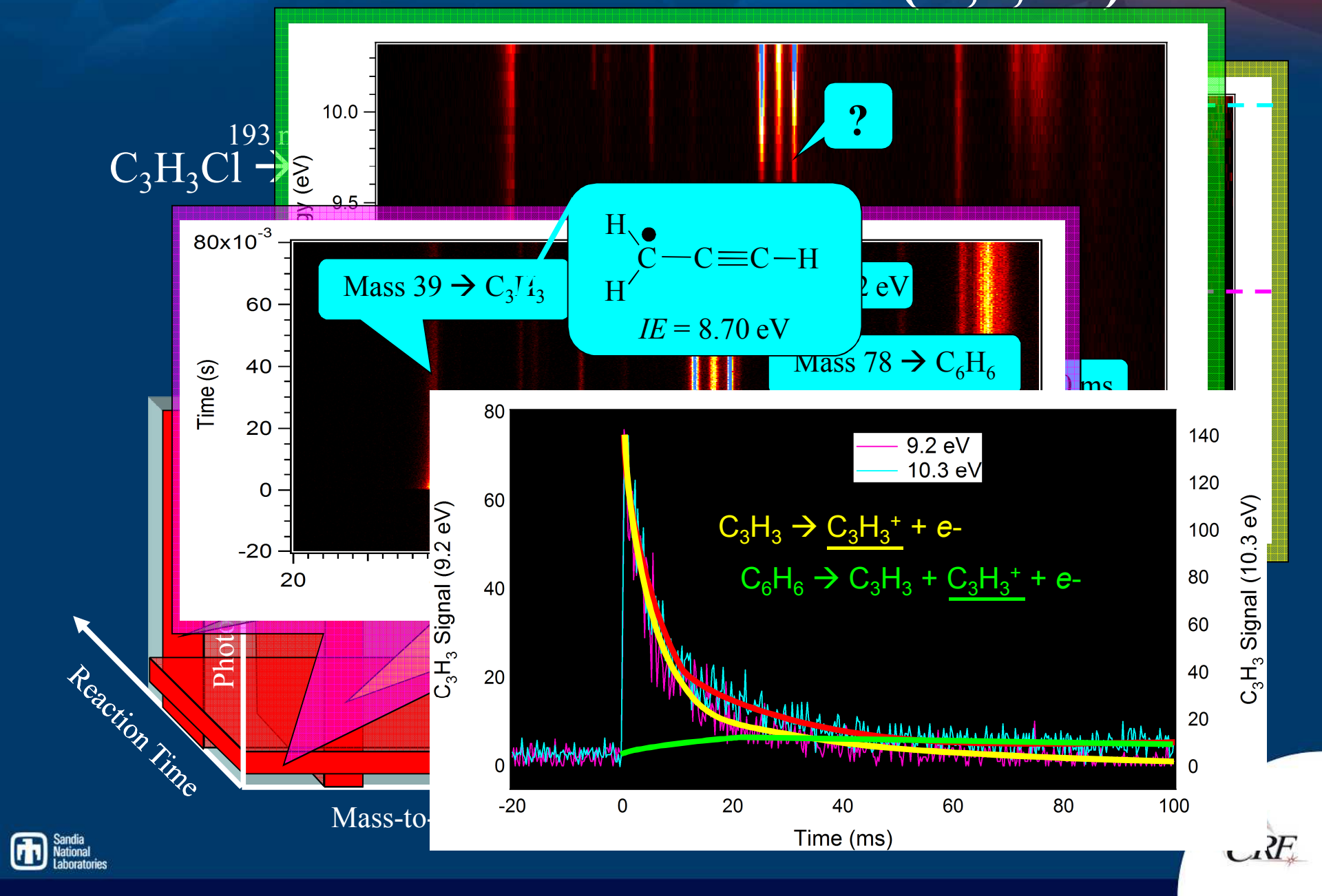
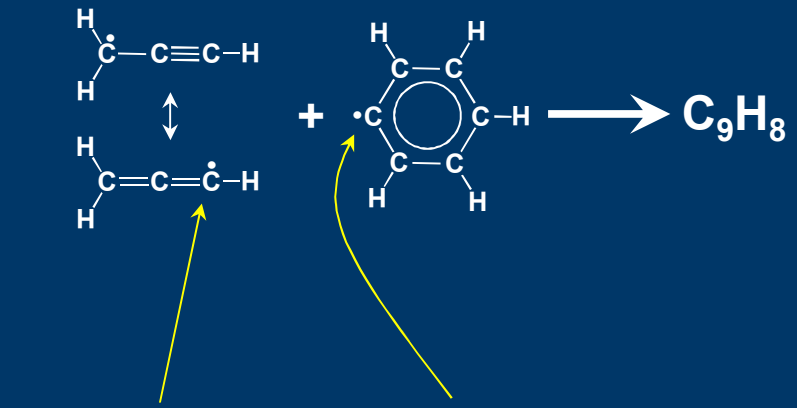
Three-Dimensional Data: $S(m, t, h\nu)$



The 2nd aromatic ring in PAH formation

- $C_3H_3 + C_3H_3 \rightarrow C_6H_6$ is an important reaction forming the first benzene ring
  - Resonance stabilization is key
- $C_3H_3 + C_6H_5$ may be significant in formation of the 2nd aromatic ring



unpaired electrons

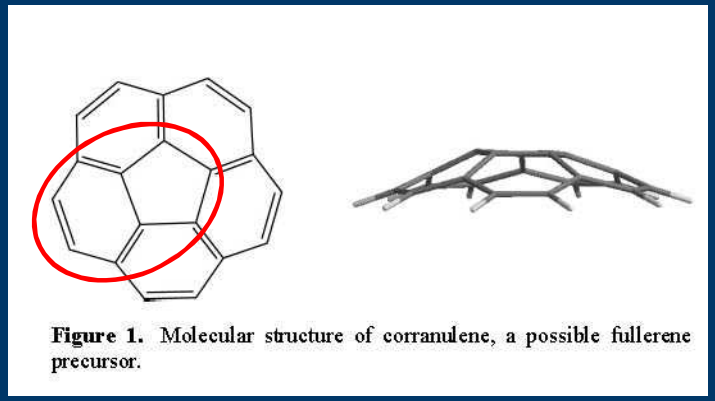
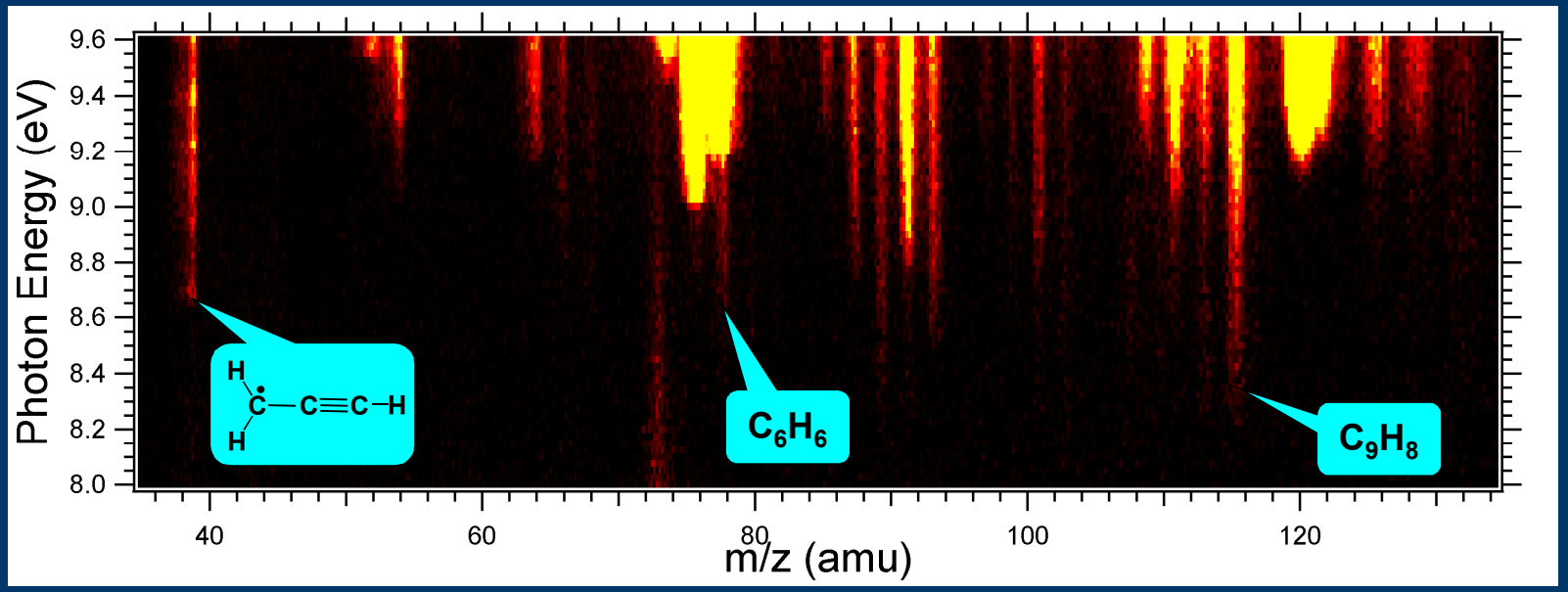


Figure 1. Molecular structure of corranulene, a possible fullerene precursor.

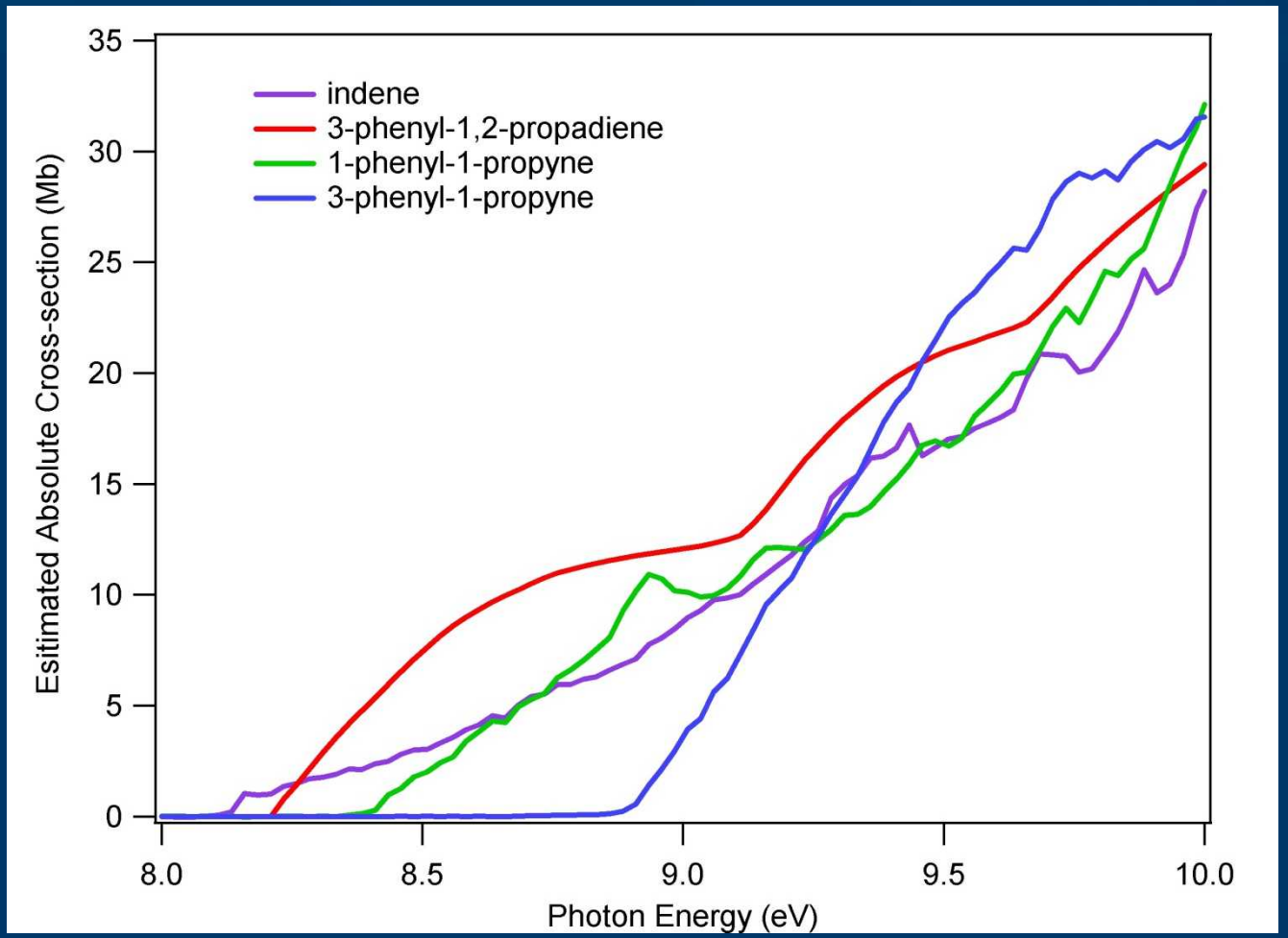
Kislov and Mebel, *J. Phys. Chem. A* **111**, 3922 (2007).

$C_3H_3 + C_6H_5 \rightarrow C_9H_8$

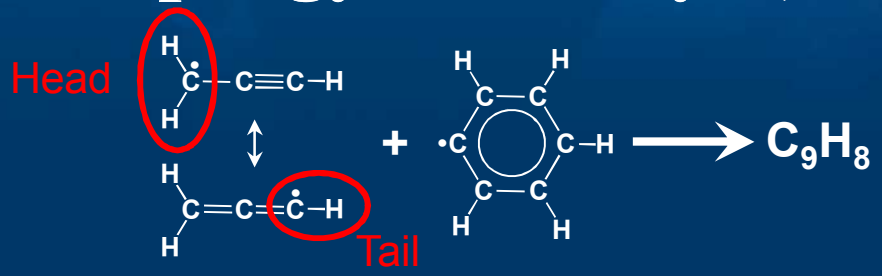
C_3H_3Br / C_6H_5Br + 248 nm, T = 300K, P = 4 torr

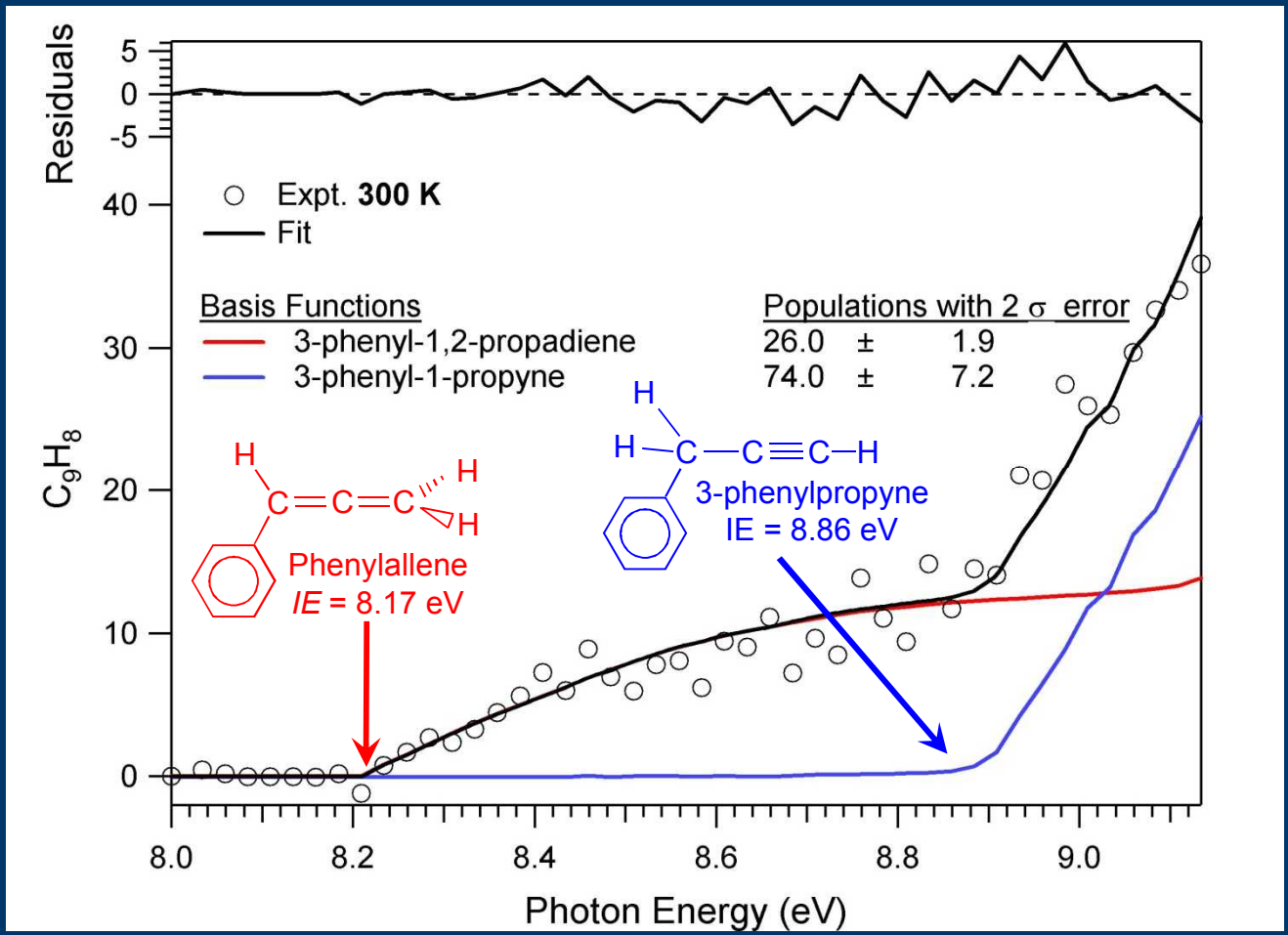


C_9H_8 Reference Photoionization Spectra

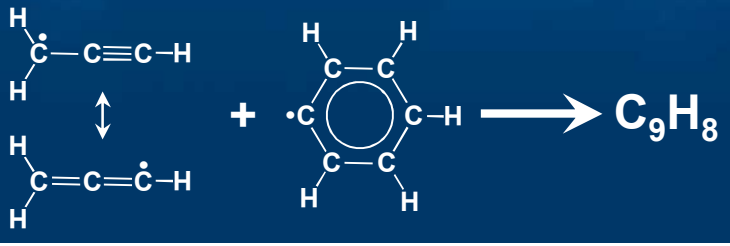


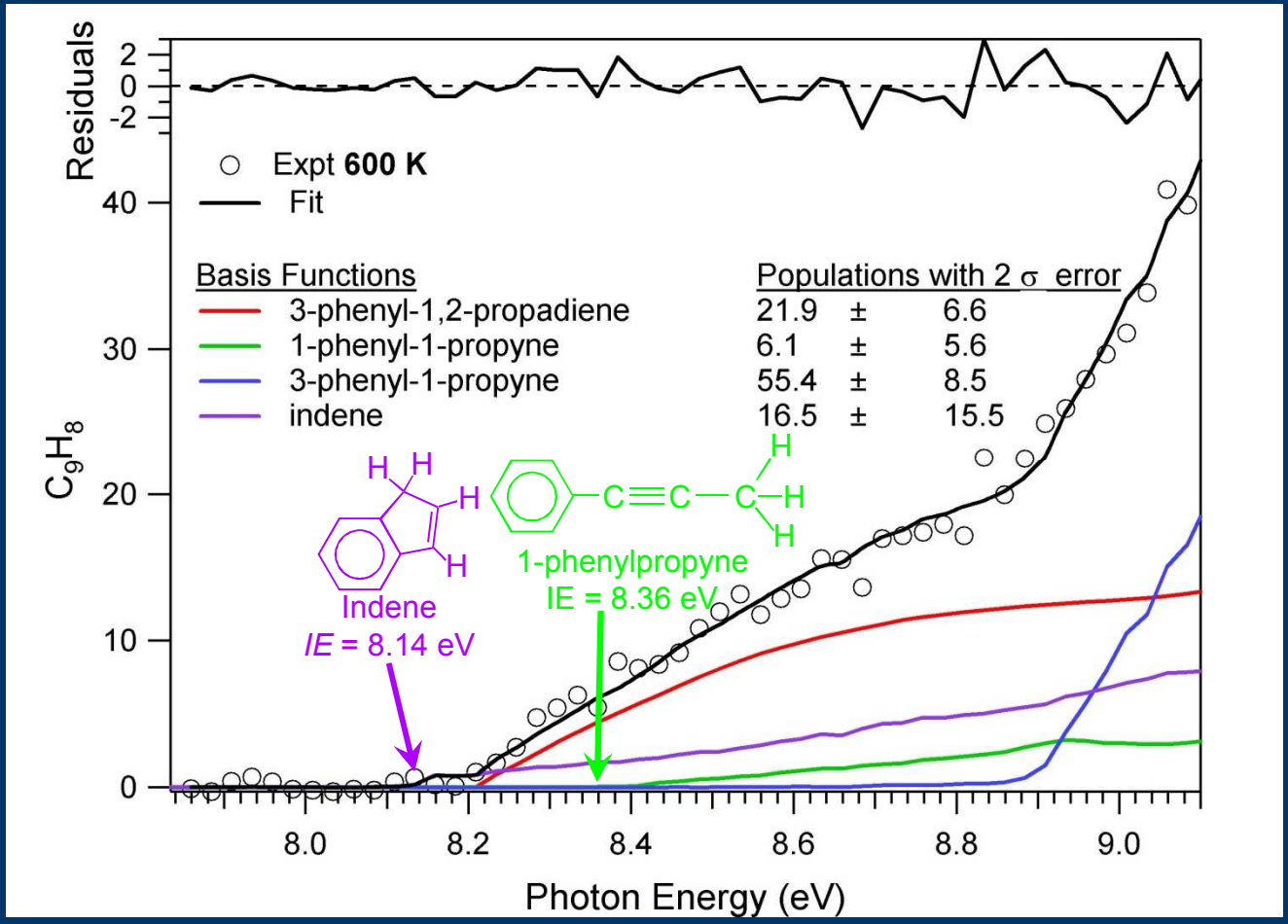
Propargyl + Phenyl (300K)



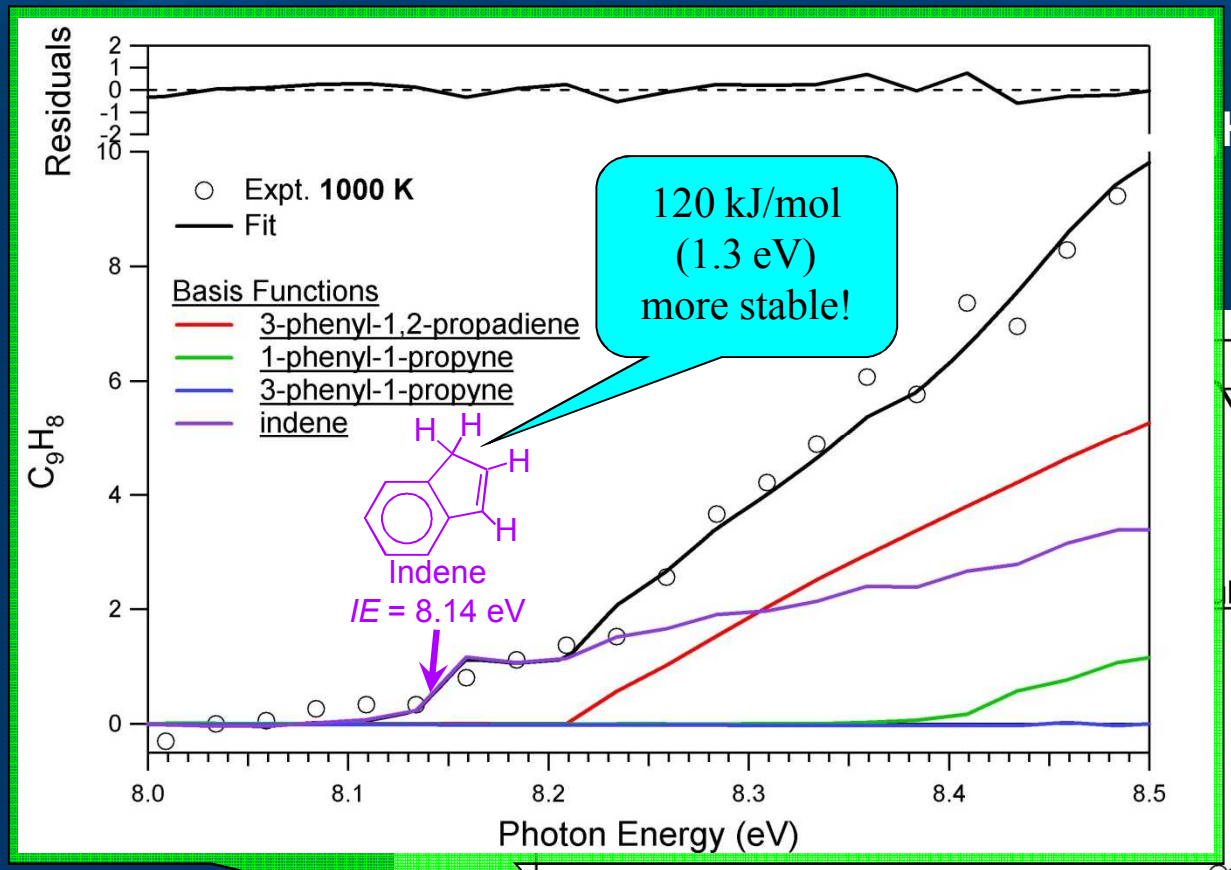


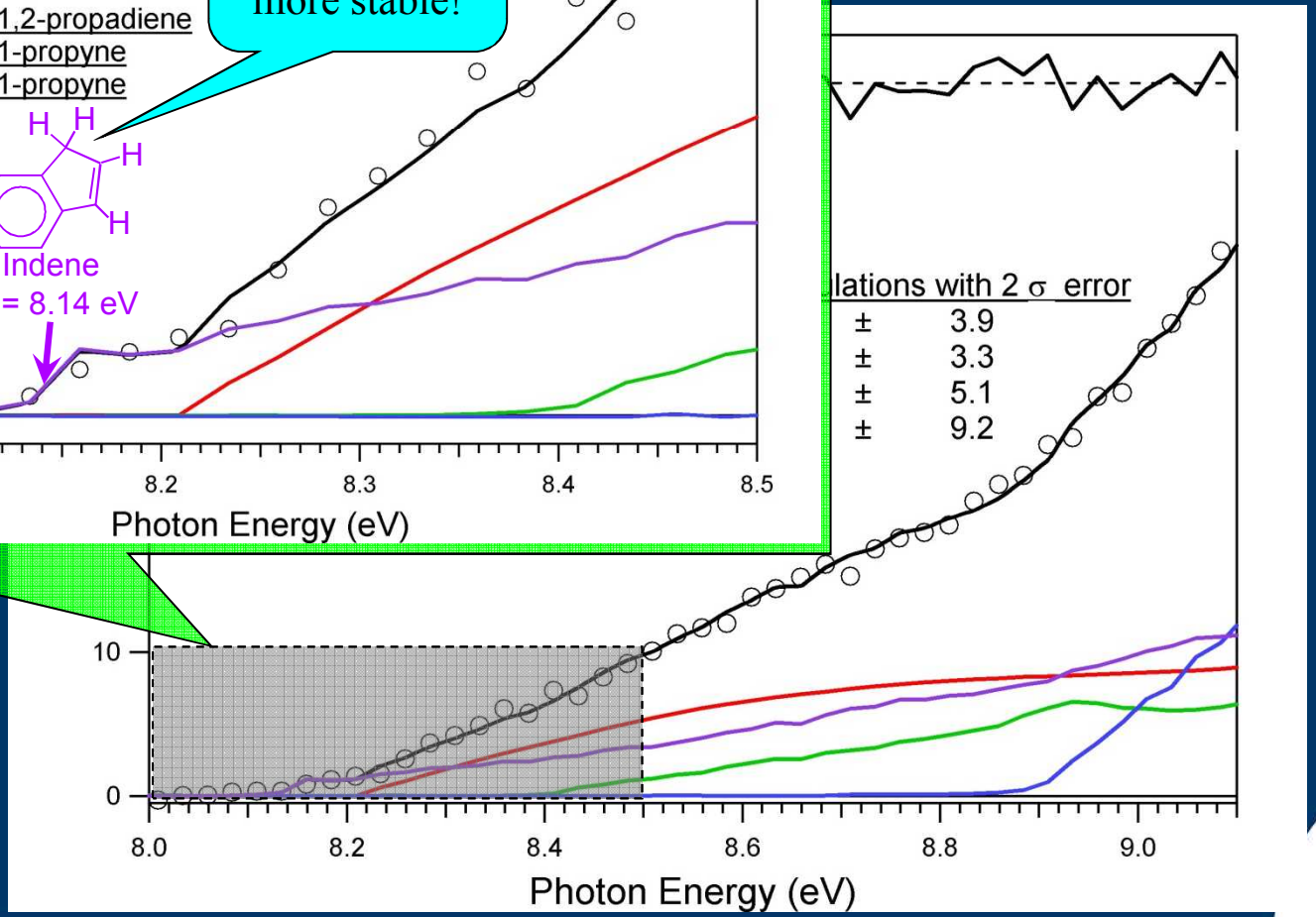
Propargyl + Phenyl (600K)





Propargyl + Phenyl (1000K)





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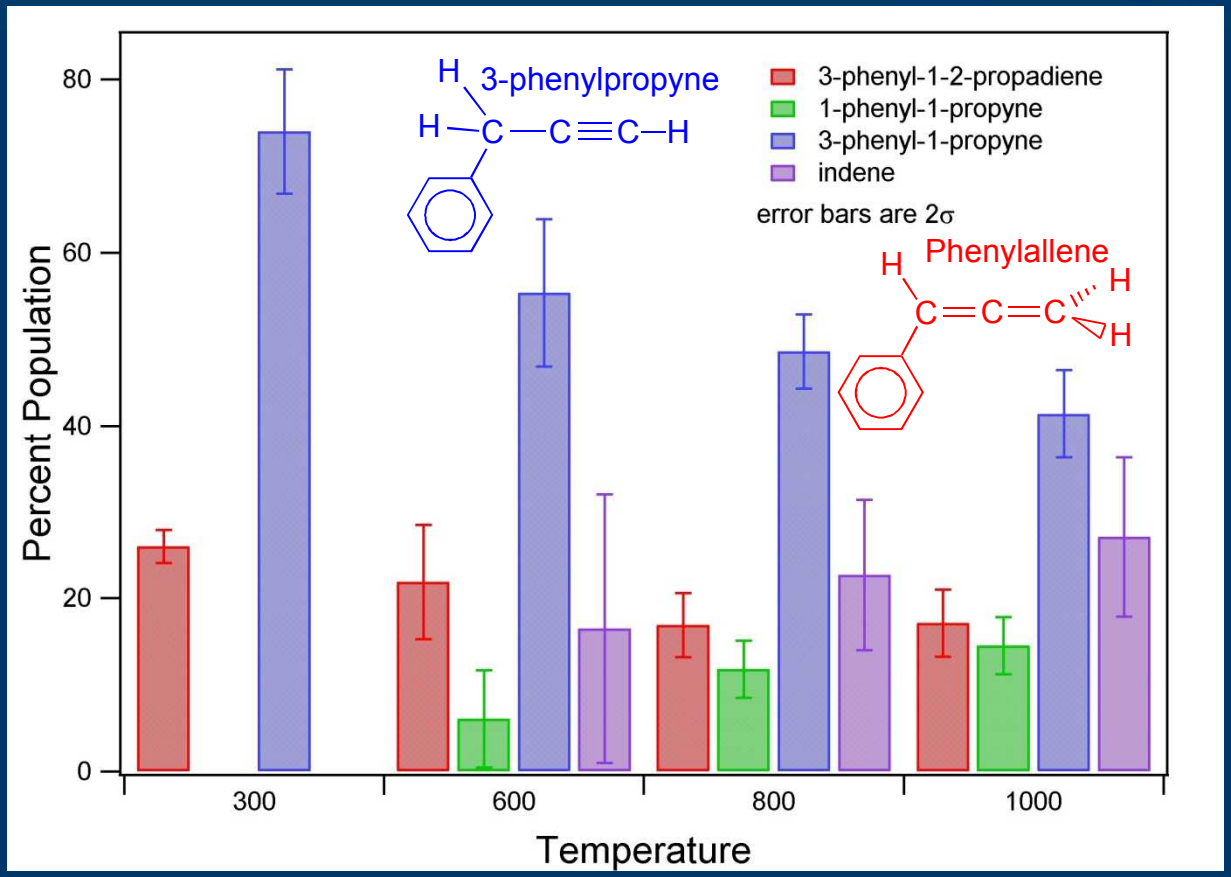
Preliminary Isomer Ratios

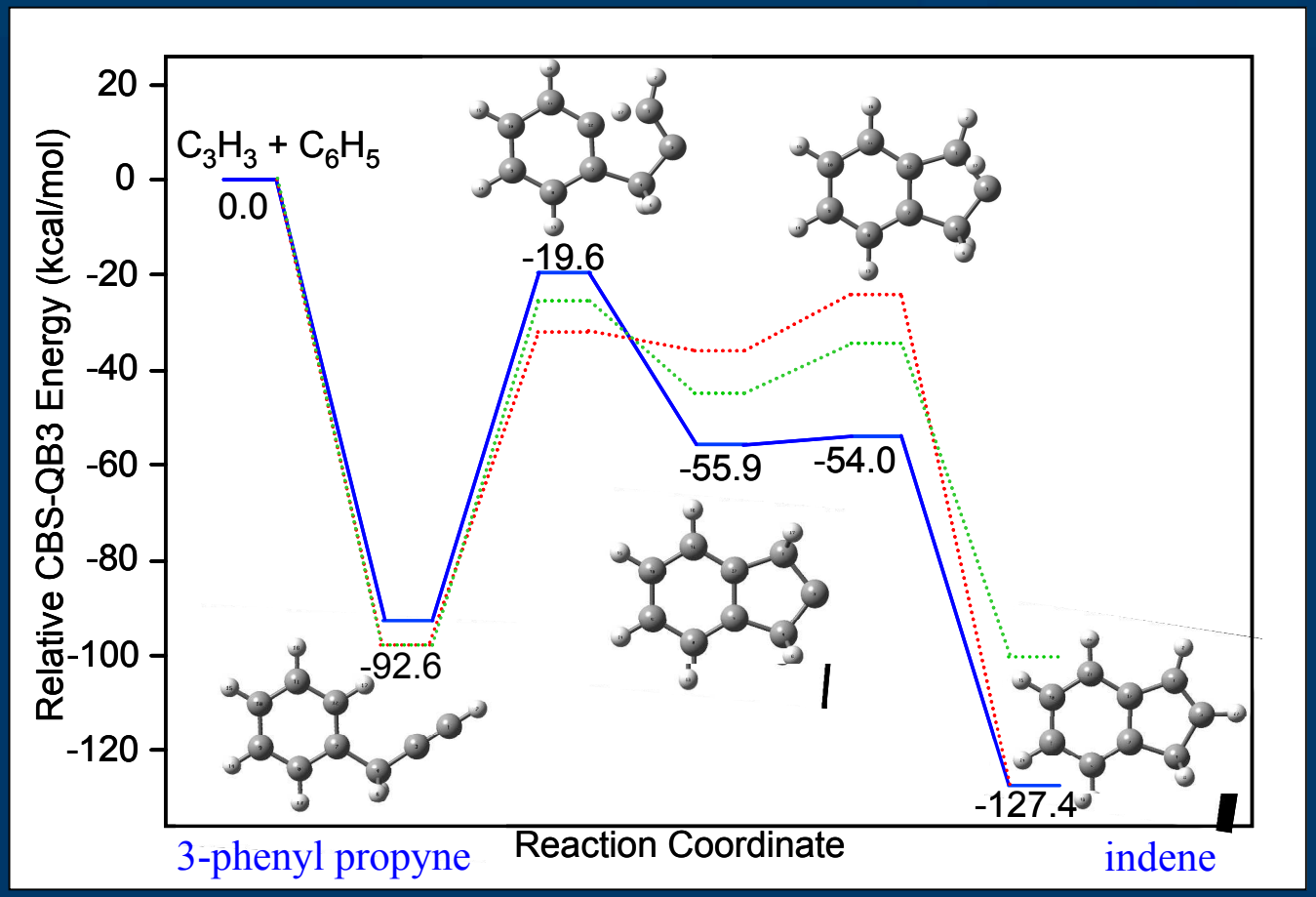


Open Questions:

Is it easier for the propyne-like adduct to isomerize?

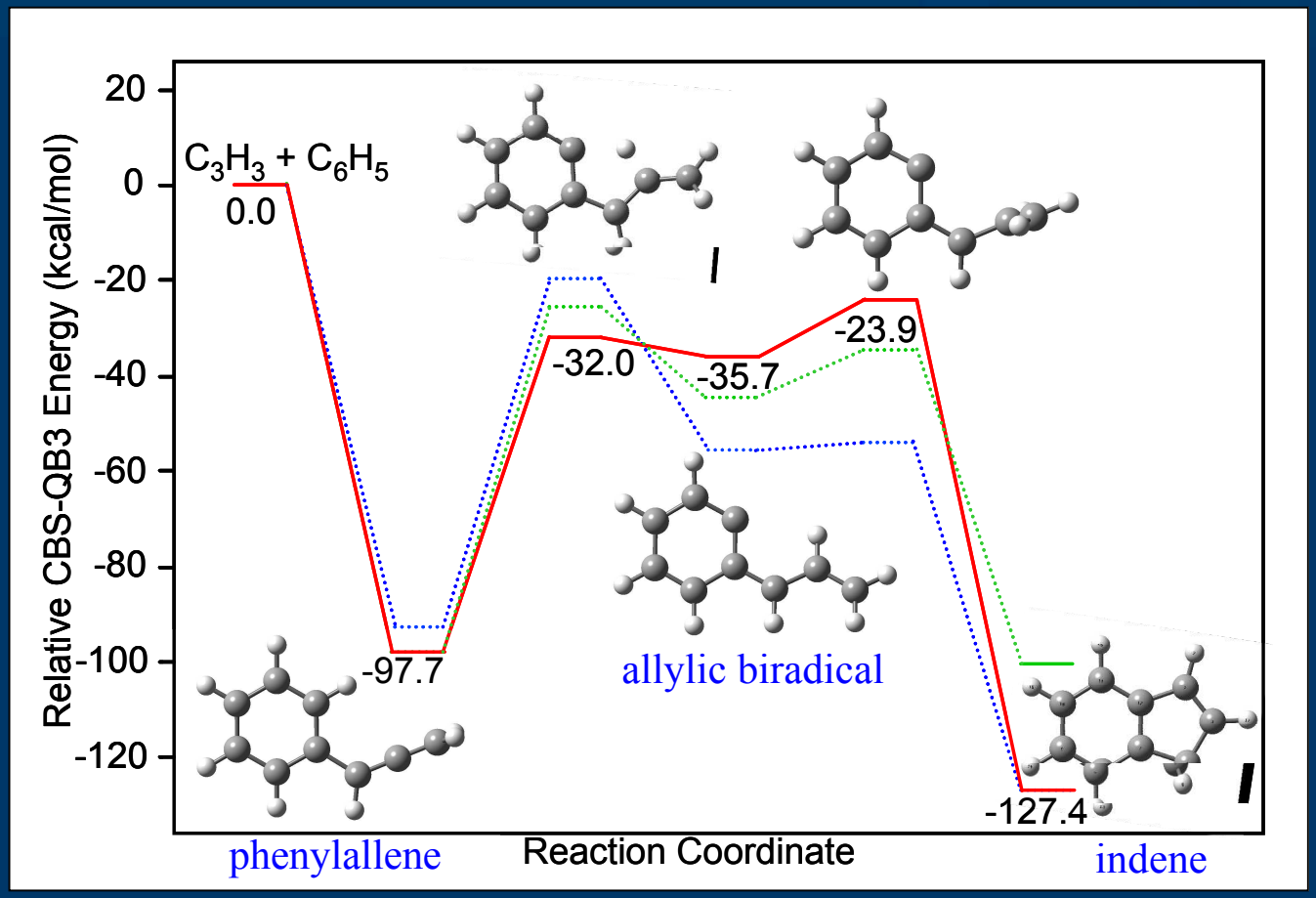
Cross sections are estimated. How much error does this introduce?

C_3H_3 head addition to phenyl



H atom-assisted isomerization: V. V. Kislov and A. M. Mebel, *J. Phys. Chem. A* **111**, 3922 (2007).

C_3H_3 tail addition to phenyl



H atom-assisted isomerization: V. V. Kislov and A. M. Mebel, *J. Phys. Chem. A* **111**, 3922 (2007).

Propargyl + Phenyl: Summary

- At low temperatures, simple adduct formation
- At higher temperatures, isomerization to more stable species

- Next steps:
  - Pressure dependence of the reaction
  - Variational treatment of entrance channels (A. Jasper)
  - Multi-well master equation calculations (A. Jasper, J. Zador, J. A. Miller)

Conclusions

- $C_3H_3 + C_6H_5$
  - Simple adduct formation at T < 600 K
  - Isomerizations from 800 – 1000 K → indene, a two-ring aromatic.
- Direct observation of Criegee intermediates should open a new chapter in their study
  - Reaction rates
  - Products
  - Other forms of spectroscopy
- Multiplexed Photoionization Mass Spectrometry can identify unexpected intermediates in a complex web of chemistry

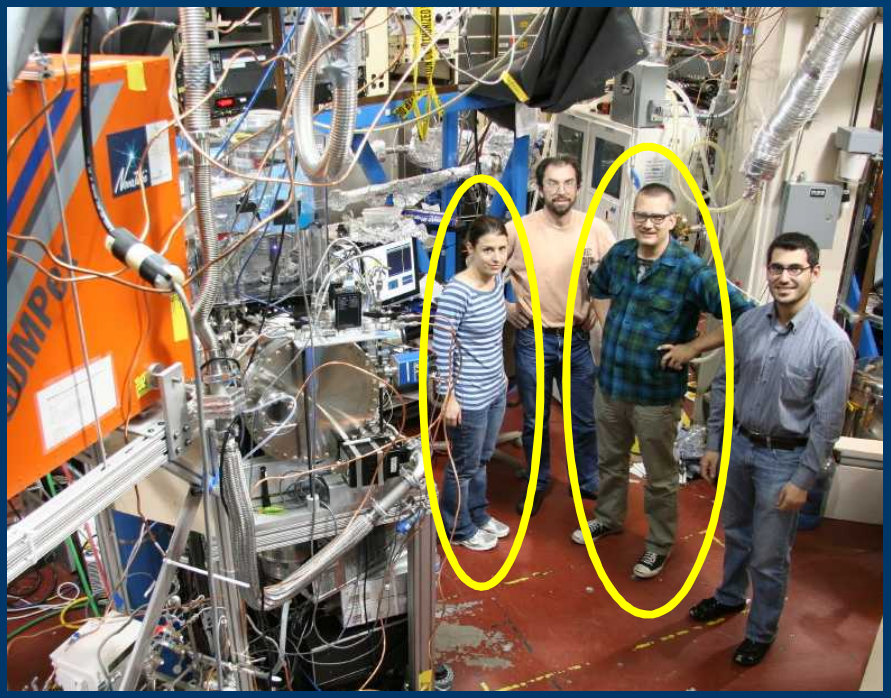
Acknowledgements

Adam Trevitt

Fabien Goulay

Musa Ahmed

Kevin Wilson



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Carl Percival

Dudley Shallcross

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U.S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under Contract DE-AC04-94-AL85000.

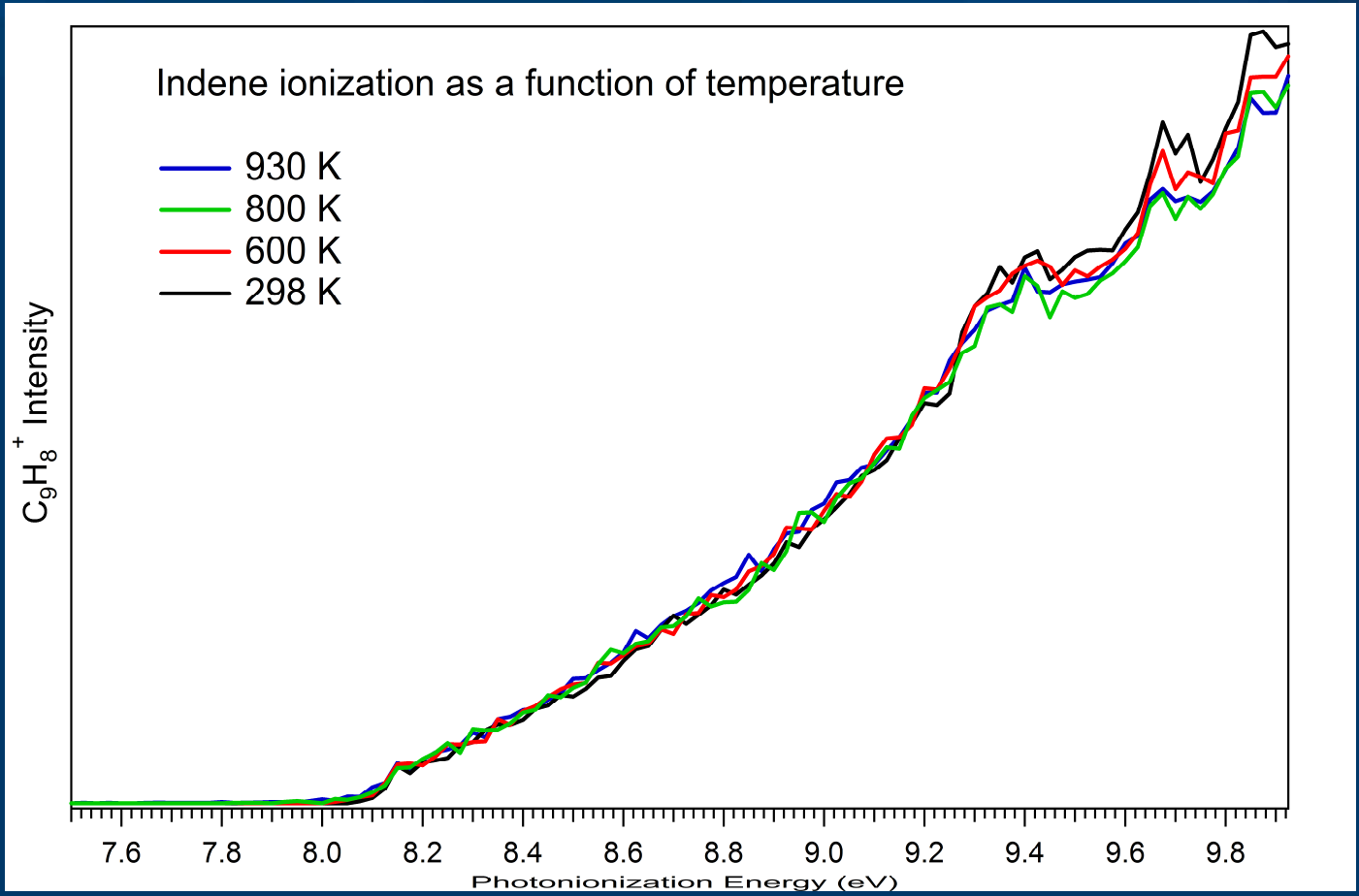
Challenges of High Pressure

- 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 = $-d/dt\,[C_2H_3] = k[C_2H_3][O_2]$
- 0.01 atm → 100 atm increased dilution by 10^4.
- Best solution is increase of VUV photon flux by 10^4.

Our Needs / Wants in a Light Source

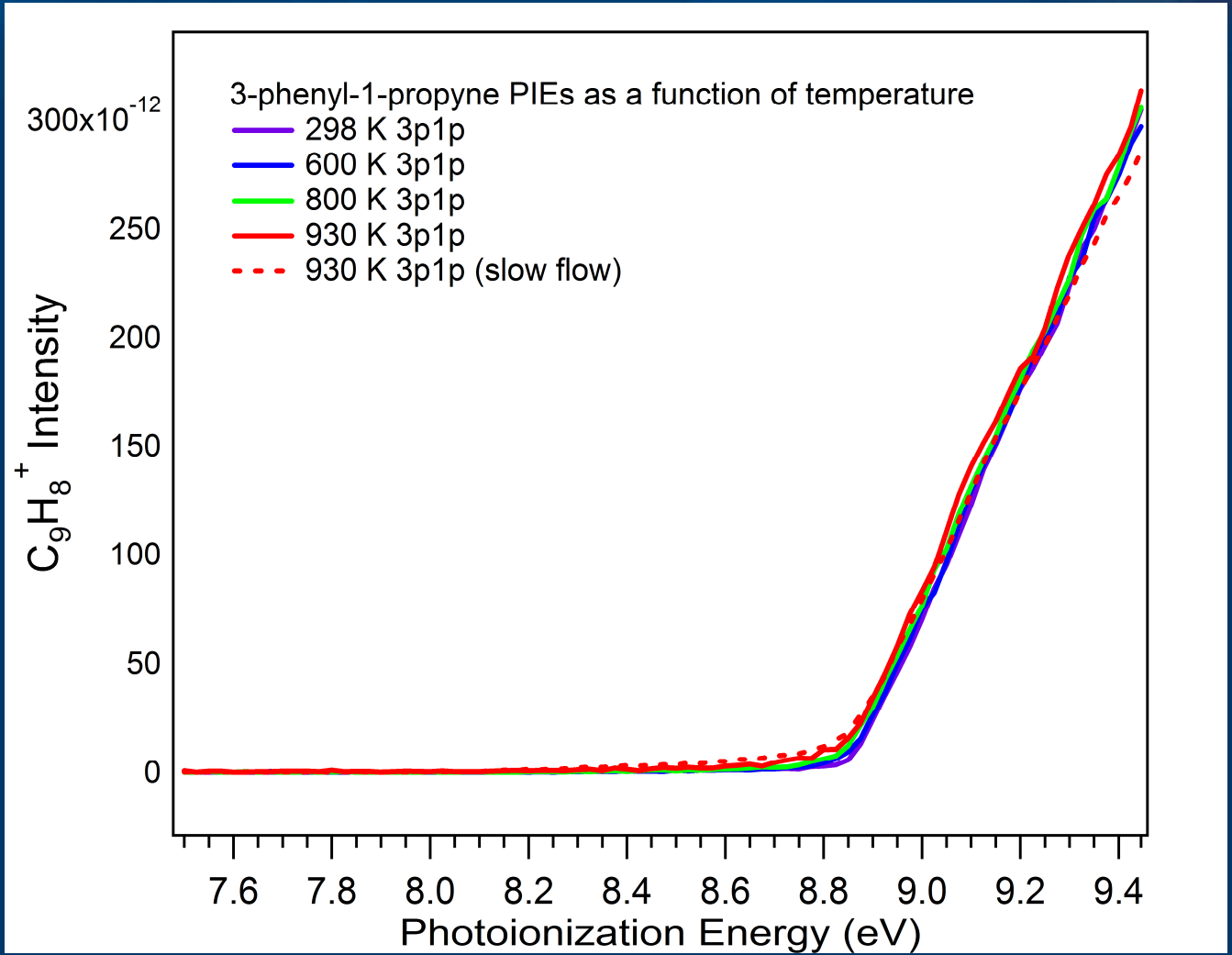
- Needs
  - Repetition Rate 50 kHz or greater
  - High average power (> 10^{13} photons / s at 0.1% bandwidth)
  - Continuous, rapid tunability (7.3 – 16 eV)
  - Light with no harmonics (at least 1 part in 10^4)
  - High brightness (spot size ~ 1 x 1 mm)
- Wants
  - Much higher average power (10^{17}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

Photoionization Energy Dependence



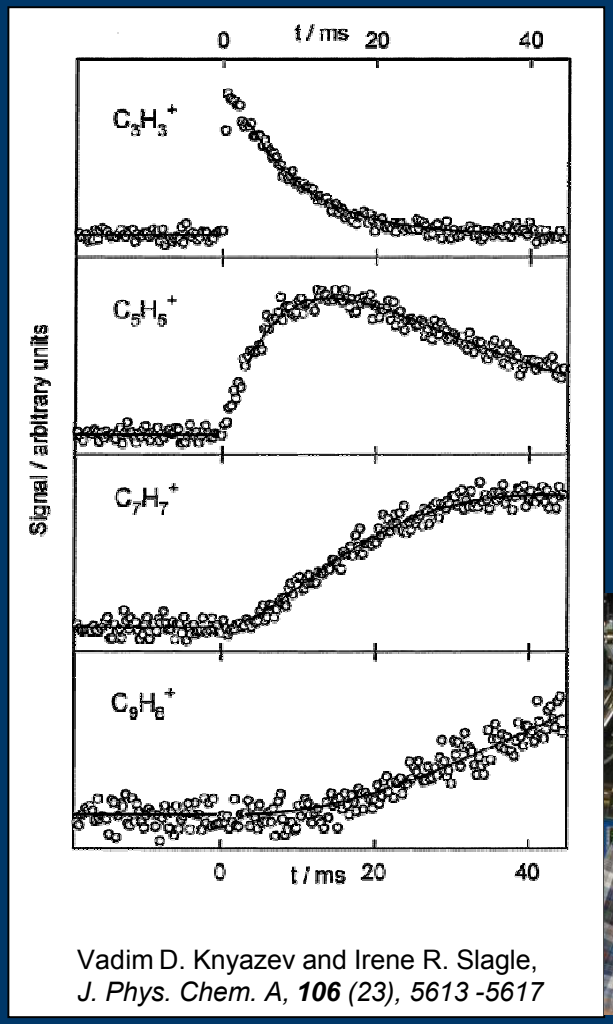
Indene photoionization is essentially temperature independent

Photoionization Energy Dependence



3-phenyl propyne photoionization has a mild temperature dependence

Following Reaction Sequences: Propargyl + Acetylene



Vadim D. Knyazev and Irene R. Slagle,
J. Phys. Chem. A, ***106*** *(23), 5613 -5617*

$C_3H_3 + C_2H_2 \rightarrow C_5H_5$ (linear or cyclic?)
$C_5H_5 + C_2H_2 \rightarrow C_7H_7$
$C_7H_7 + C_2H_2 \rightarrow C_9H_8 + H$

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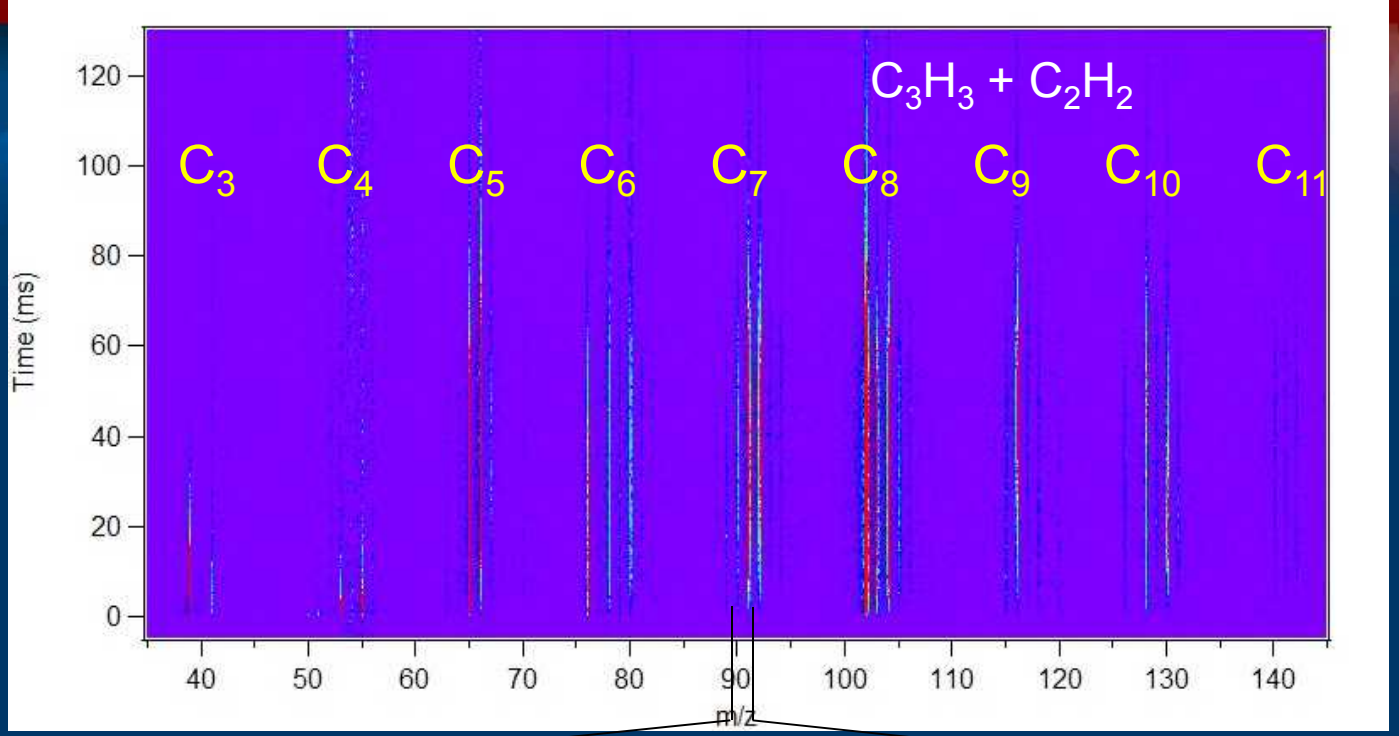
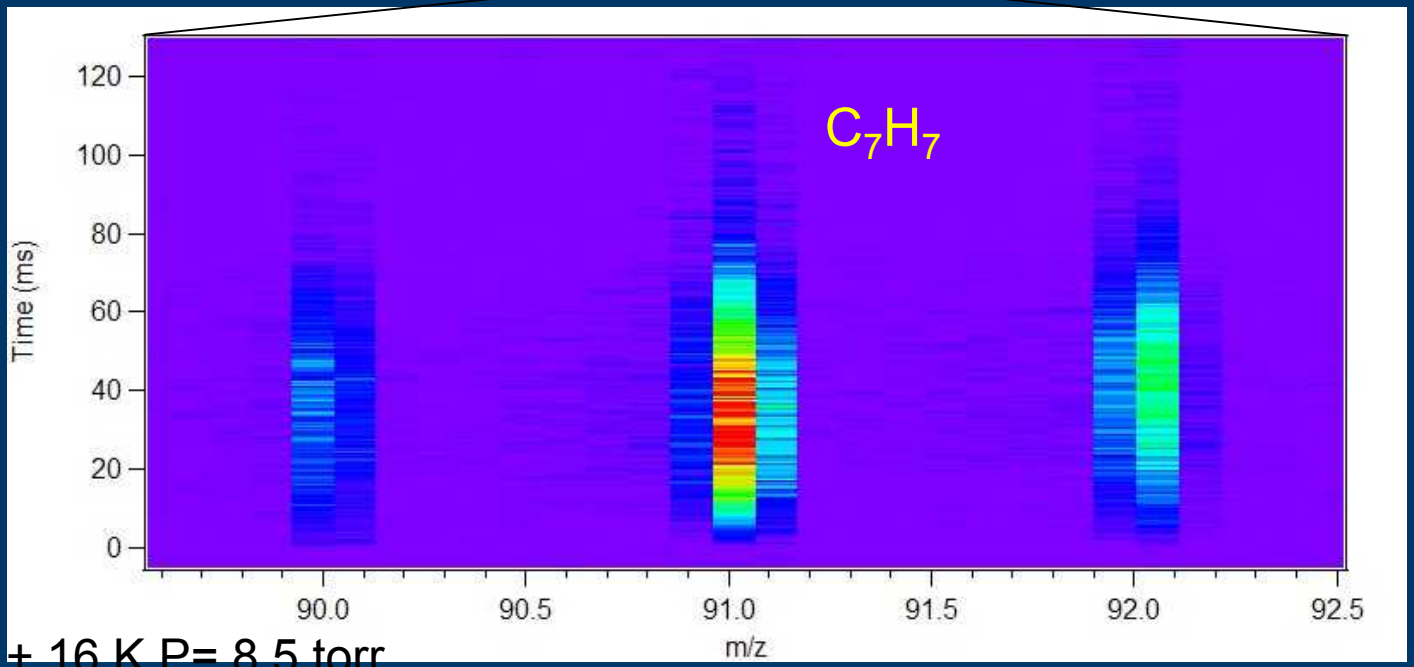
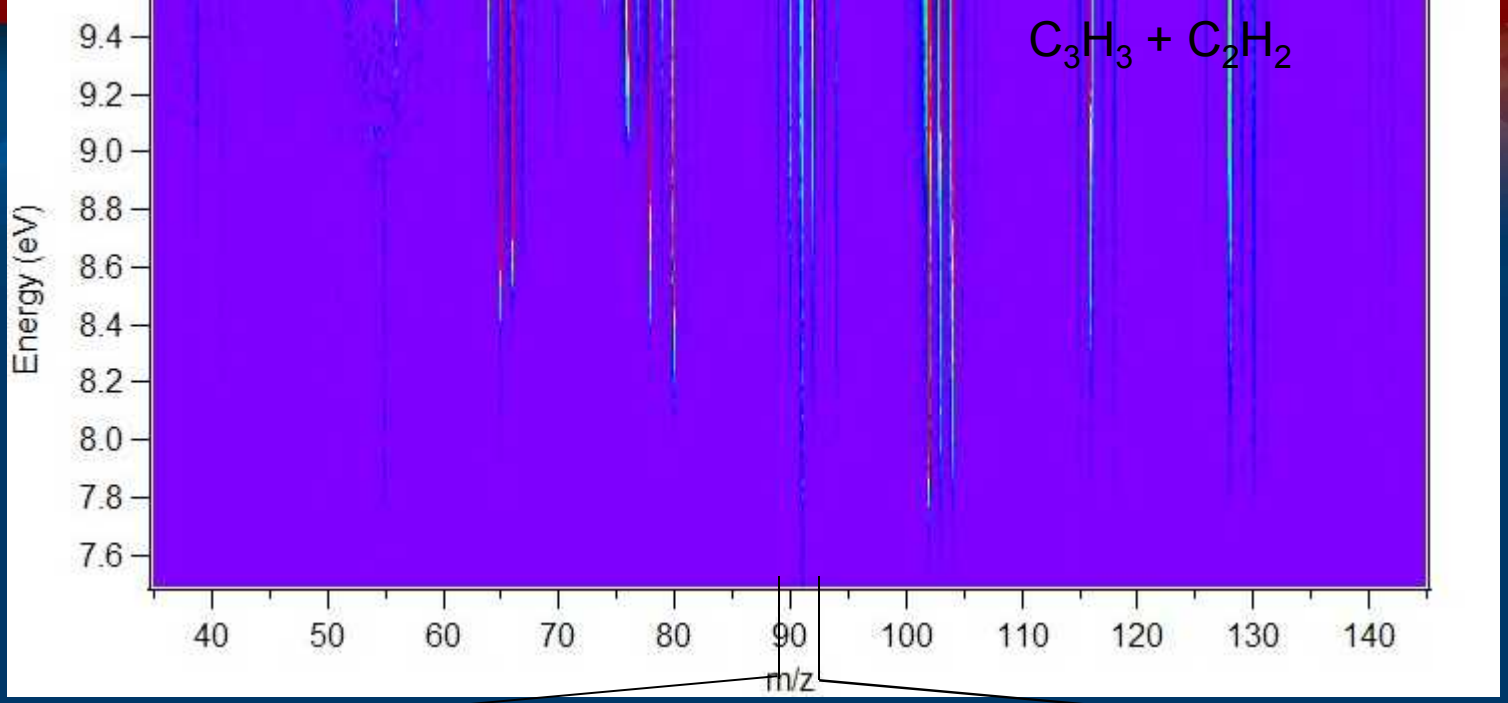
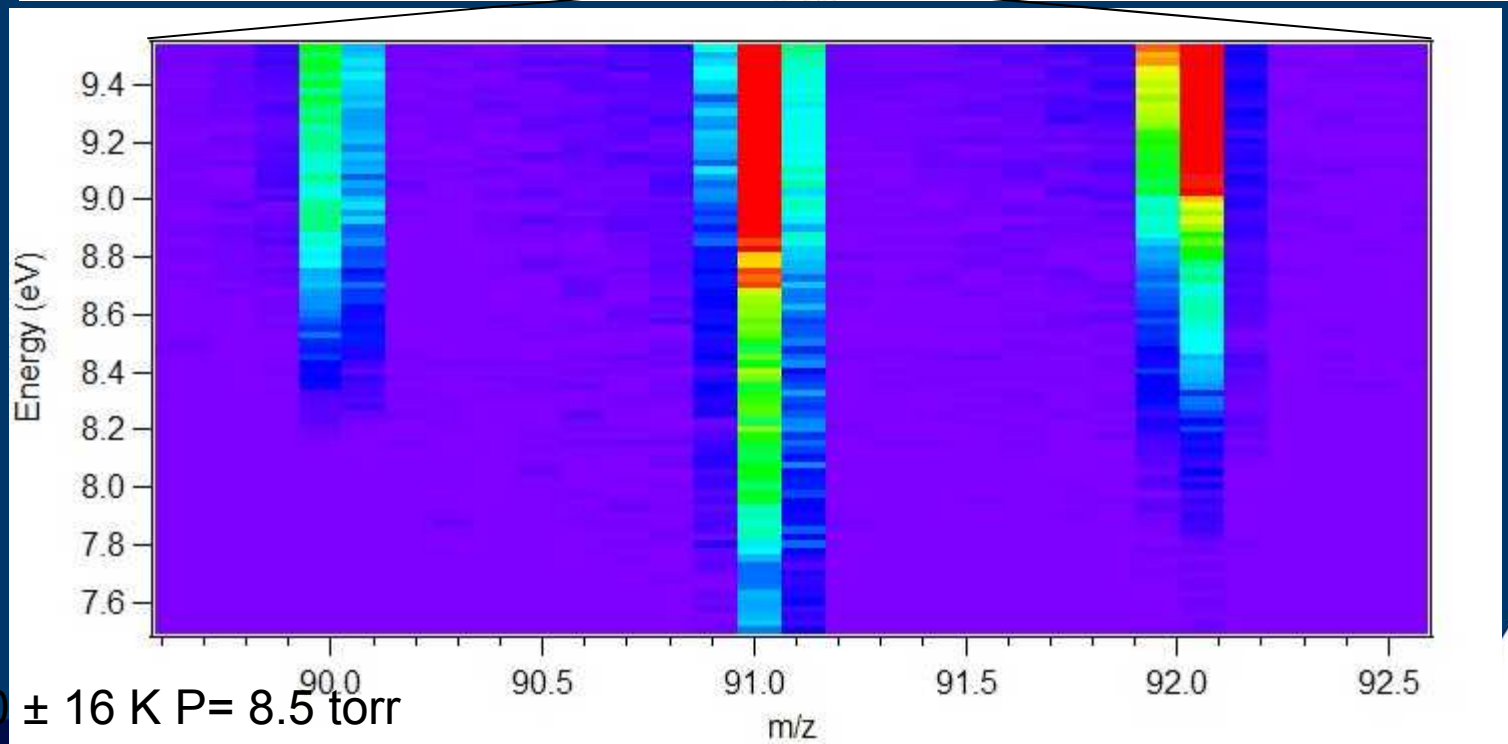




T= 990 ± 16 K P= 8.5 torr



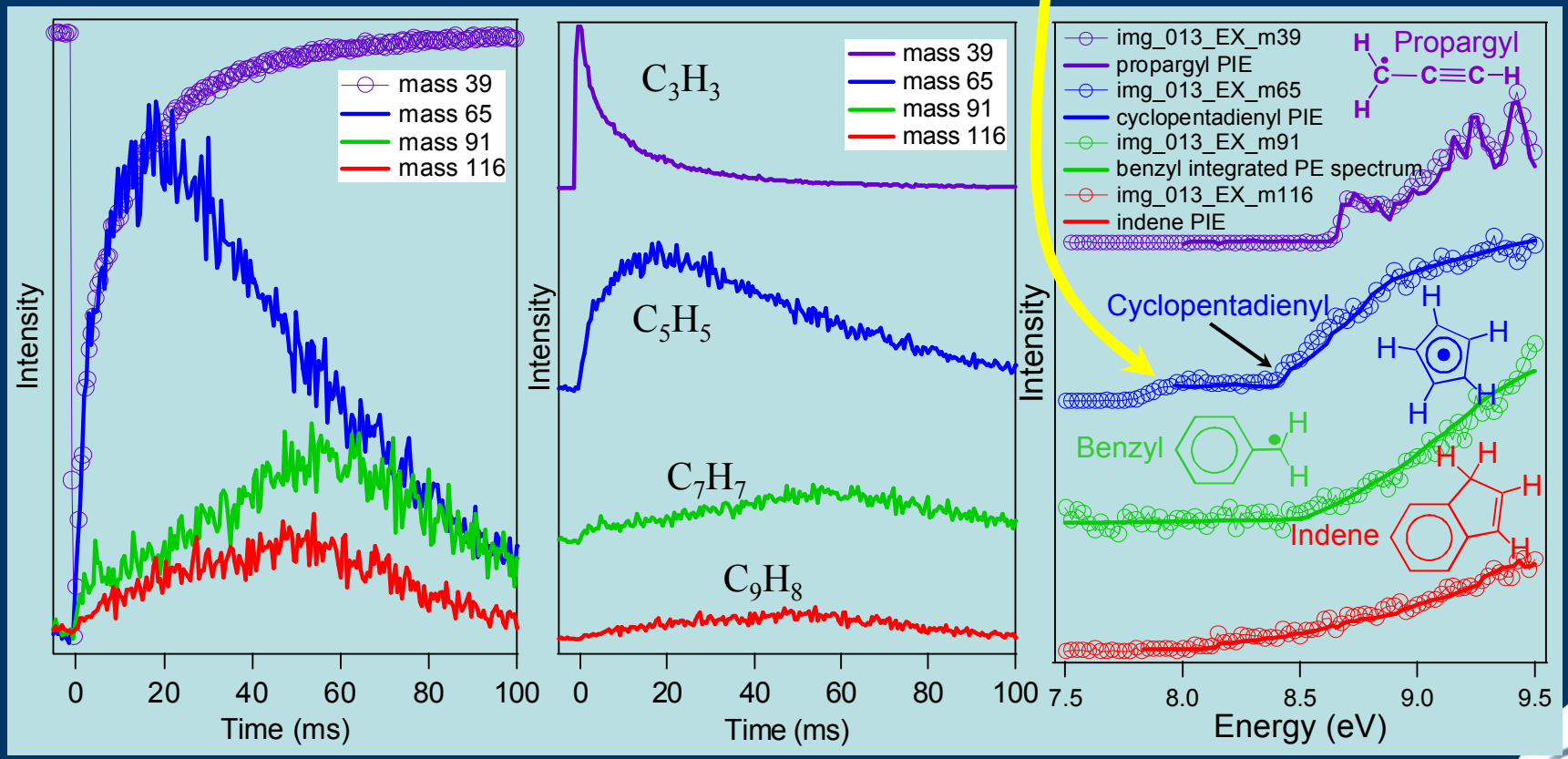


T= 990 ± 16 K P= 8.5 torr

$C_3H_3 + C_2H_2$ at 800 K

$C_3H_3 + C_2H_2 \rightarrow C_5H_5 + C_2H_2 \rightarrow C_7H_7$

T = 800 ± 5 K
P = 7.4 torr



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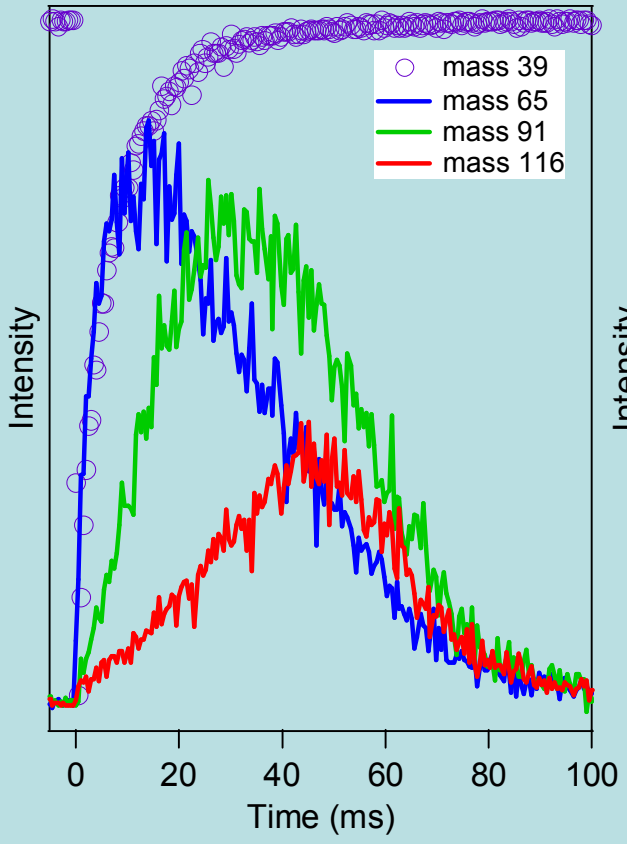
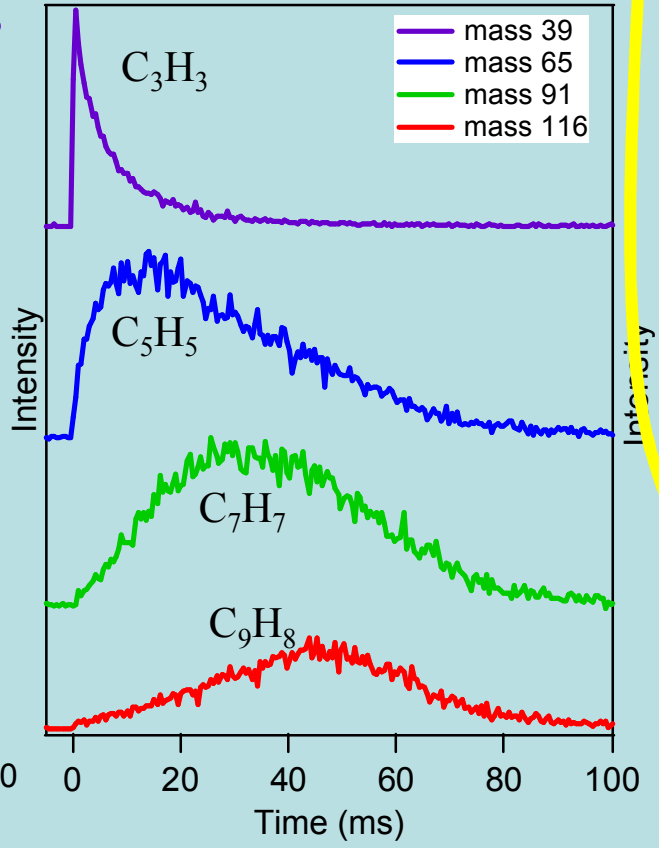
$C_3H_3 + C_2H_2$ at 990 K

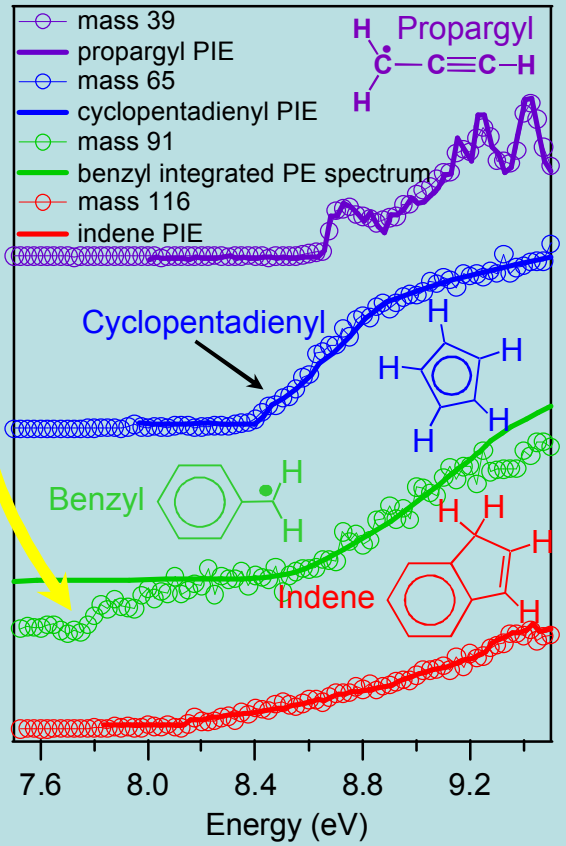
$$C_3H_3 + C_2H_2 \rightarrow C_5H_5 + C_2H_2 \rightarrow C_7H_7 + C_2H_2 \rightarrow C_9H_8 + H$$

T = 990 ± 16 K
P = 8.5 torr

linear C_7H_7 isomer(s)



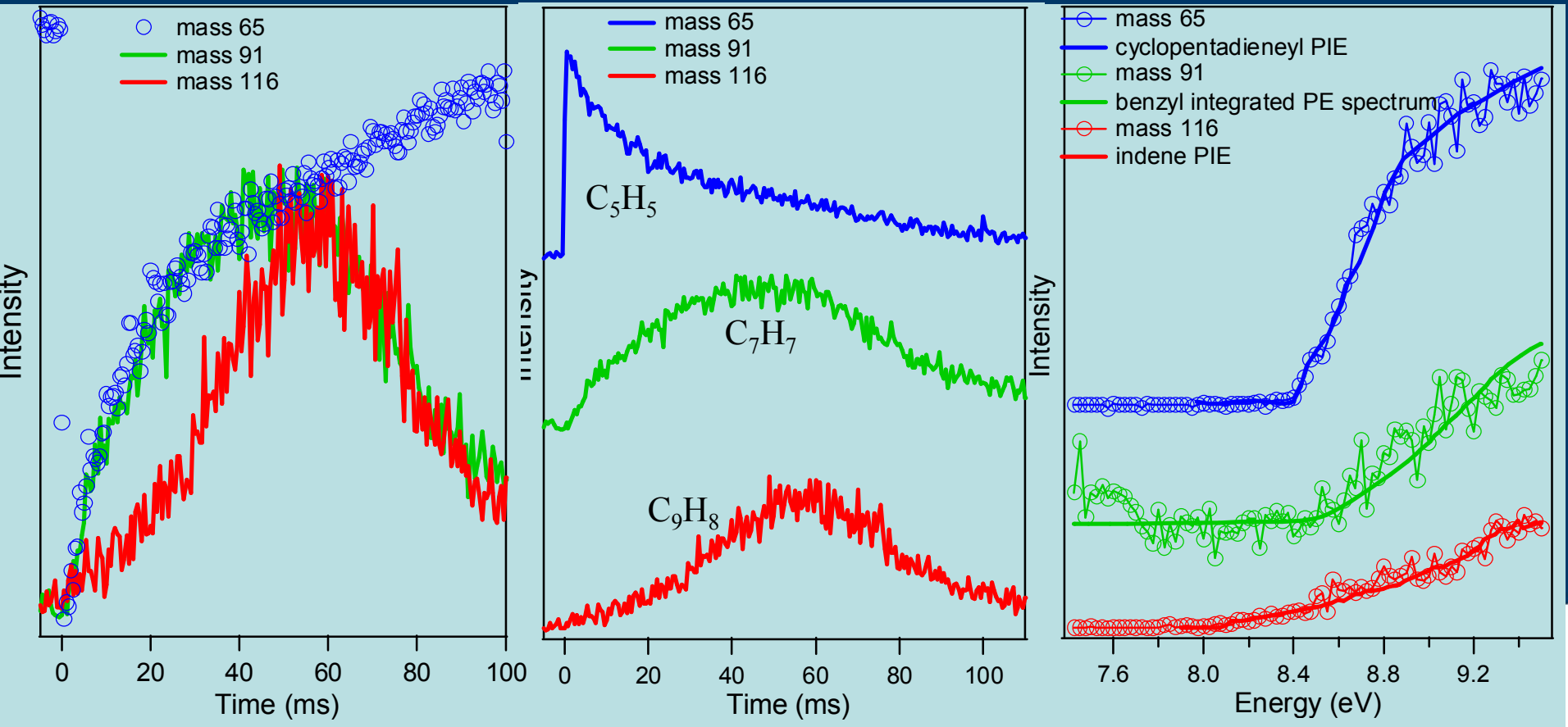




$C_5H_5 + C_2H_2$ at 990 K

$C_3H_3 + C_2H_2 \rightarrow C_5H_5 + C_2H_2 \rightarrow C_7H_7 + C_2H_2 \rightarrow C_9H_8 + H$

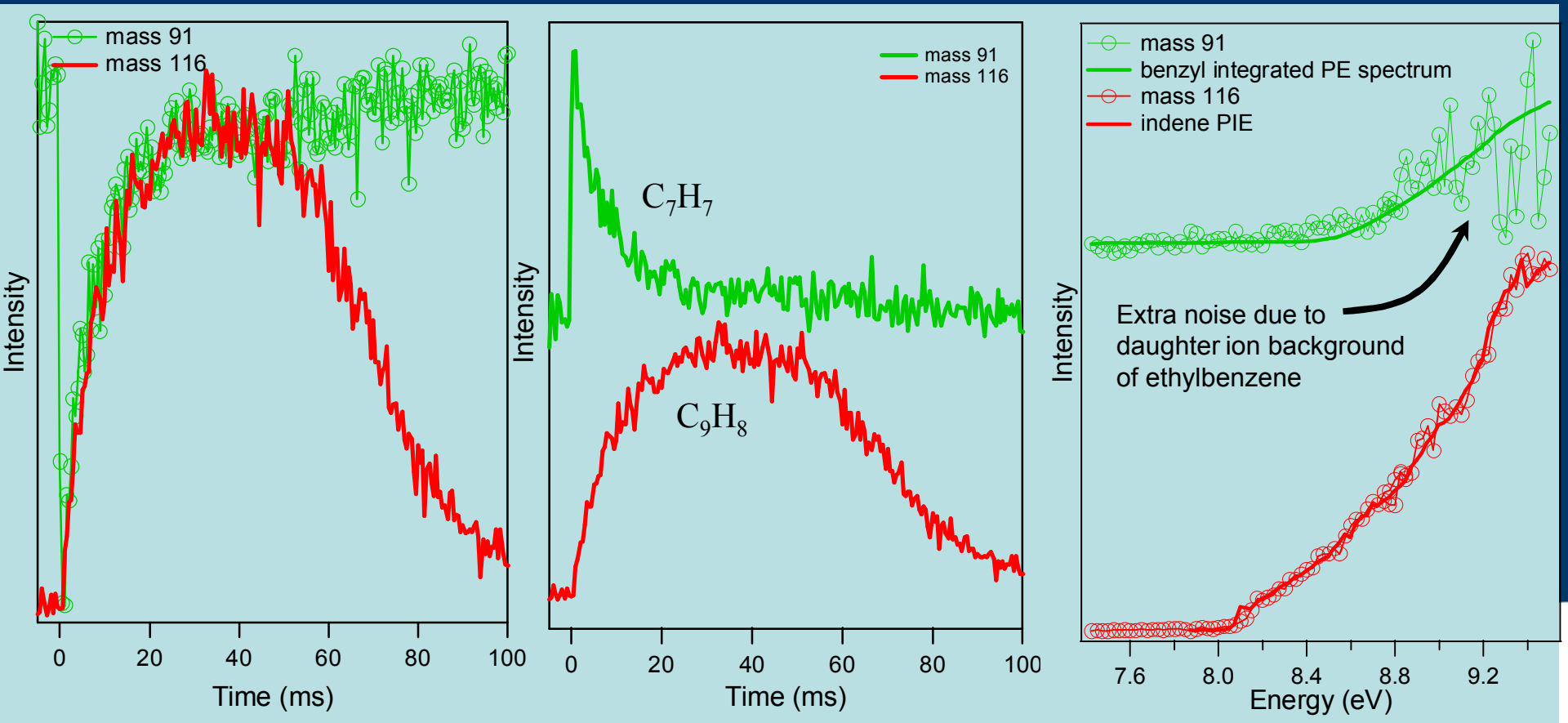
T = 920 ± 40 K
P = 8.0 torr



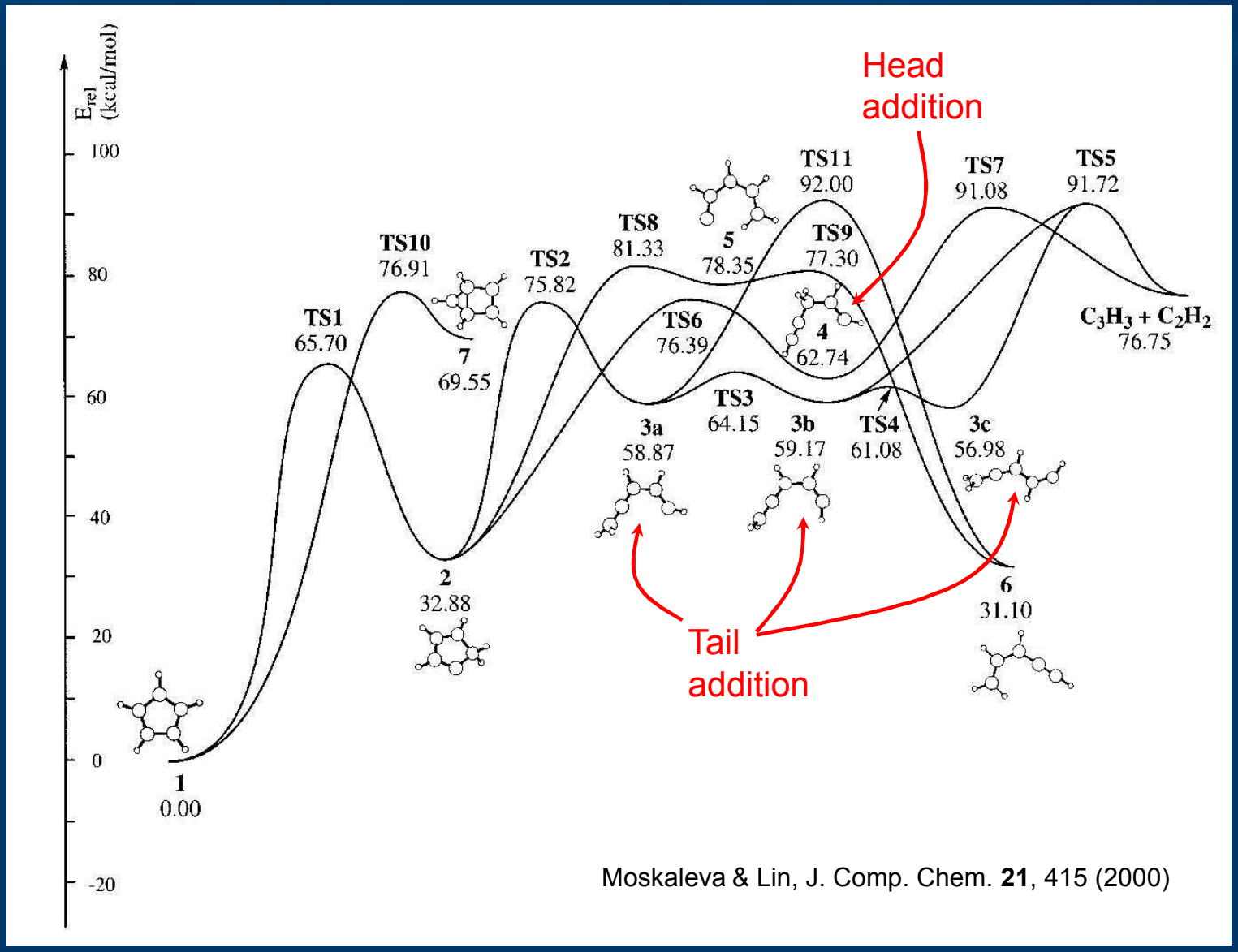
$C_7H_7 + C_2H_2$ at 990 K

$C_3H_3 + C_2H_2 \rightarrow C_5H_5 + C_2H_2 \rightarrow C_7H_7 + C_2H_2 \rightarrow C_9H_8 + H$

T = 900 ± 30 K
P = 8.0 torr

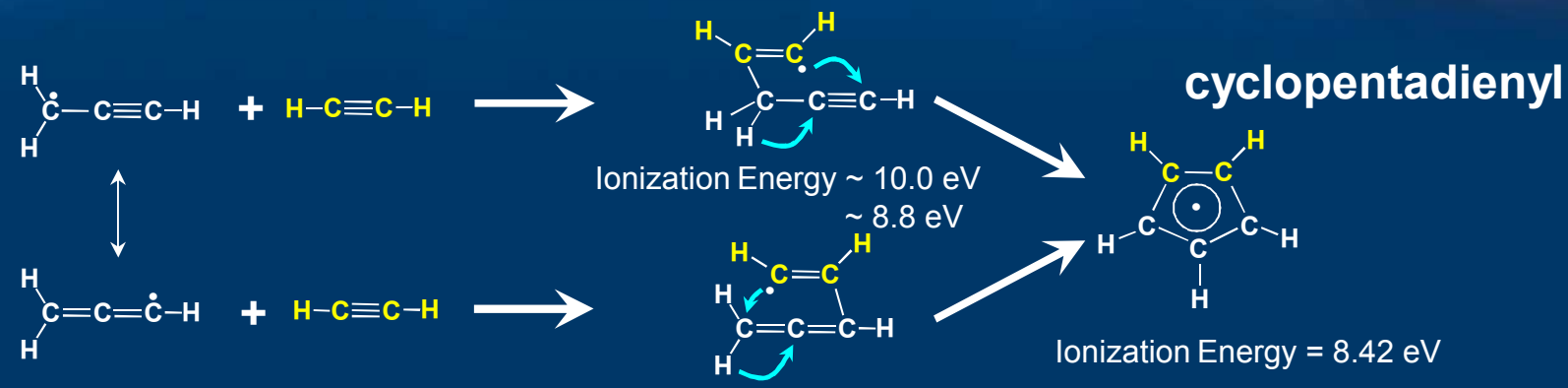


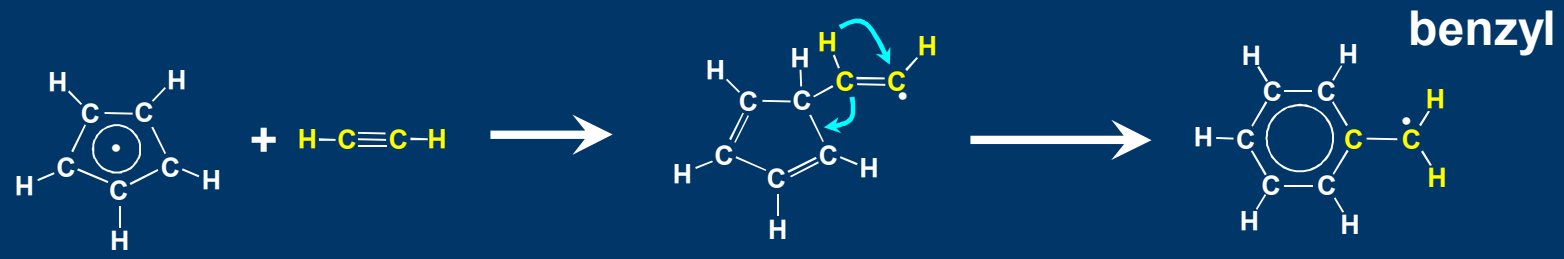
C_5H_5 Potential Energy Surface

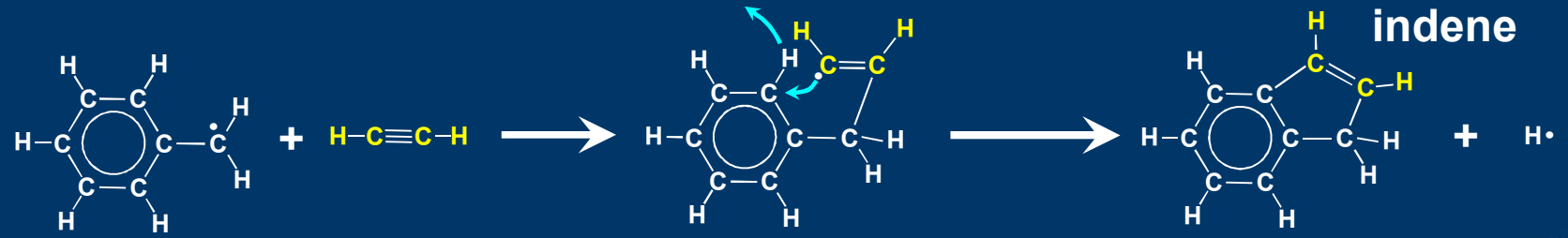


Moskaleva & Lin, J. Comp. Chem. **21**, 415 (2000)

$C_3H_3 + C_2H_2$ Reaction Pathways





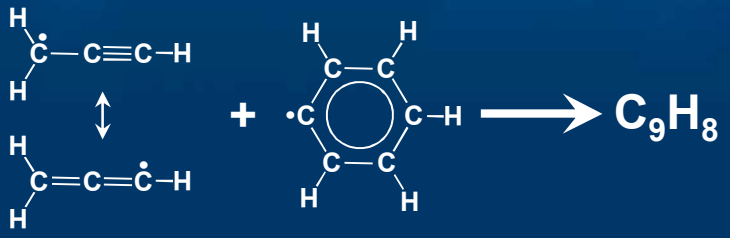


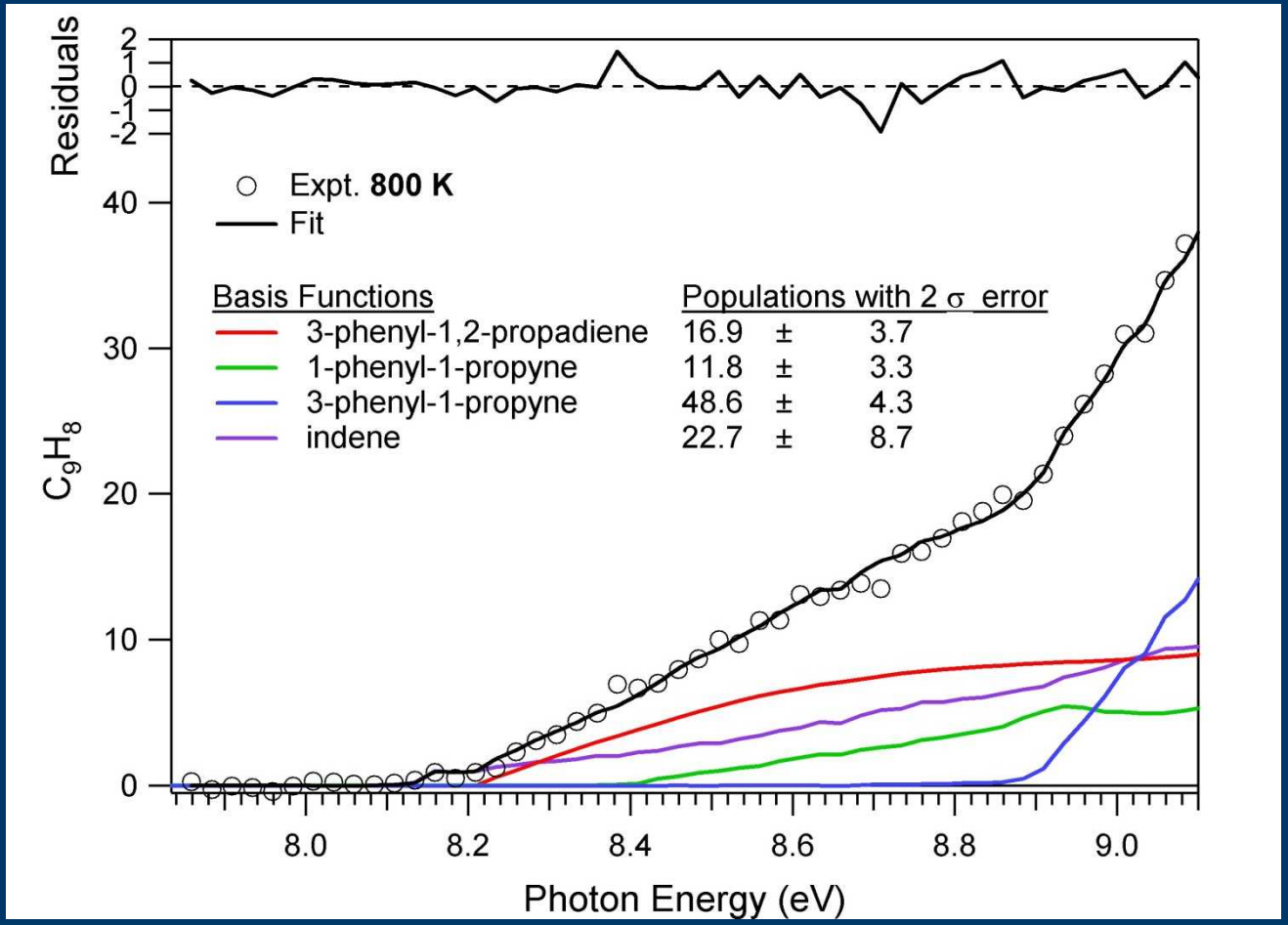
Conclusions

- Multiplexed Photoionization Mass Spectrometry is a powerful tool to unravel pathway-specific chemical mechanisms.
- Single reactions and reaction sequences can be studied in unprecedented detail.
- $C_6H_5 + C_3H_3$ shows substantial onset of isomerization between 300 – 1000 K, forming 2-ring compounds.
- $C_3H_3 + C_2H_2$ reaction demonstrates a molecular weight growth sequence with acyclic and aromatic intermediates.

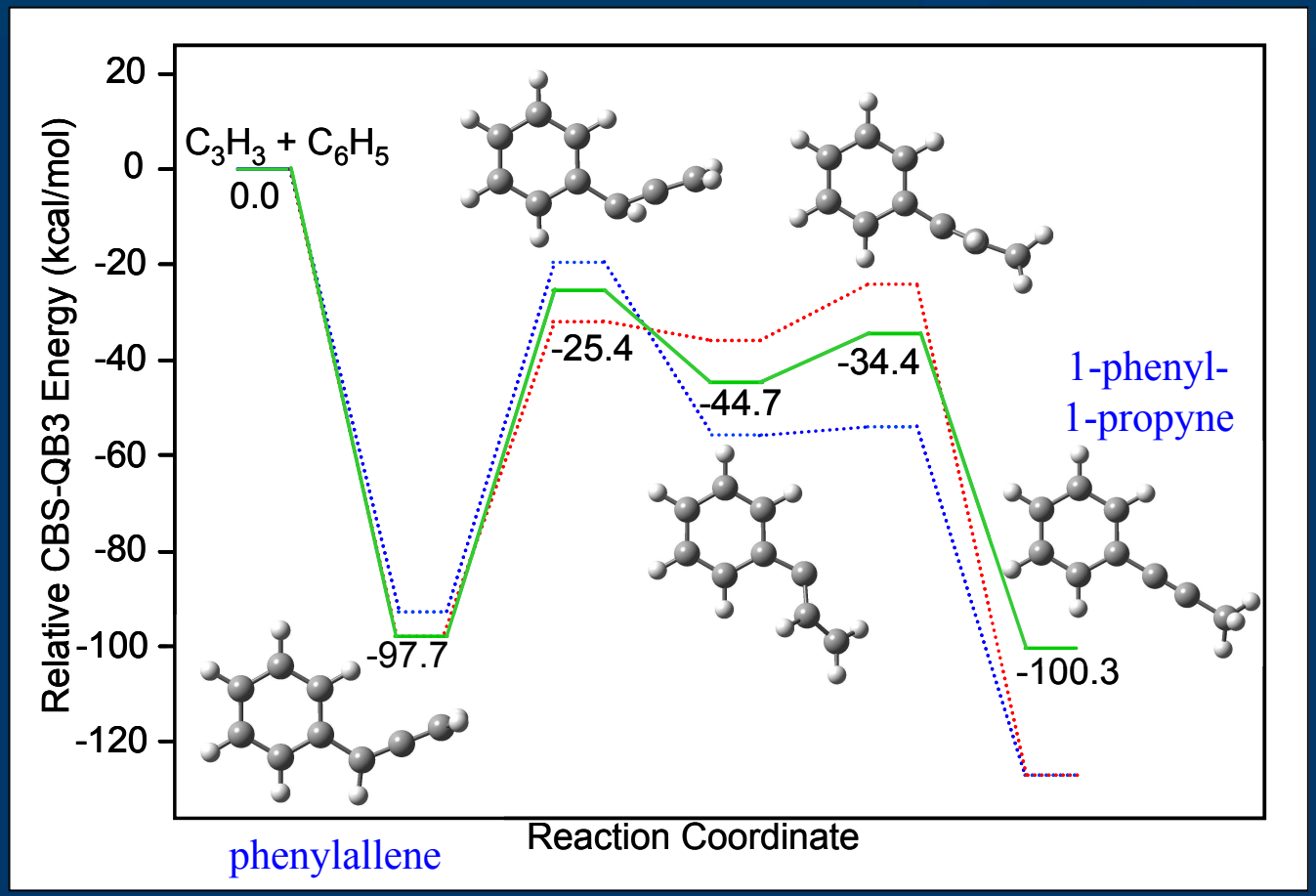
We have sensitive and selective probes of potentially important molecular weight growth reactions. Determining the relevance of any particular sequence requires comparisons with combustion models.

Propargyl + Phenyl (800K)



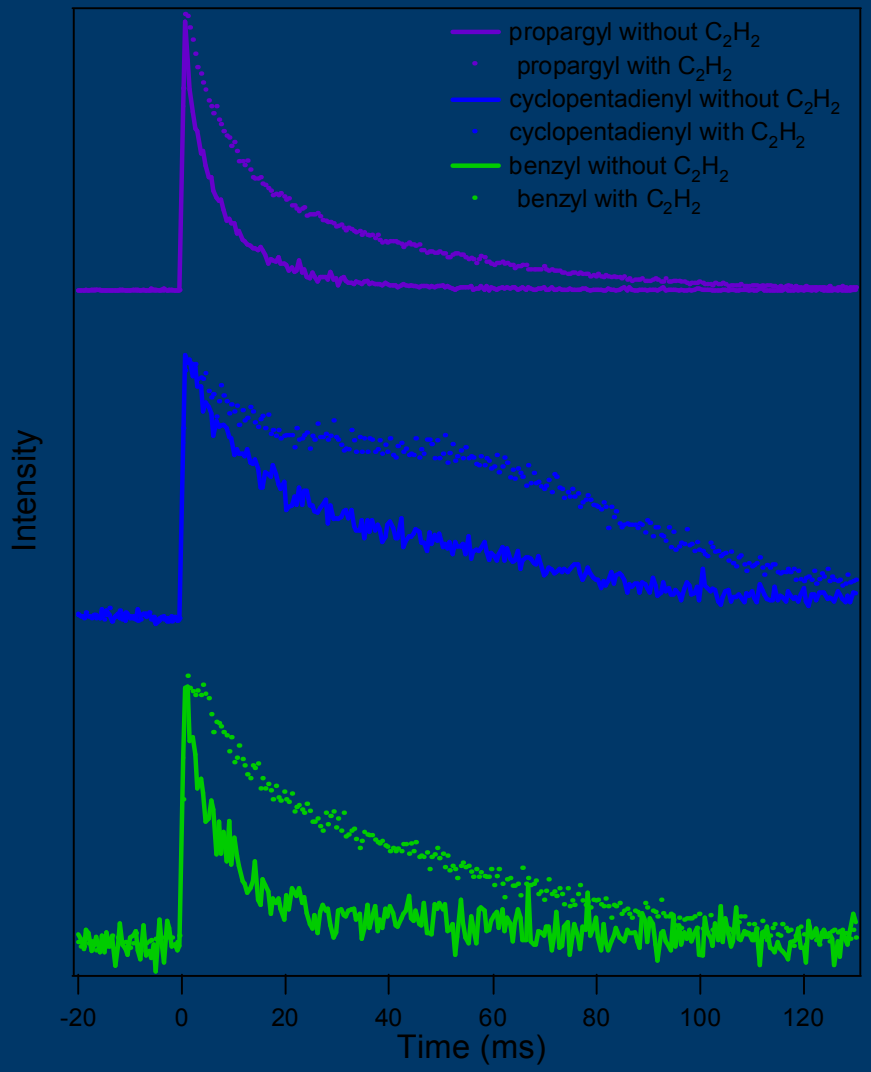


C_3H_3 tail addition to phenyl



H atom-assisted isomerization: V. V. Kislov and A. M. Mebel, *J. Phys. Chem. A* **111**, 3922 (2007).

Comparison of precursor radical time profiles with and without acetylene

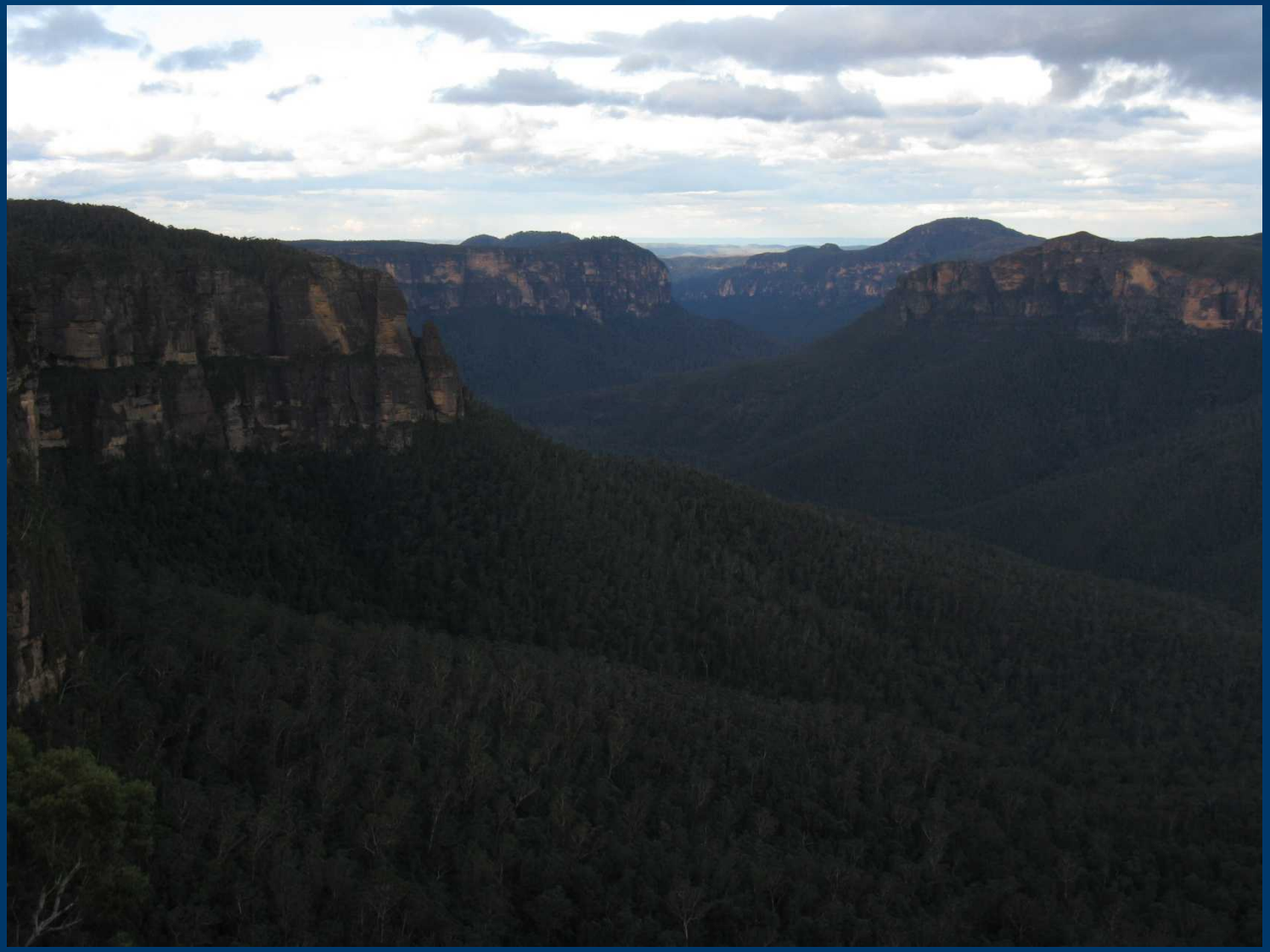


Still not sure of source of time profile of C5H5 without C2H2….I am looking more closely at C5H5 self reaction—I will get back to you.

Mass Spectrometer Upgrade

- Present sector mass spectrometer
  - (+) 100% duty cycle
  - (-) low mass resolution ($m/\Delta m$ ~ 150)
  - (-) cannot detect H or D
  - (-) calibration changes with time
- Time-of-flight
  - (-) < 100% duty cycle (usually much less)
  - (-) mismatch of photons (quasi-cw) with mass spec (pulsed)
  - (+) much improved resolution ($m/\Delta m$ > 1000)
  - (+) mass range unlimited (can see H and D)
  - (+) mass calibration should be more robust

Why are the Blue Mountains Blue?



Ozone formation in the troposphere

- In urban environments, a primary source of ozone is

$$\bullet OH + RH \rightarrow R\bullet + H_2O$$

$$R\bullet + \bullet O_2 \rightarrow ROO\bullet$$

$$ROO\bullet + NO\bullet \rightarrow RO\bullet + NO_2\bullet$$

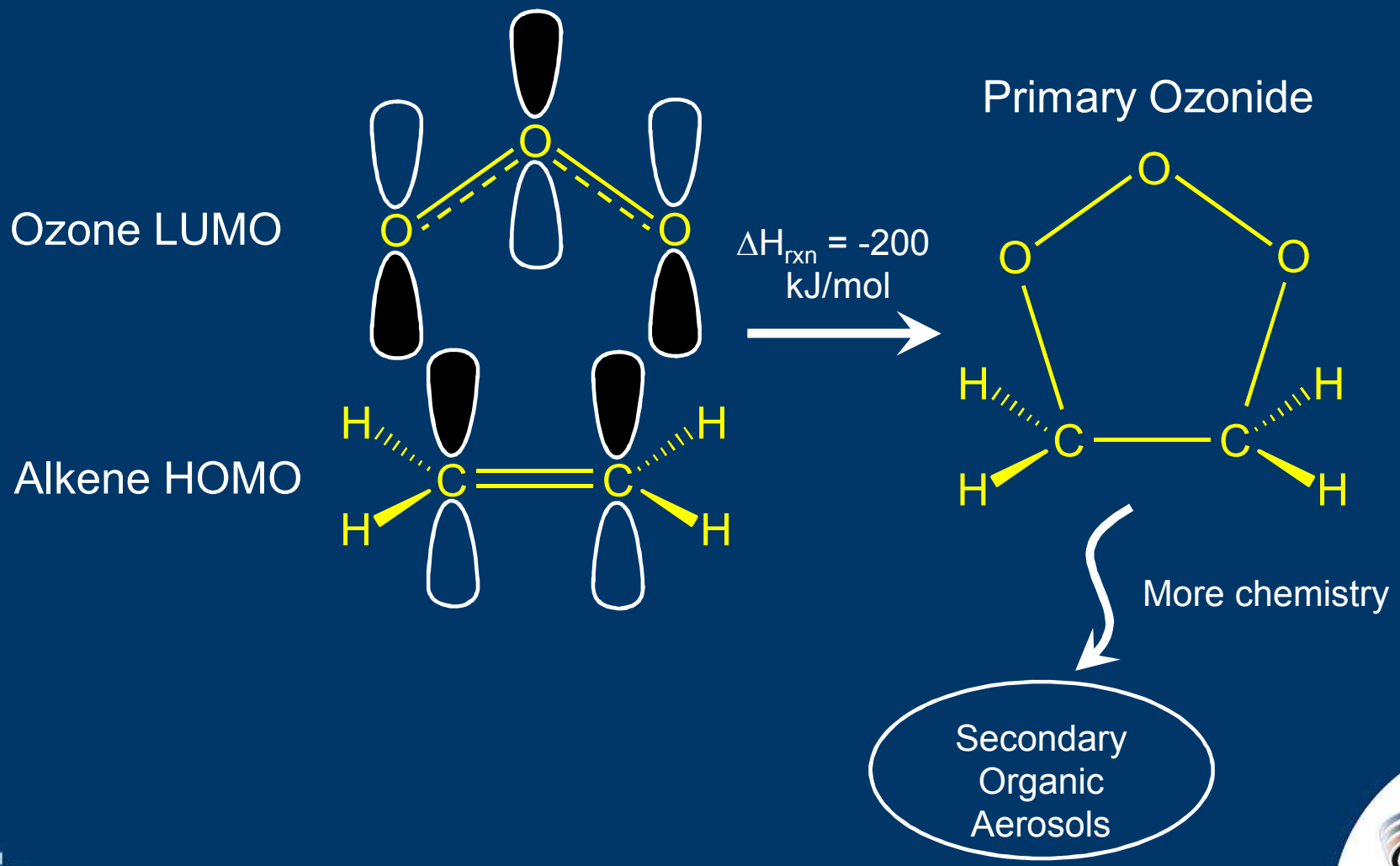
$$NO_2\bullet + \text{sunlight} \rightarrow \bullet O(^3P) + NO\bullet$$

$$\bullet O(^3P) + \bullet O_2\ (+ N_2) \rightarrow O_3\ (^1A_1)\ (+ N_2)$$

Alkenes in the troposphere

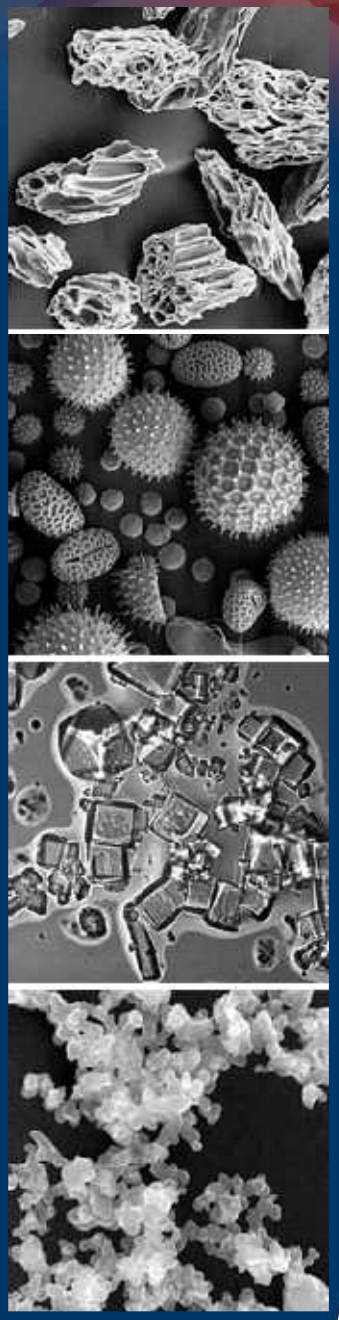
- Significant biogenic and man-made sources of alkenes
  - Plants (trees & shrubs) emit 5 x 10^{11} kg / year of isoprene
  - Additional biogenic production of monoterpenes / sesquiterpenes
  - Alkenes from industrial emissions
  - Alkenes ~ 15% of non-methane hydrocarbons

Ozonolysis of Alkenes



Atmospheric aerosols

- Primary aerosols
  - Injected directly to the atmosphere
    - Sea spray
    - Dust
- Secondary aerosols
  - Formed *in* the atmsophere
    - Physical (condensation via cooling)
    - Chemical (reactions)
- Aerosols cool the earth
  - Direct reflection of sunlight
  - Cloud condensation nuclei
- Detrimental to human health
- Give the Blue Mountains their name



Volcanic ash

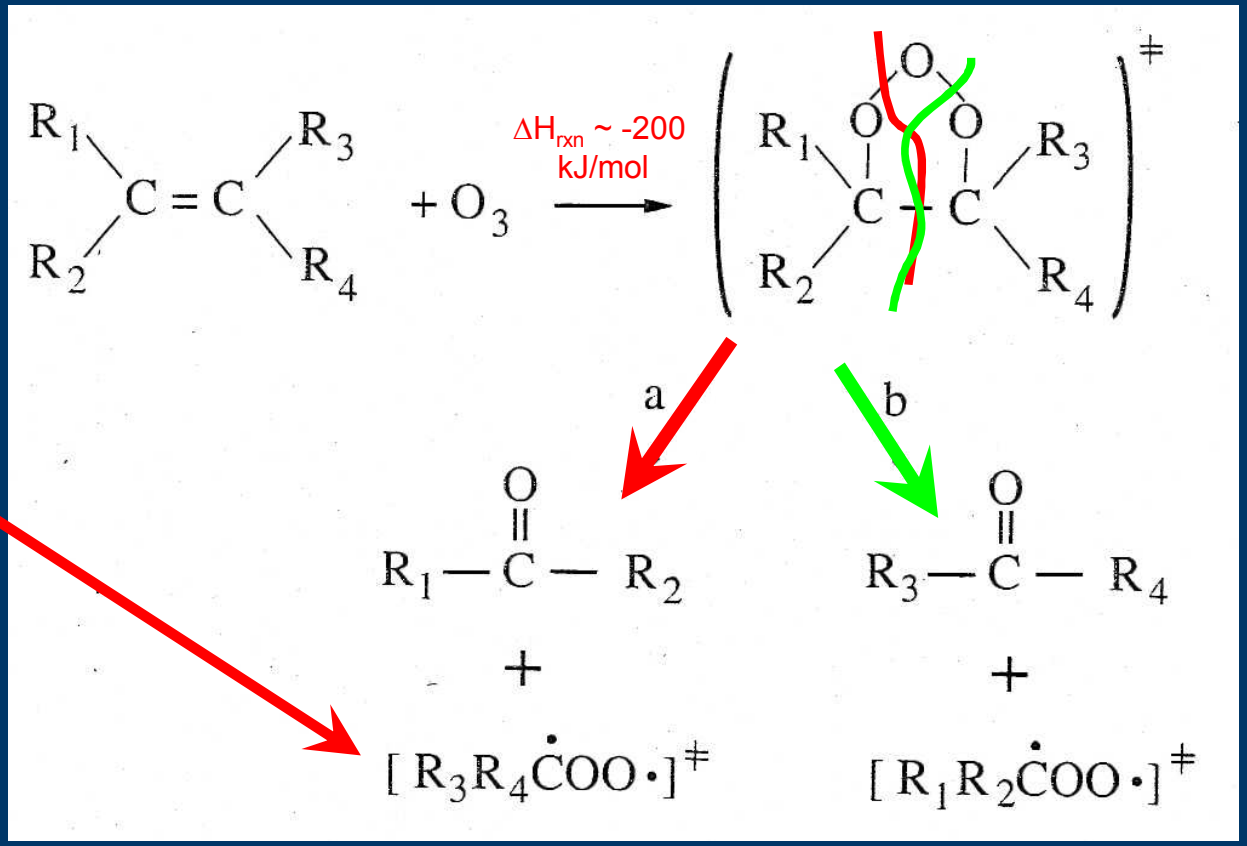
Pollen

Sea Salt

Soot

The Criegee intermediate mechanism

- In 1949 Rudolf Criegee proposed the following mechanism



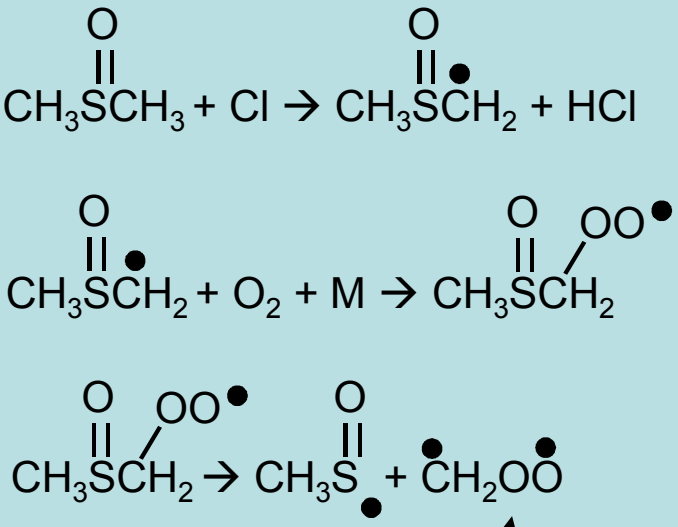
Can we observe the Criegee intermediate?

- David Johnson & George Martson, Chemical Society Reviews, **37**, 699 (2008)

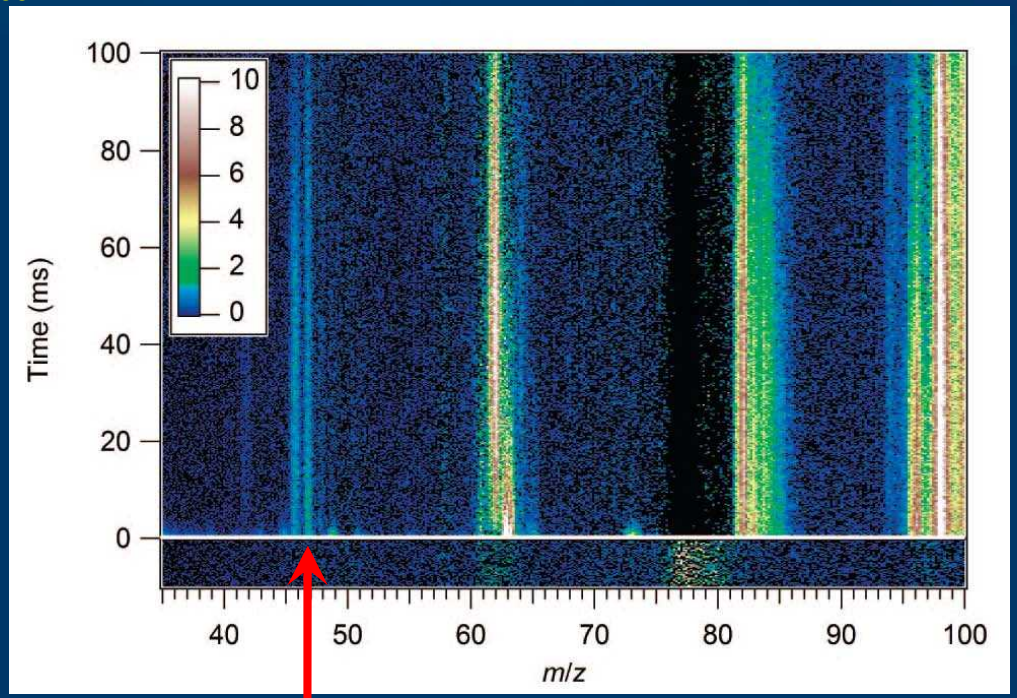
> "…it is worth noting that chemical species attributed as being Criegee intermediates have not, to date, been observed directly in the gas phase, despite their intermediacy in ozone-alkene reactions first being postulated by Criegee in 1949."

Criegee intermediates from DMSO oxidation

Dimethyl Sulfoxide (DMSO) oxidation may form CH_2OO (Asatryan and Bozzelli, PCCP 10, 1769 (2008))



Dioxirane is 25 kcal/mol more stable than CH_2OO



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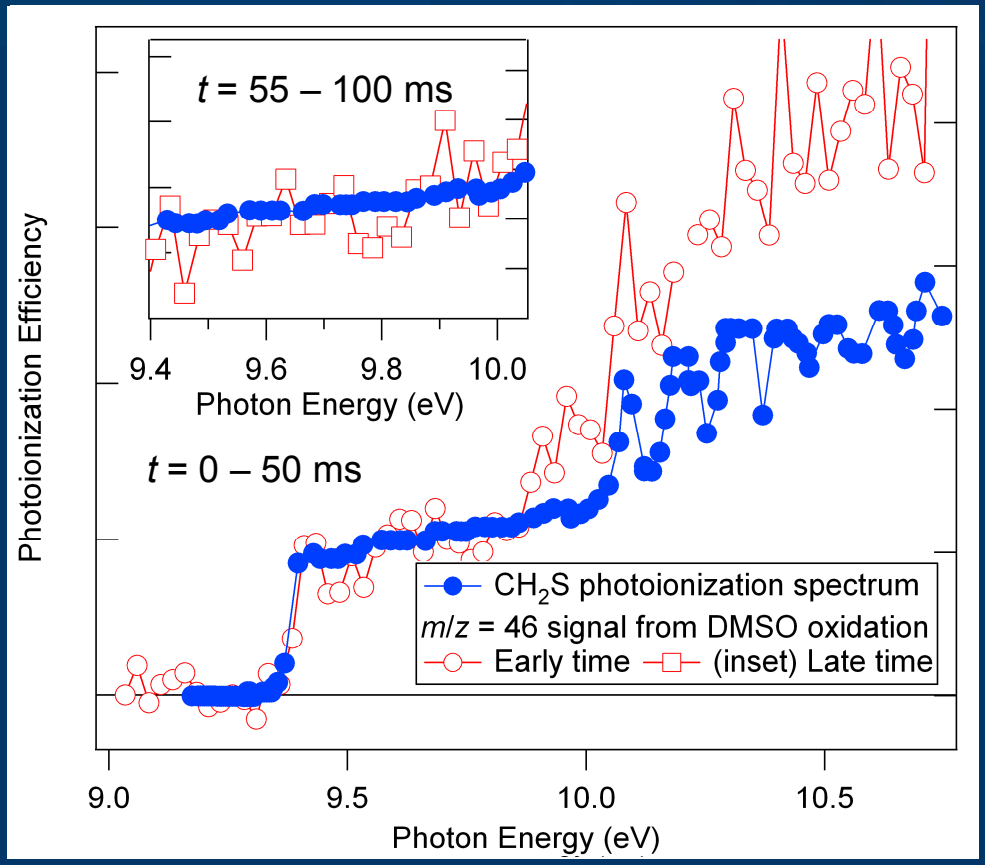
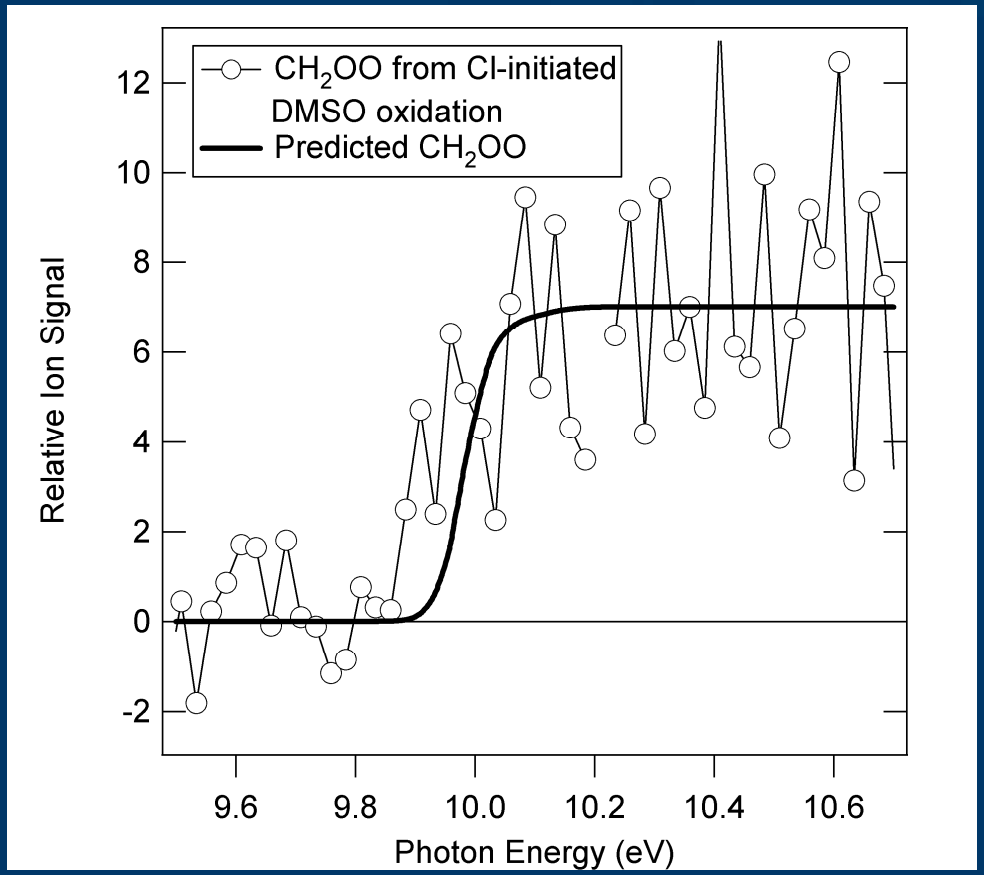
Photoionization spectrum identifies CH_2OO

- New species has IE ~ 9.9 eV
  - HCOOH (IE = 11.33 eV)
  - C_2H_5OH (IE = 10.48 eV)
  - CH_3OCH_3 (IE = 10.025 eV)
- CH_2OO absent after 50 ms

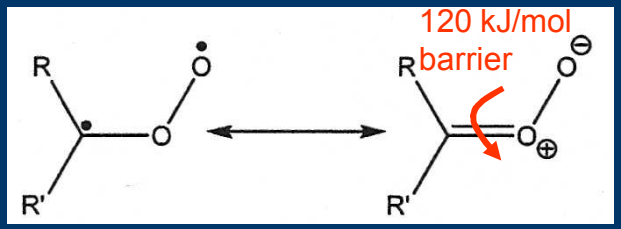


Comparison with Franck-Condon Factors

- CCSD(T)/CBS IE = 9.98 eV
- Ab initio photoionization spectrum agrees in both shape and position



Biradical "Zwitterion"

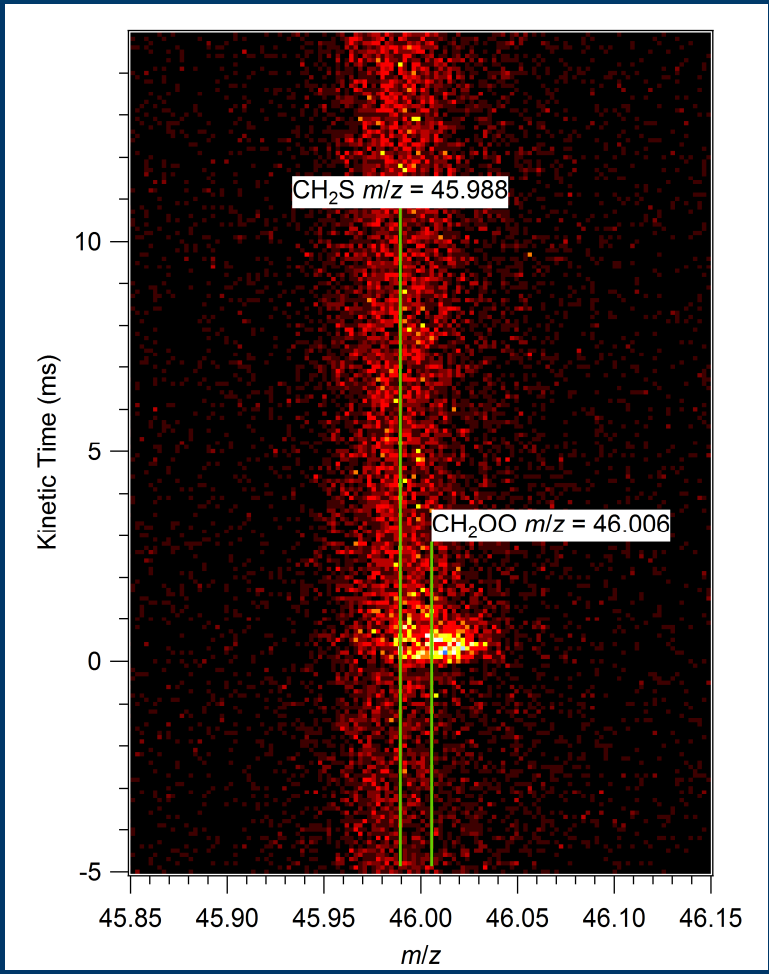


Non-vertical (broad)

Vertical (sharp)

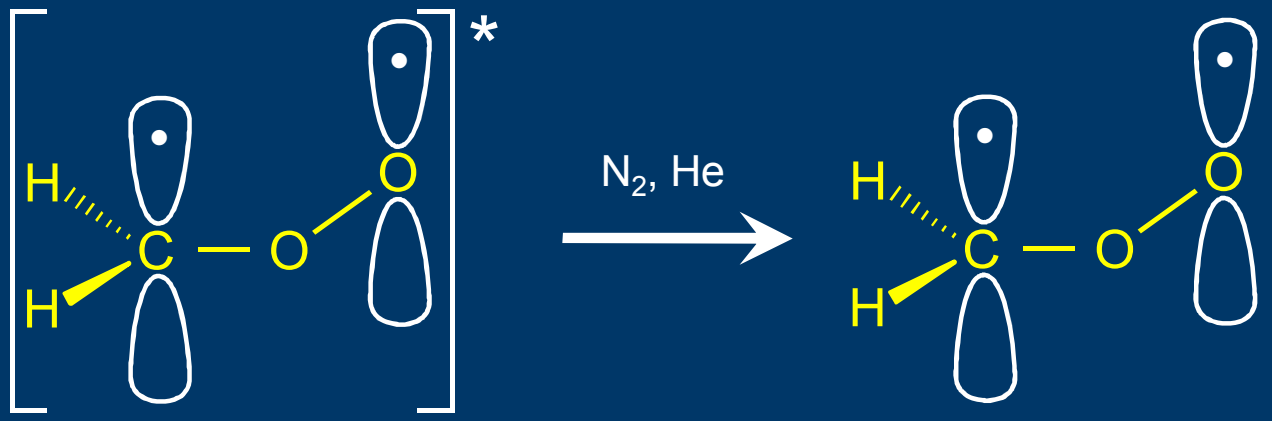
Higher resolution with time of flight mass spectrometry

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

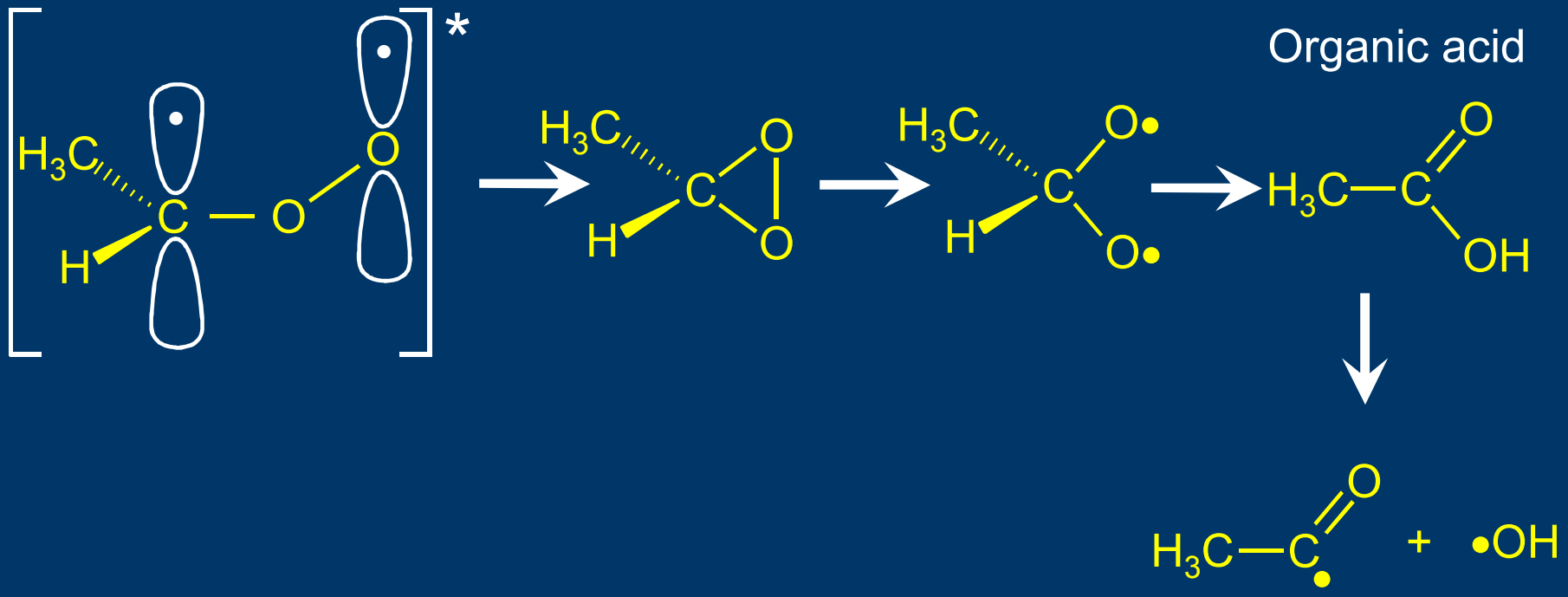


Reactions of Criegee intermediates?

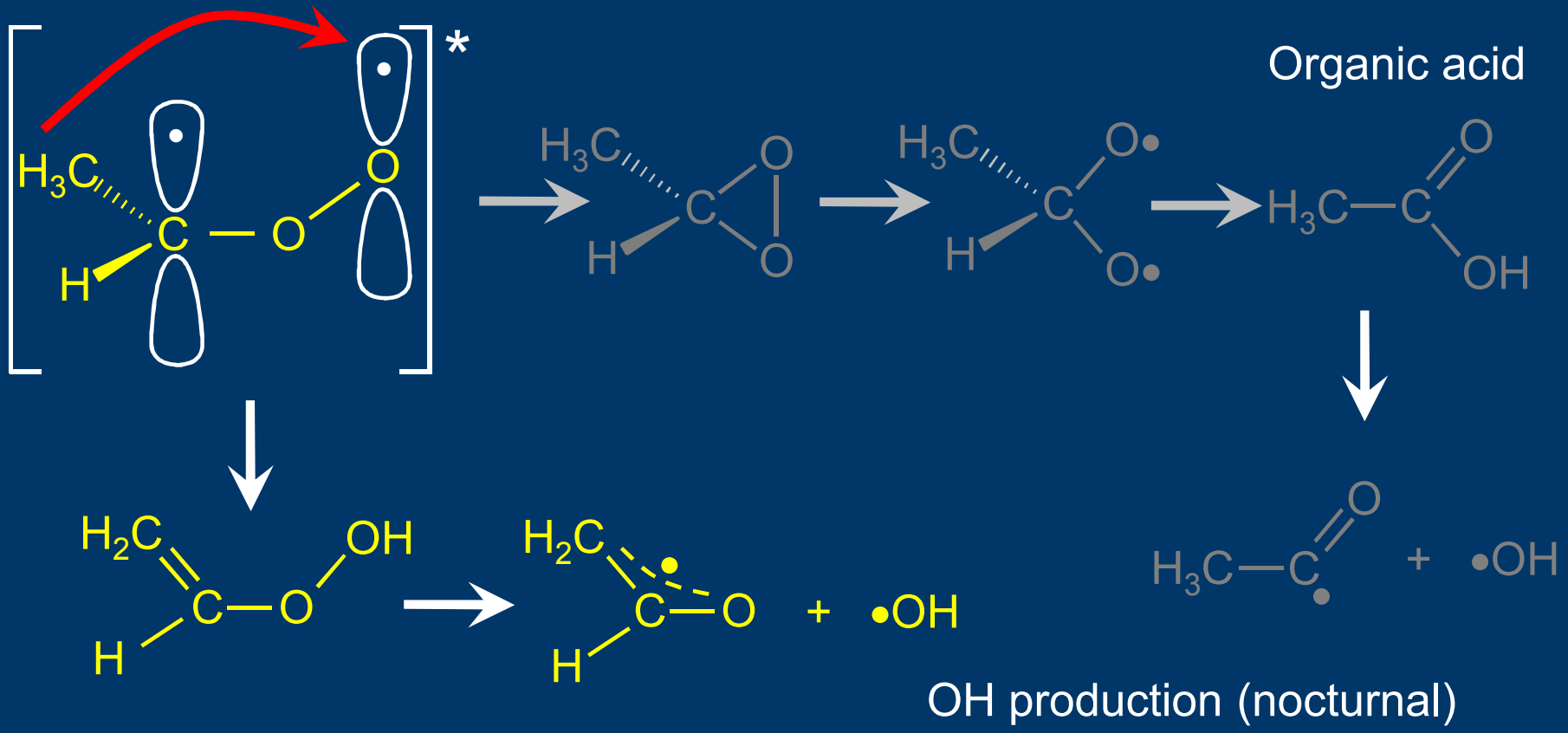
Stabilization (via collisions)



Unimolecular reactions of Criegee intermediates?



Unimolecular reactions of Criegee intermediates?



Volatility and aerosol formation

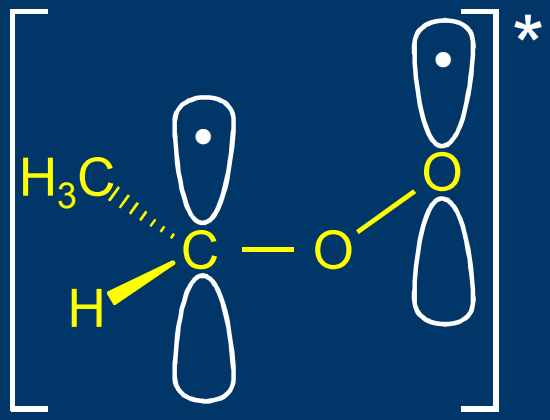
Increasing oxidation →

Species	C_2H_4	H_2CO	HCOOH
Boiling point	163 K	254 K	374 K

Decreasing volatility →

Increasing aerosol formation

Bimolecular reactions of Criegee intermediates?



+ H_2O
SO_2
NO
NO_2

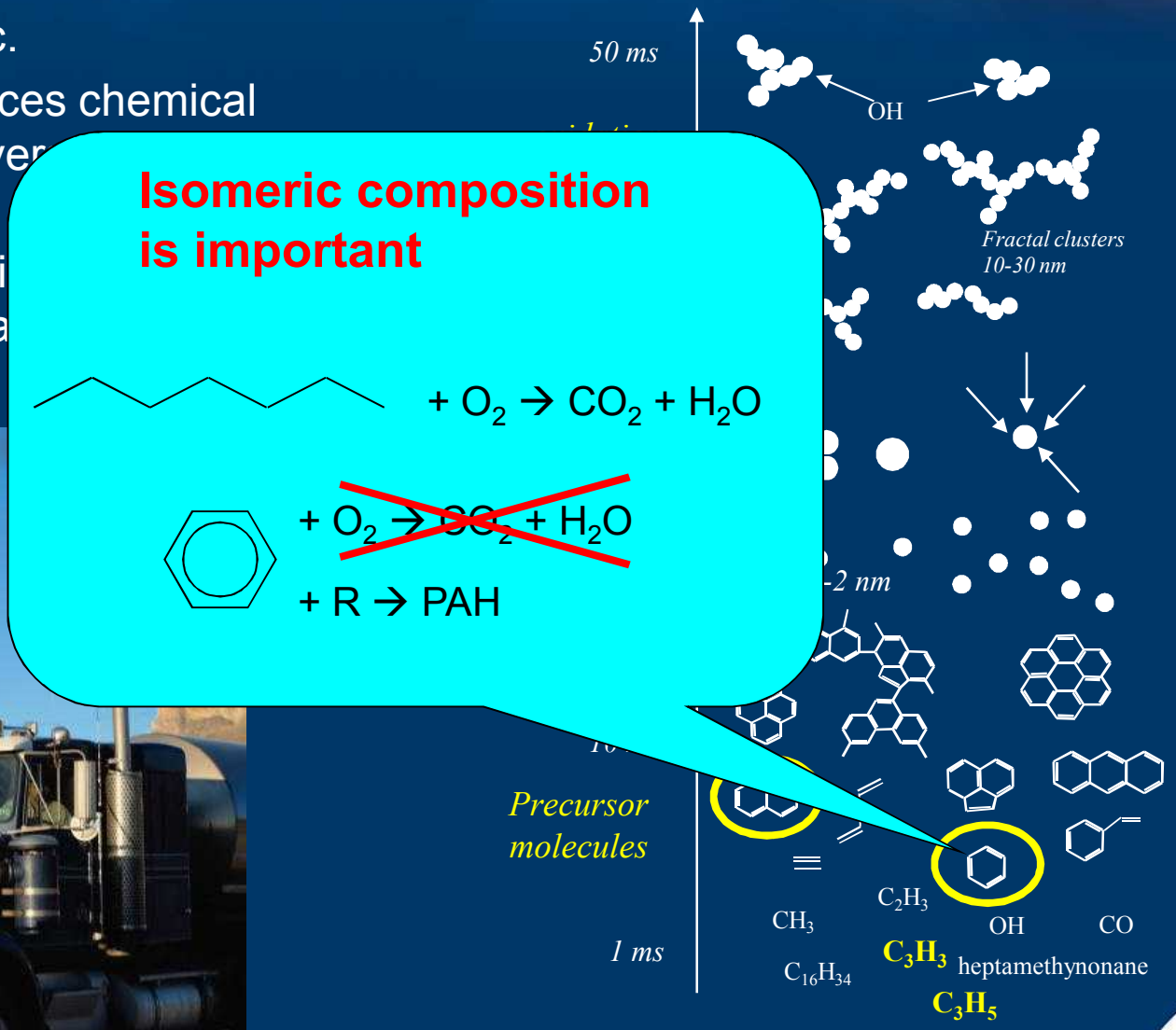
Rates ??

Products ??

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

Molecular Weight Growth Leads to Soot

- Soot is carcinogenic.
- Soot formation reduces chemical energy to work conver 30%
- Black carbon deposi accelerate global wa



Isomeric composition is important

$+ O_2 \rightarrow CO_2 + H_2O$

~~$+ O_2 \rightarrow CO_2 + H_2O$~~

$+ R \rightarrow PAH$

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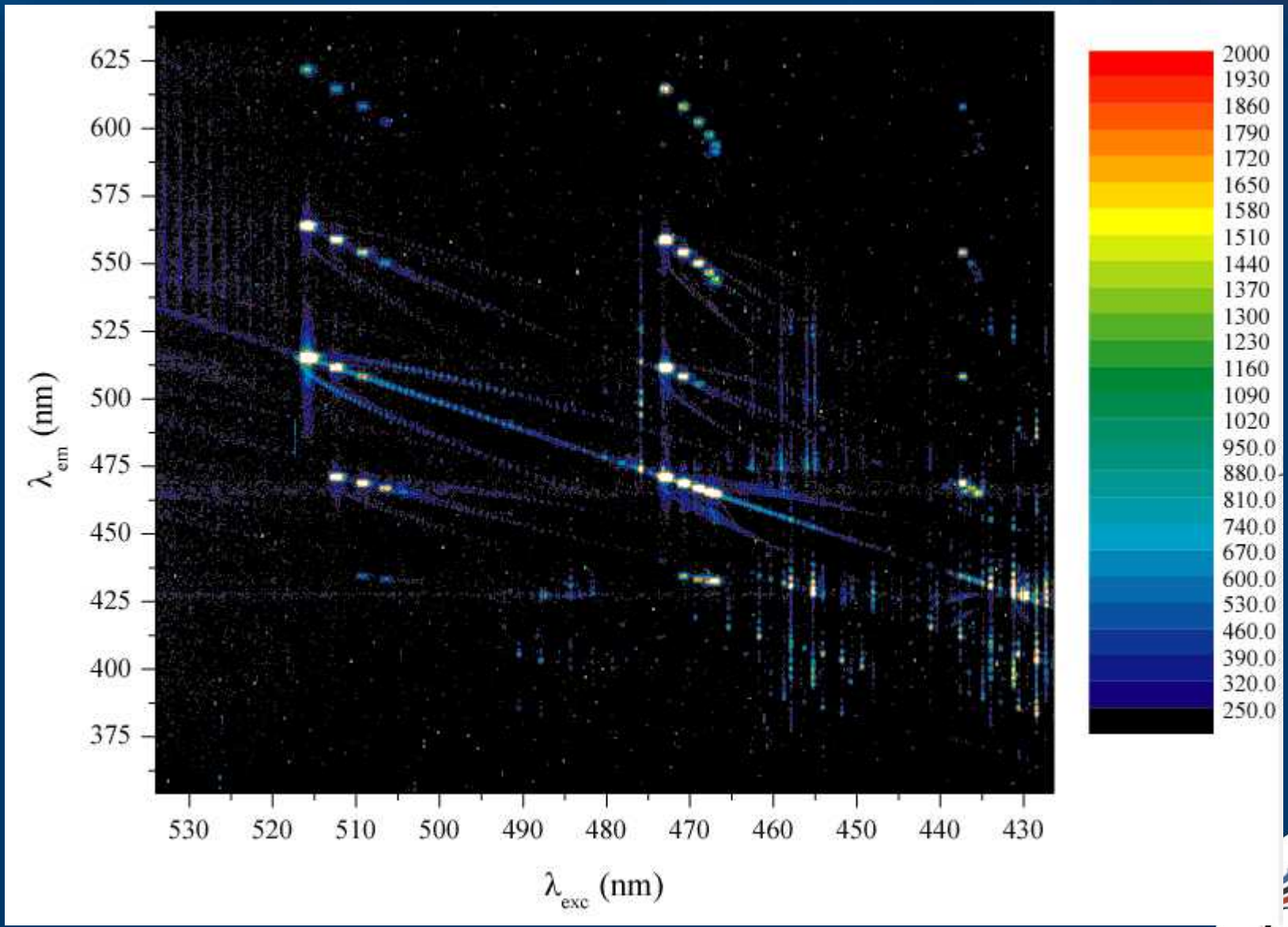
2-D laser-induced fluorescence image of a benzene discharge

T.W. Schmidt, S. H. Kable, *et al*.



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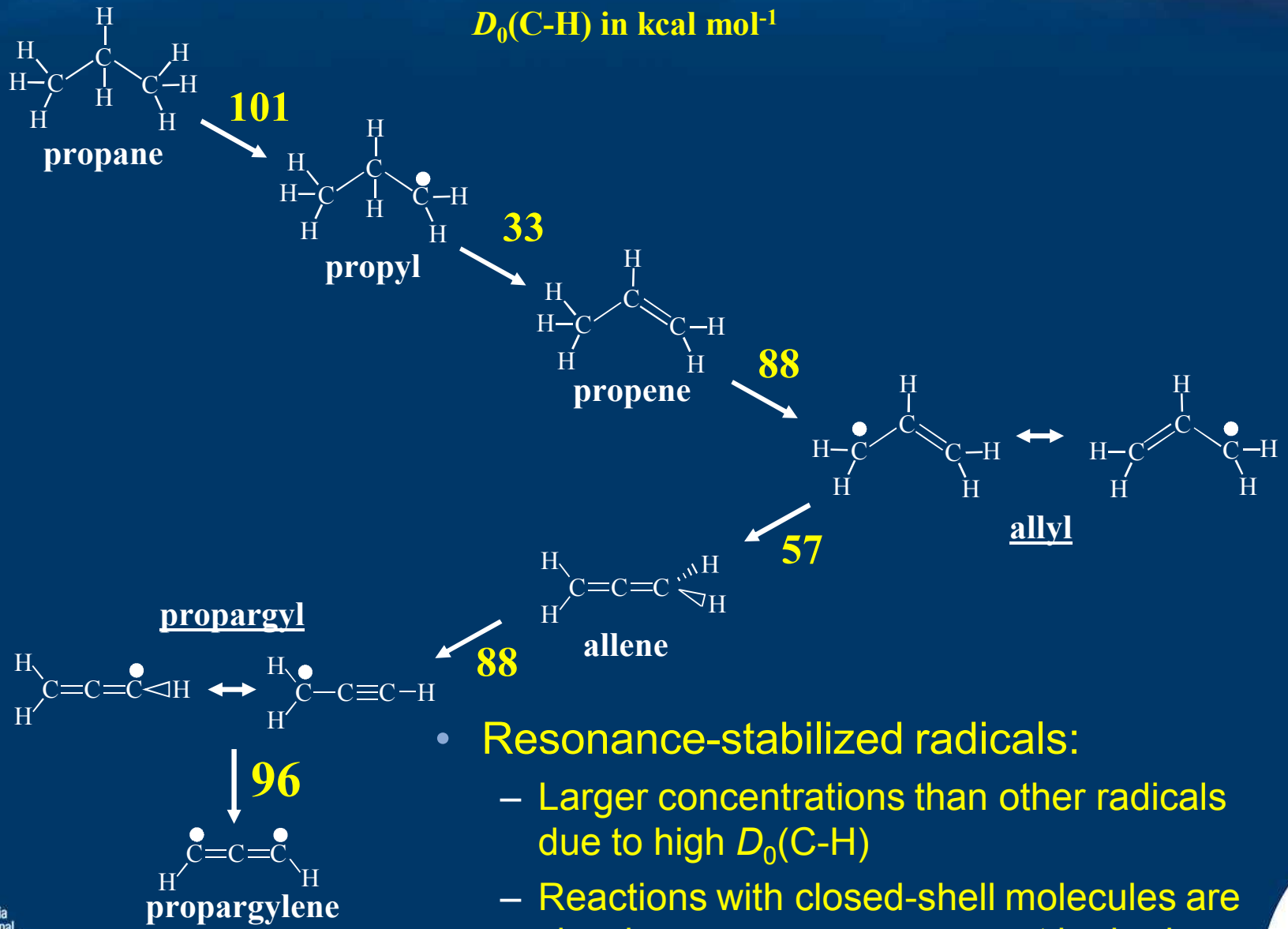
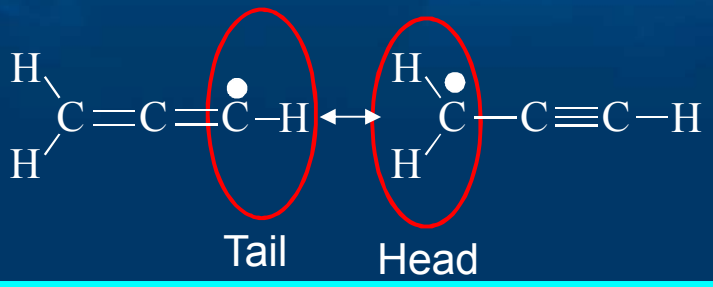
Why are Resonance-Stabilized Radicals Important?



- Resonance-stabilized radicals:
  - Larger concentrations than other radicals due to high D_0(C-H)
  - Reactions with closed-shell molecules are slow because resonance must be broken

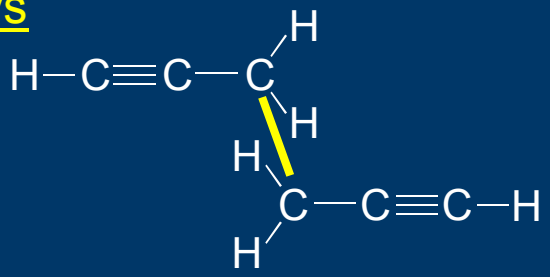
Propargyl Radical Addition Pathways



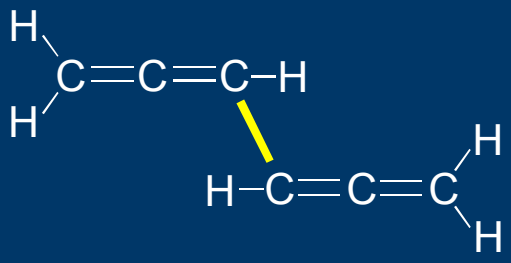
Propargyl Radical

Three addition pathways

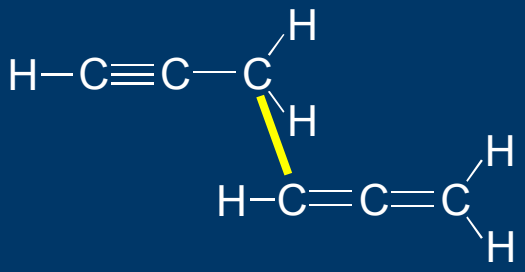
1) Head-to-Head

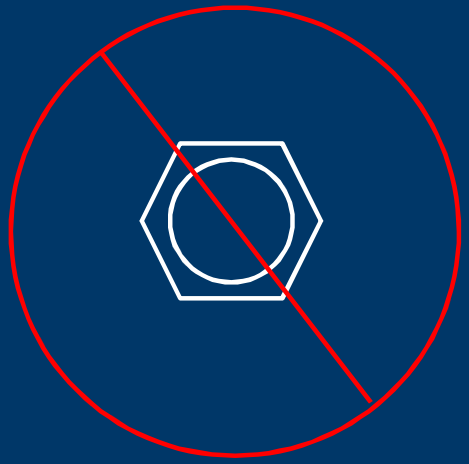


2) Tail-to-Tail



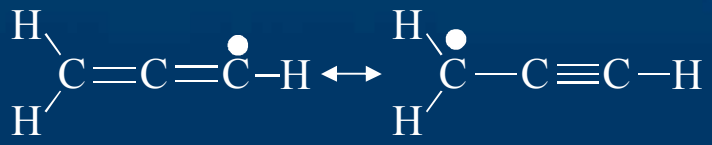
3) Head-to-Tail

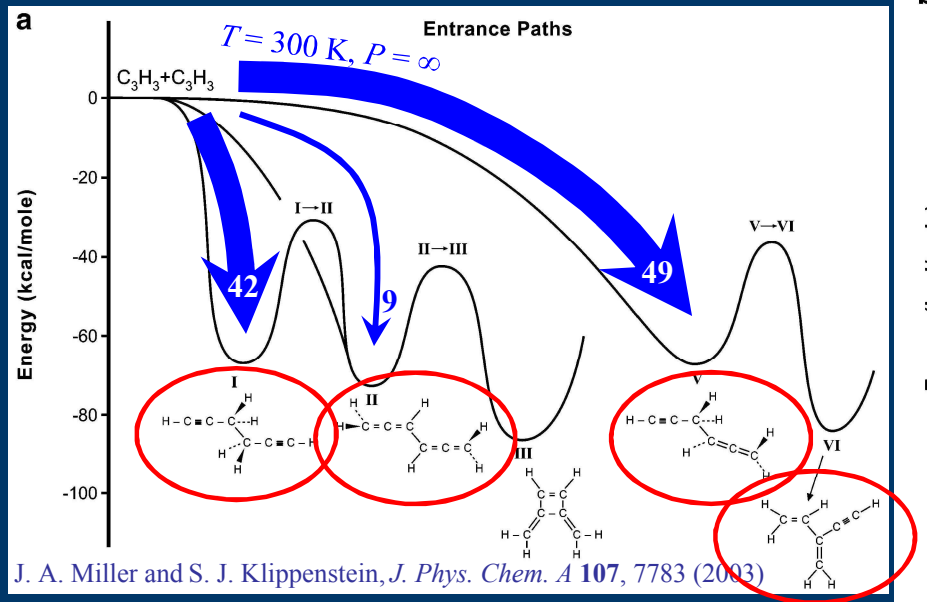




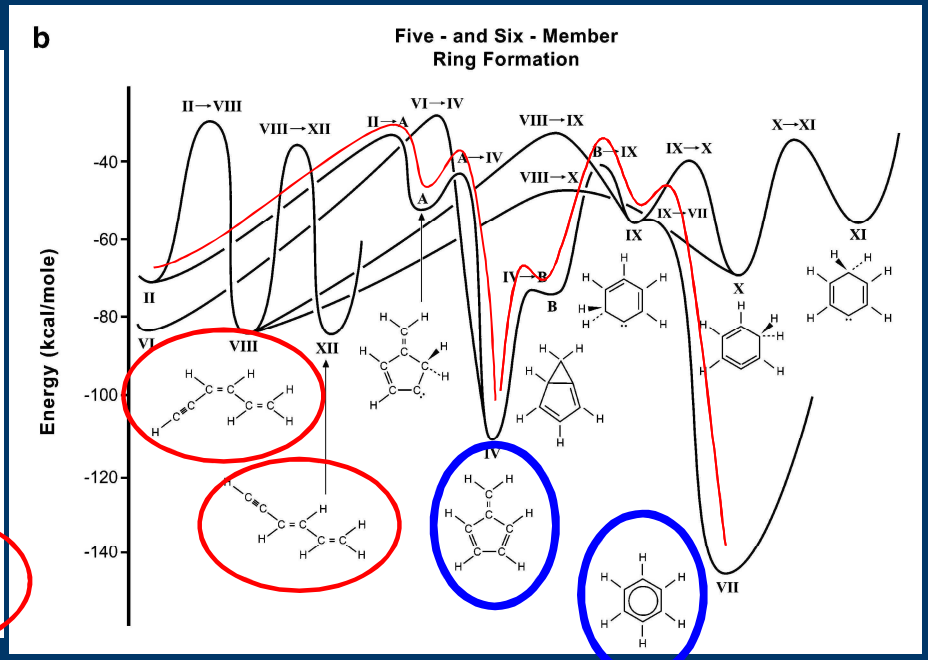
There is no direct path to benzene: Isomerization Required

Reaction pathways and isomers are important example: propargyl + propargyl





J. A. Miller and S. J. Klippenstein, *J. Phys. Chem. A* **107**, 7783 (2003)



Acyclic: easier to oxidize

~~PAH / SOOT~~

Cyclic aromatics: harder to oxidize

PAH / SOOT

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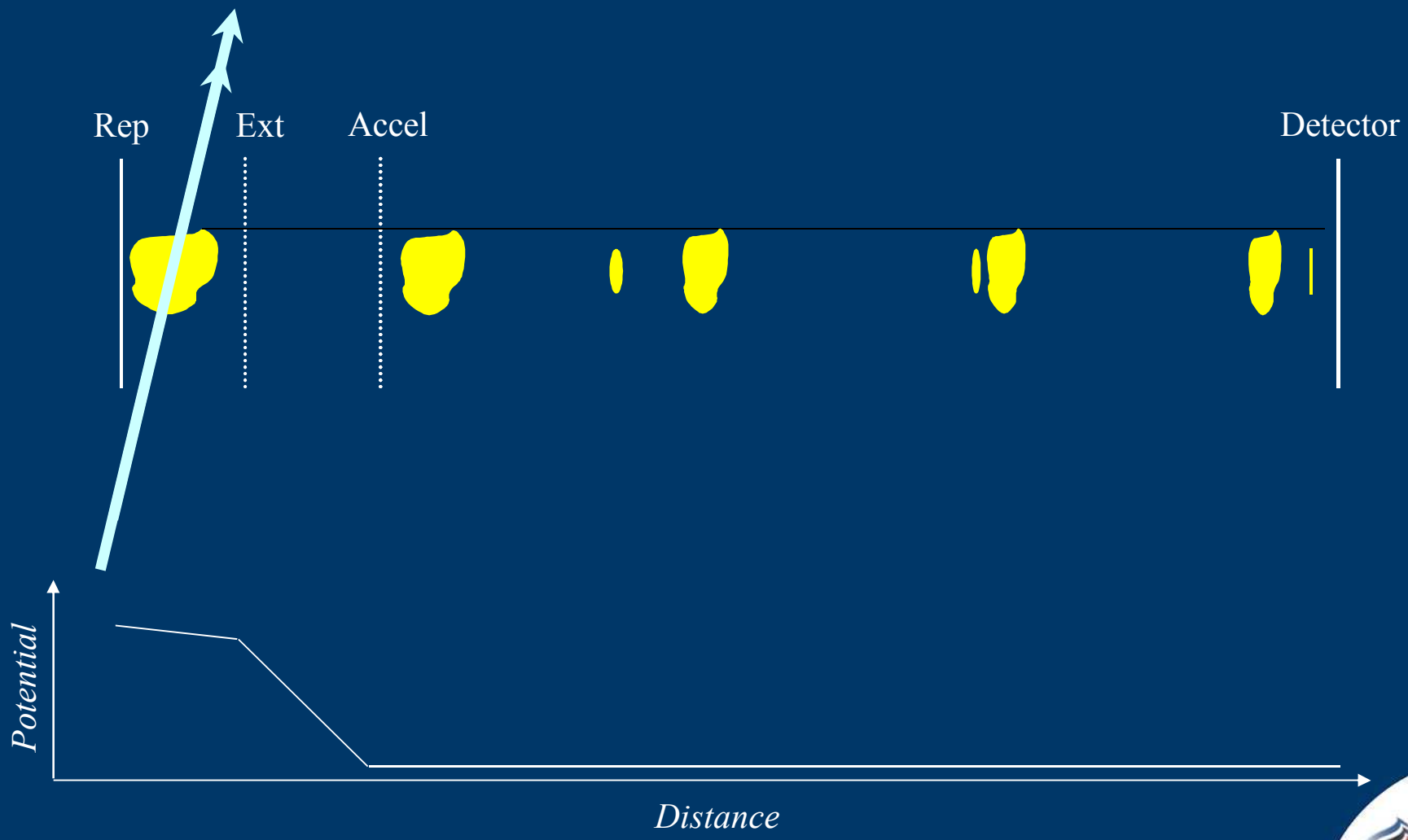
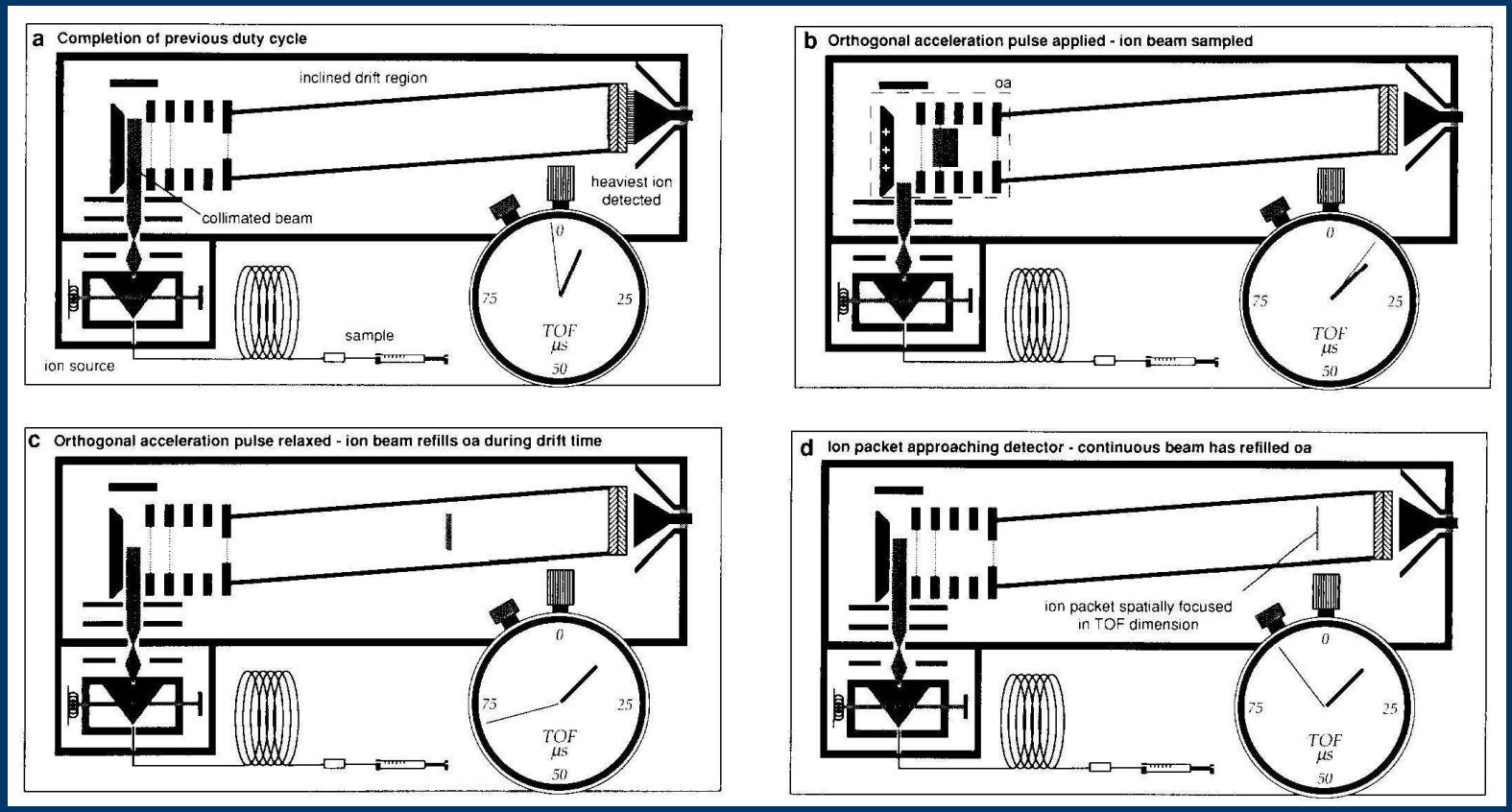
TOF mismatch

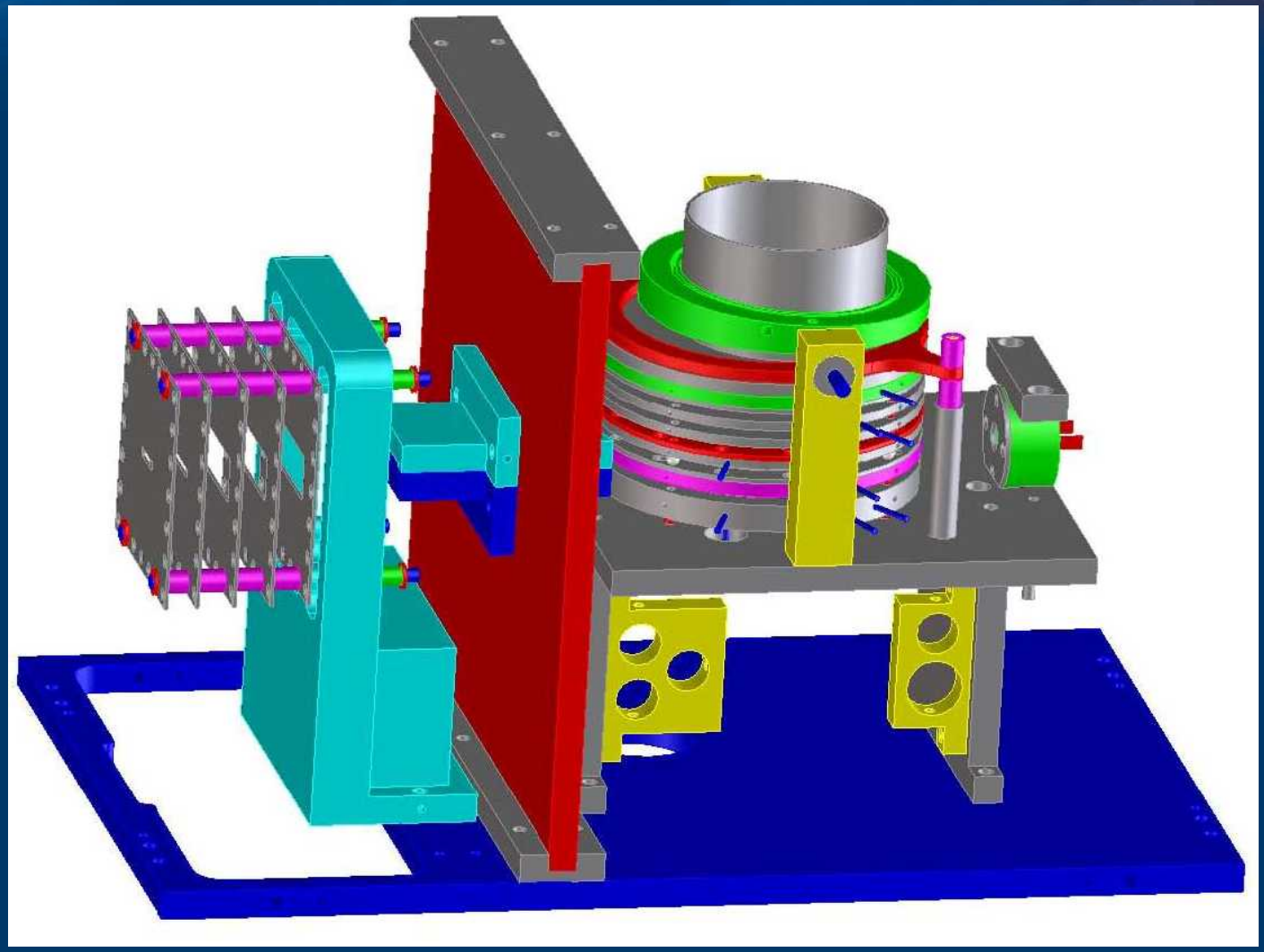


Orthogonal Extraction Time-of-Flight



Coles and Guilhaus, *Trends in Analytical Chemistry*, **12**, 203 (1993).

Sandia OA-TOF

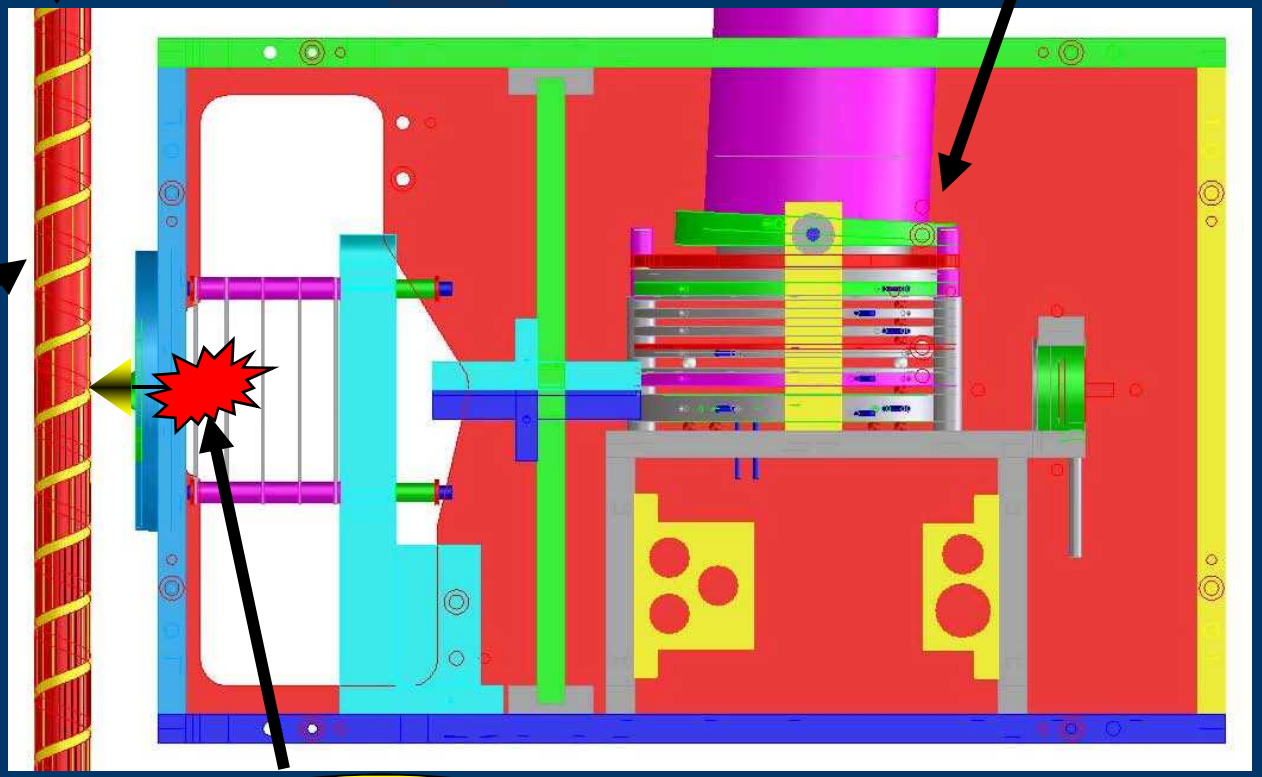


continuous ion optics

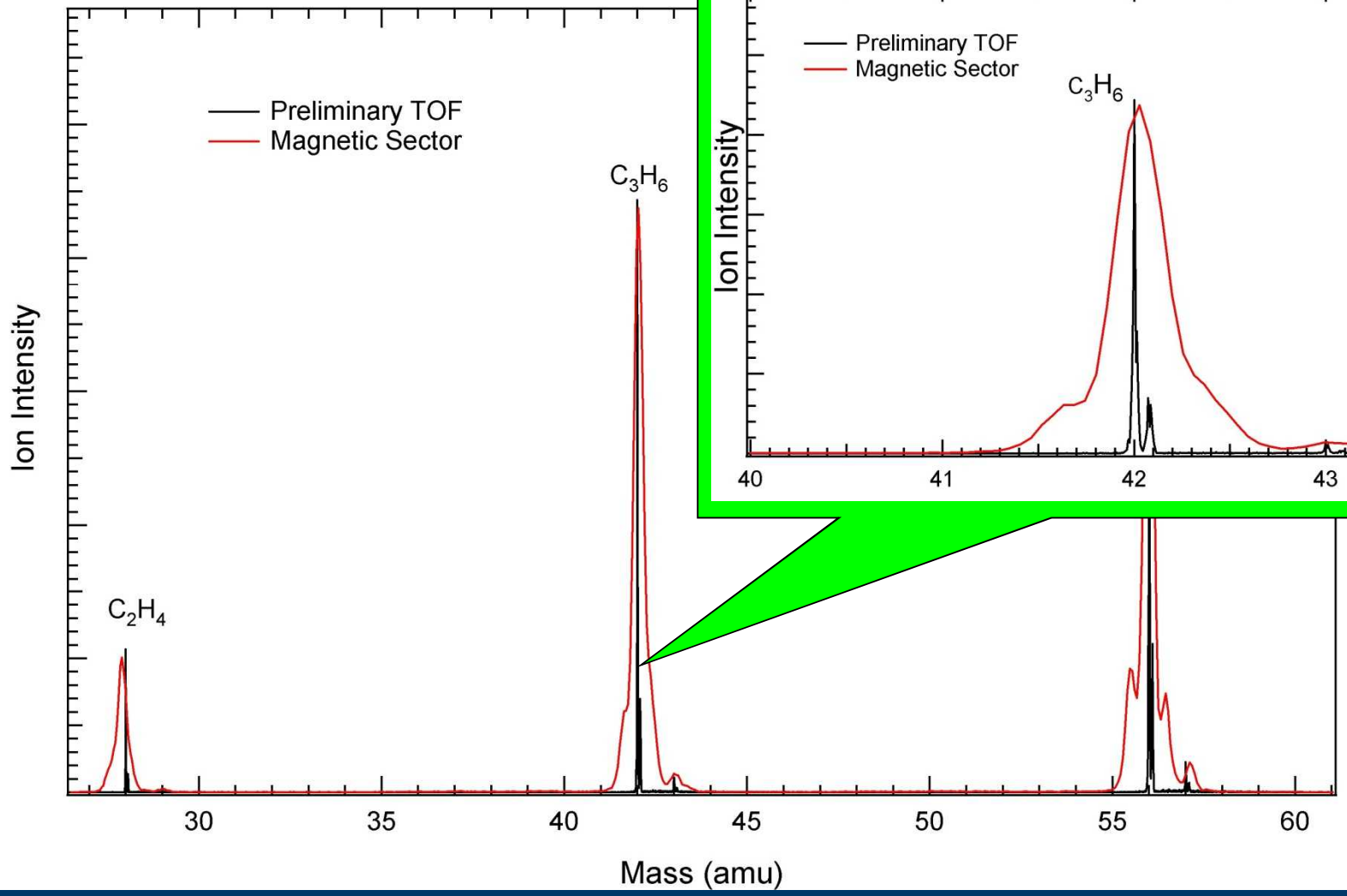
differential-pumping wall

orthogonal extractor

Experimental Design



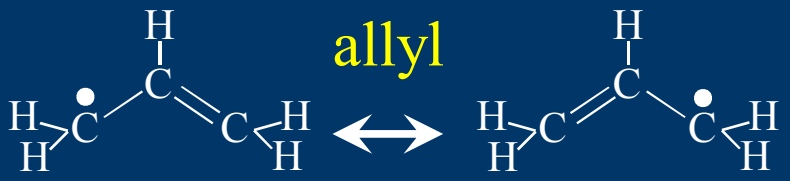
Preliminary OA-TOF spectra

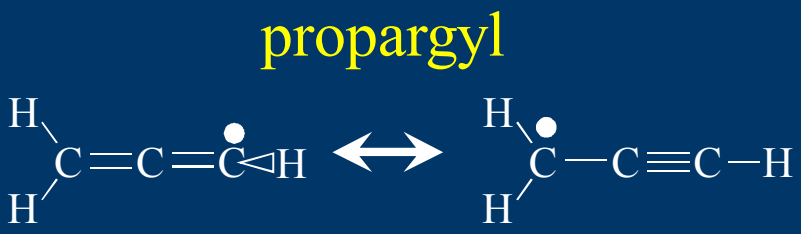


Allyl + Allyl

- Allyl radicals are resonance stabilized
  - But, contain only 1 π bond (compared to 2 π bonds in C_3H_3)
- Allyl radicals included in some molecular weight growth models

- Is allyl important compared to propargyl?
  - Measure rate coefficient
  - Measure product isomers

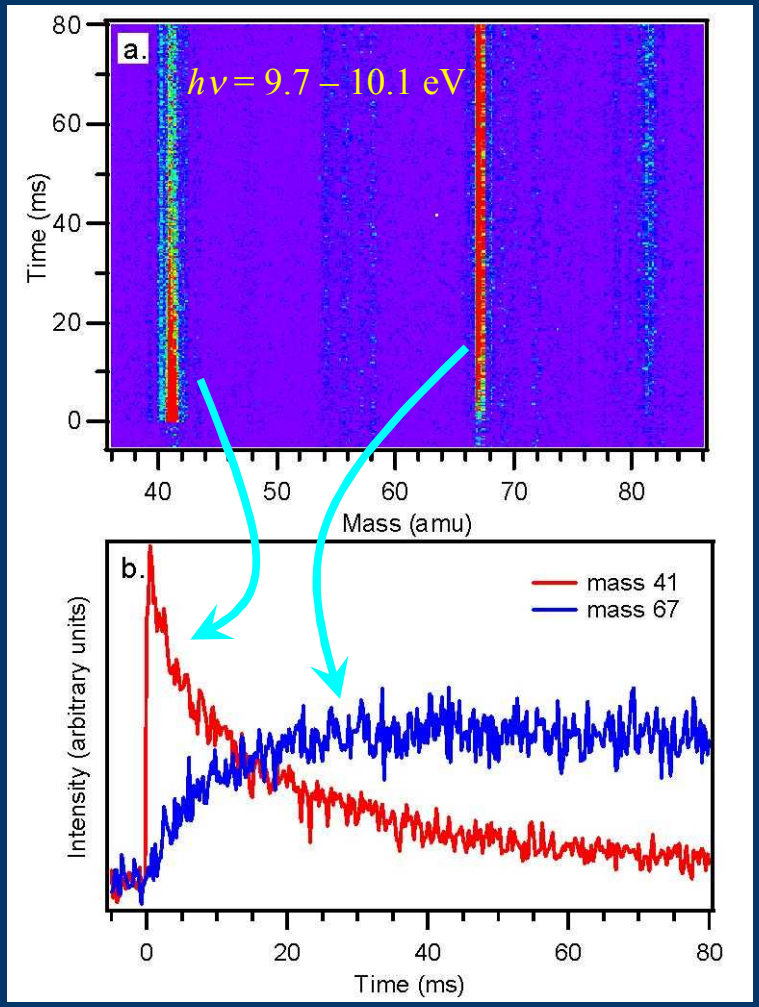




Allyl + Allyl: Kinetics & Products

$$C_3H_5 + C_3H_5 \rightarrow C_6H_{10} \quad (\Delta H°_{298} = -62 \text{ kcal/mol}) \quad (k_{1a})$$
$$\rightarrow C_3H_4 + C_3H_6 \quad (\Delta H°_{298} = -32 \text{ kcal/mol}) \quad (k_{1b})$$

- All previous rate coefficients depend on UV absorption cross section of C_3H_5.
- $k_1 = 1.4 – 4.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}
- Precursors:
  - 1,5 hexadiene (C_6H_{10}) photodissociation for kinetics studies. P = 4 Torr, T = 298 K.
  - Allyl bromide (C_3H_5Br) for product studies. P = 1 – 6 Torr, T = 298 – 600 K.



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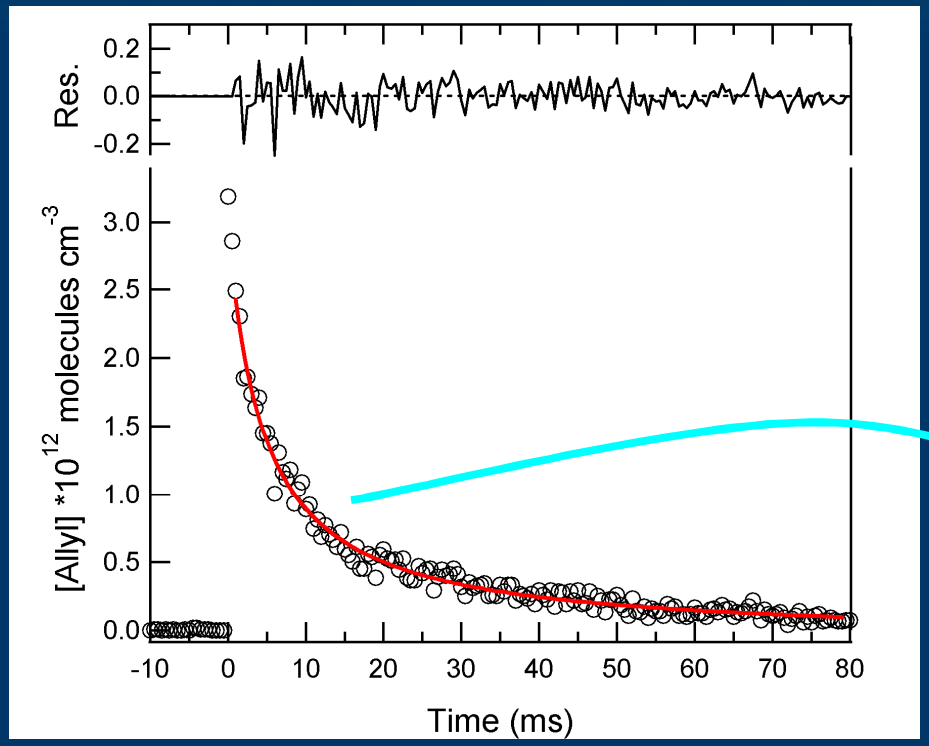
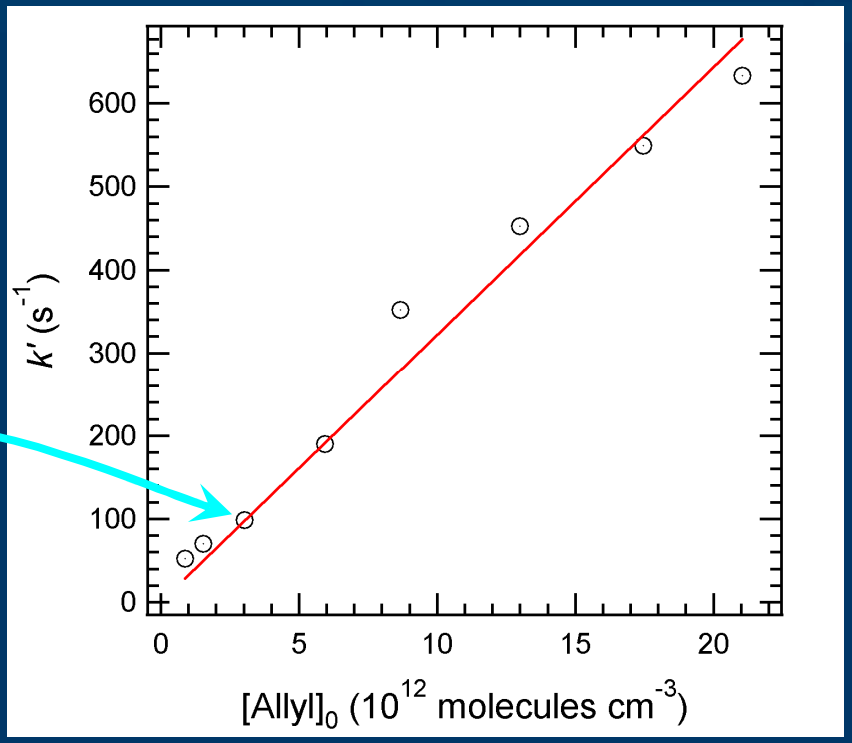
Kinetics





$k_1(298\ \mathrm{K}) = (2.7 \pm 0.7) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ (this work)

(2.65 ± 0.2)	Tulloch & Pilling, J. Phys Chem. **86**, 3812 (1982).
(3.0 ± 0.5)	Jenkin & Hayman, J. Chem. Soc. Faraday Trans. **89**, 433 (1993).

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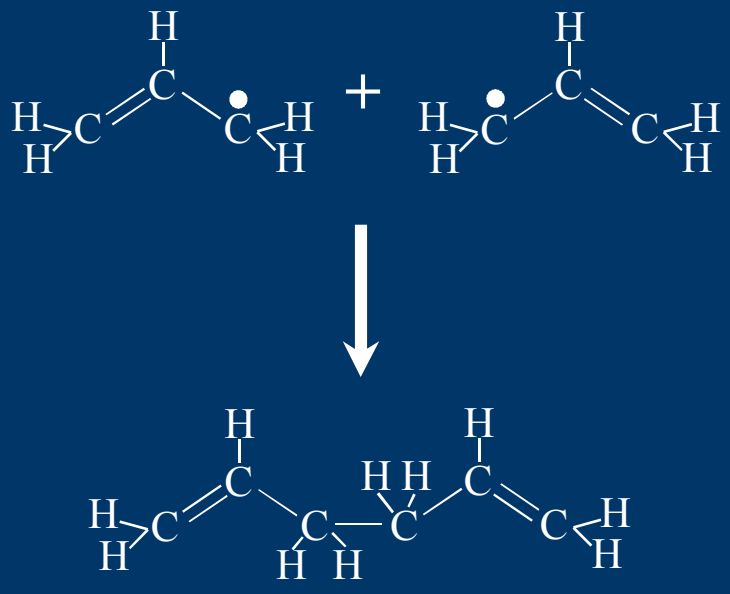
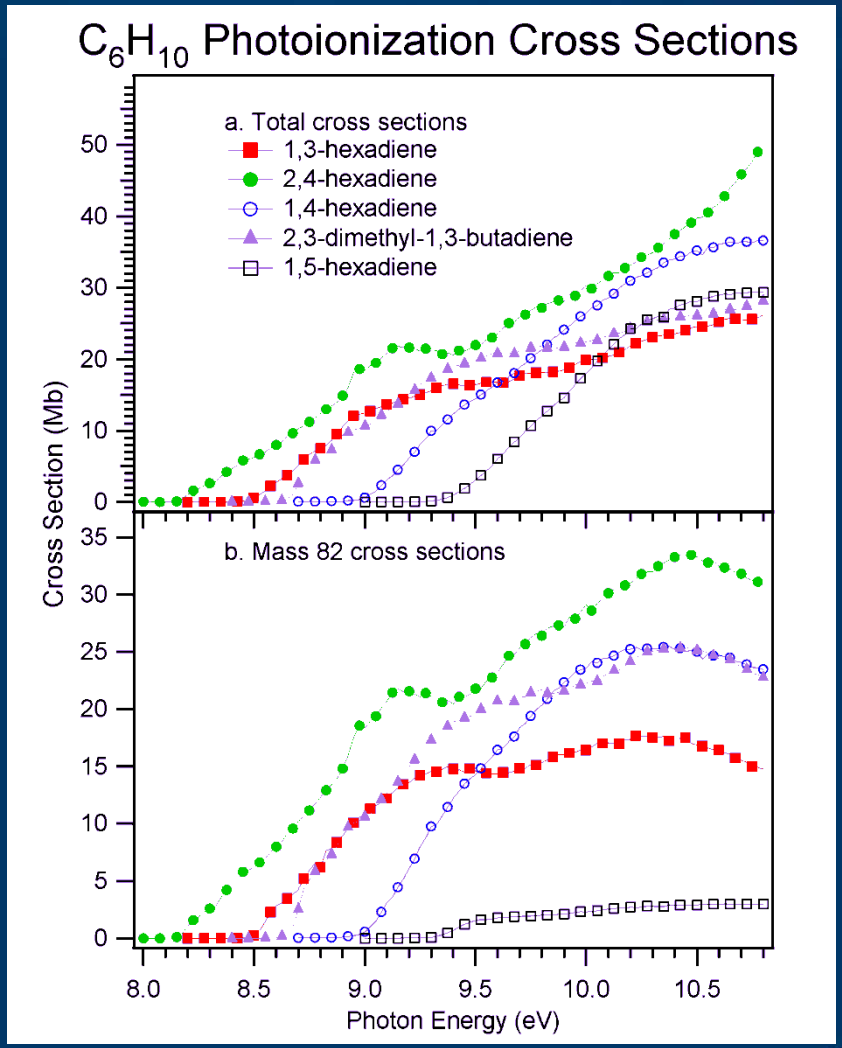
C_6H_{10} Isomers: Reference Photoionization Spectra

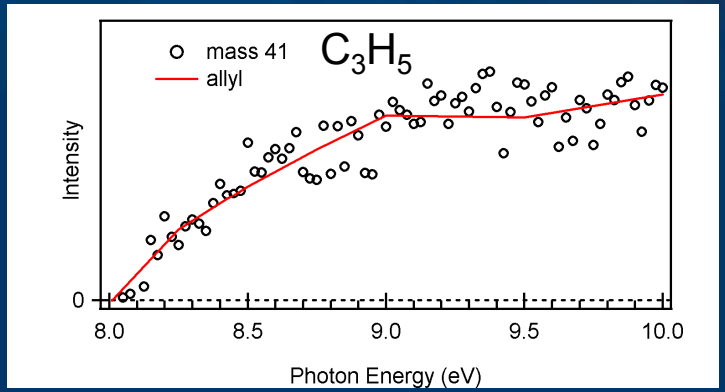


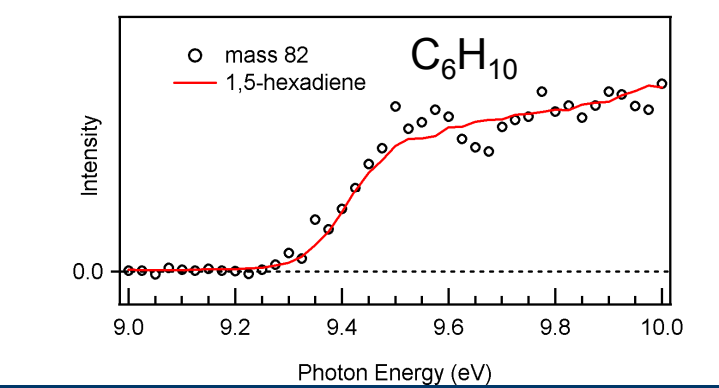
1,5-hexadiene

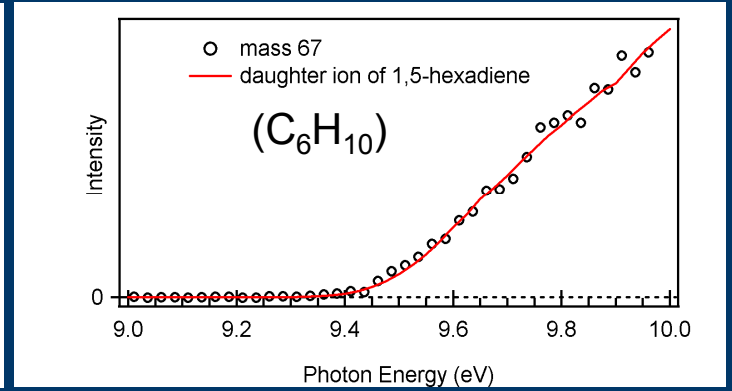


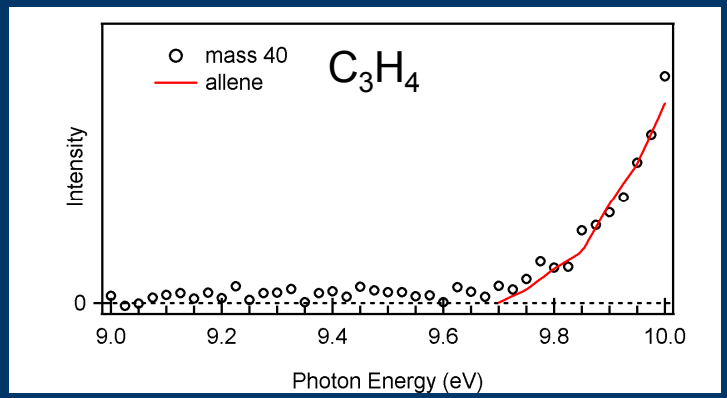
Products of the Allyl Self Reaction

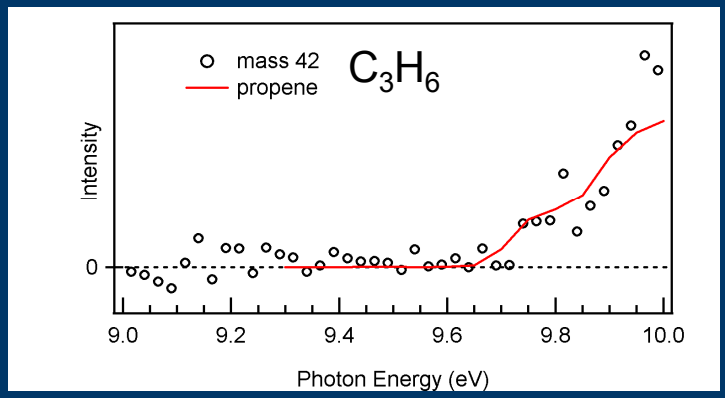
For $P = 1 - 6$ Torr
$T = 298 - 600$ K
only isomer of C_6H_{10} is
1,5 hexadiene











$k_{1b} / k_{1a} < 0.03$

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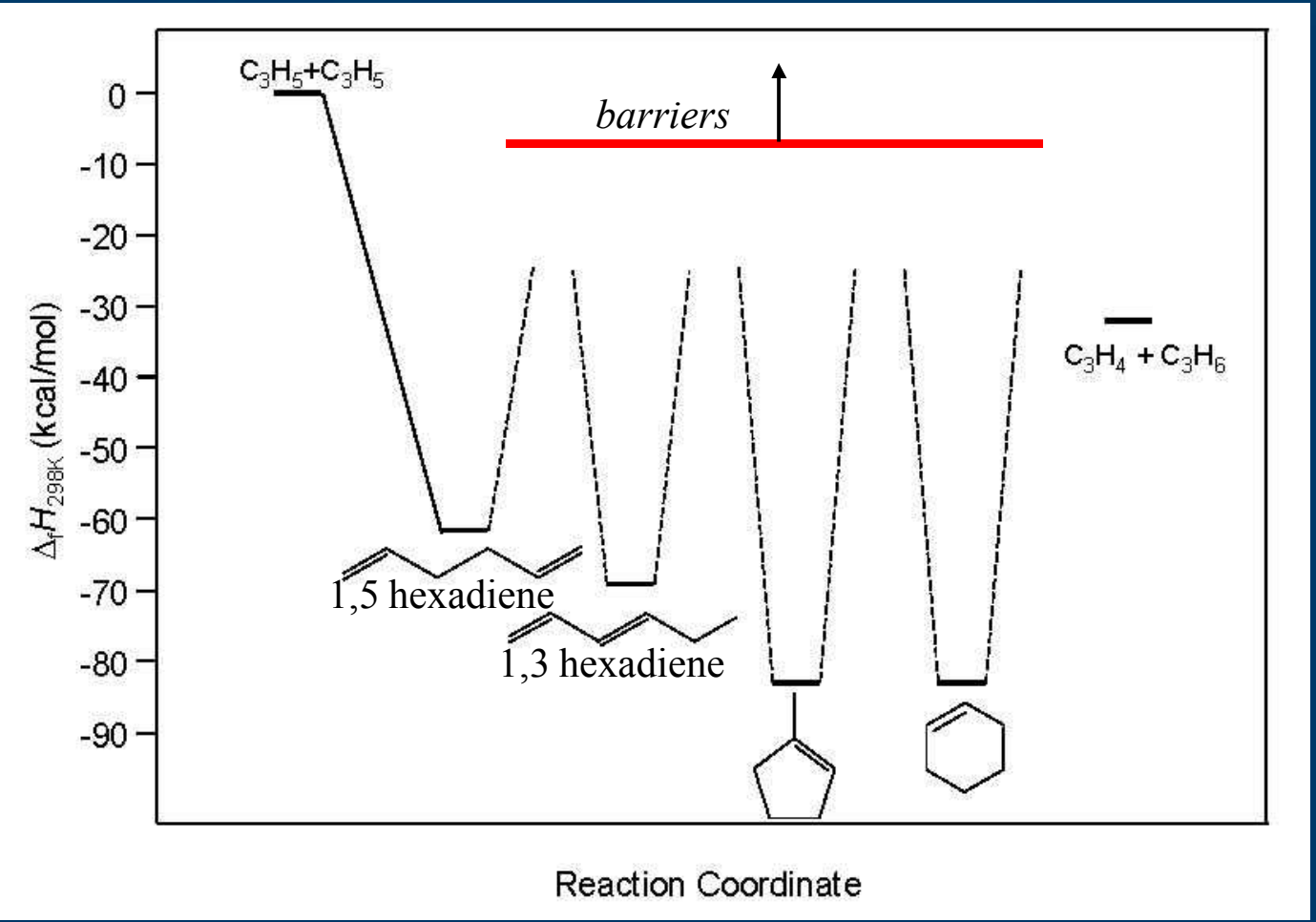
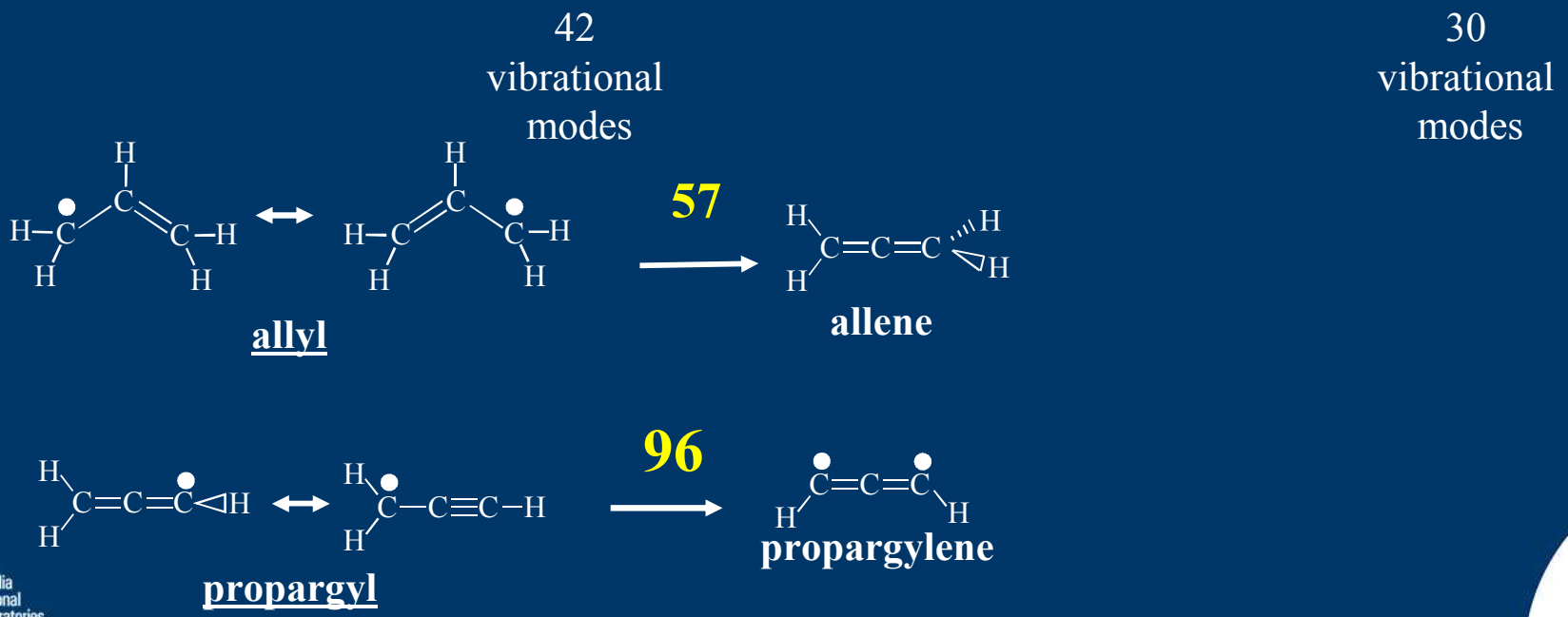
C_6H_{10} Potential Energy Surface



Allyl Self-Reaction: Conclusions

- Allyl radicals are less important than propargyl in the initial steps of soot formation chemistry
  - Lower steady-state concentration (due to weaker C-H bond)
  - Less likely to isomerize to cyclic species (higher barriers)
  - Larger adduct (C_6H_{10}) is more easily stabilized compared to C_6H_6



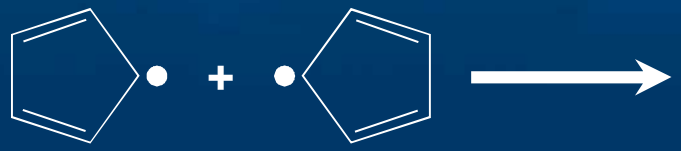
Sensitivity

$$N_{\text{req}} = 1.74 \times 10^{6} \frac{S}{\sigma * n_{\text{ph}} * \Delta t_{\text{bin}} * C * \sqrt{m_i}}$$

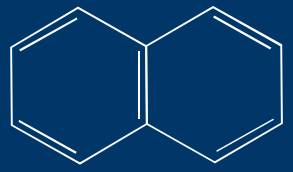
$S = 100$ counts timebin^{-1} → $S/N = 10$

$\sigma = 10$ megabarns (1×10^{-17} cm^2 molecule^{-1})
$n_{\text{ph}} = 5 \times 10^{13}$ photons s^{-1}
$\Delta t_{\text{bin}} = 250$ μs
$C = 2400$ coadditions (10 minutes @ 4 Hz reprate)
$m_i = 58$ amu (acetone)
$N_{\text{req}} = 7.6 \times 10^{10}$ molecules cm^{-3}

Cyclopentadienyl radical recombination



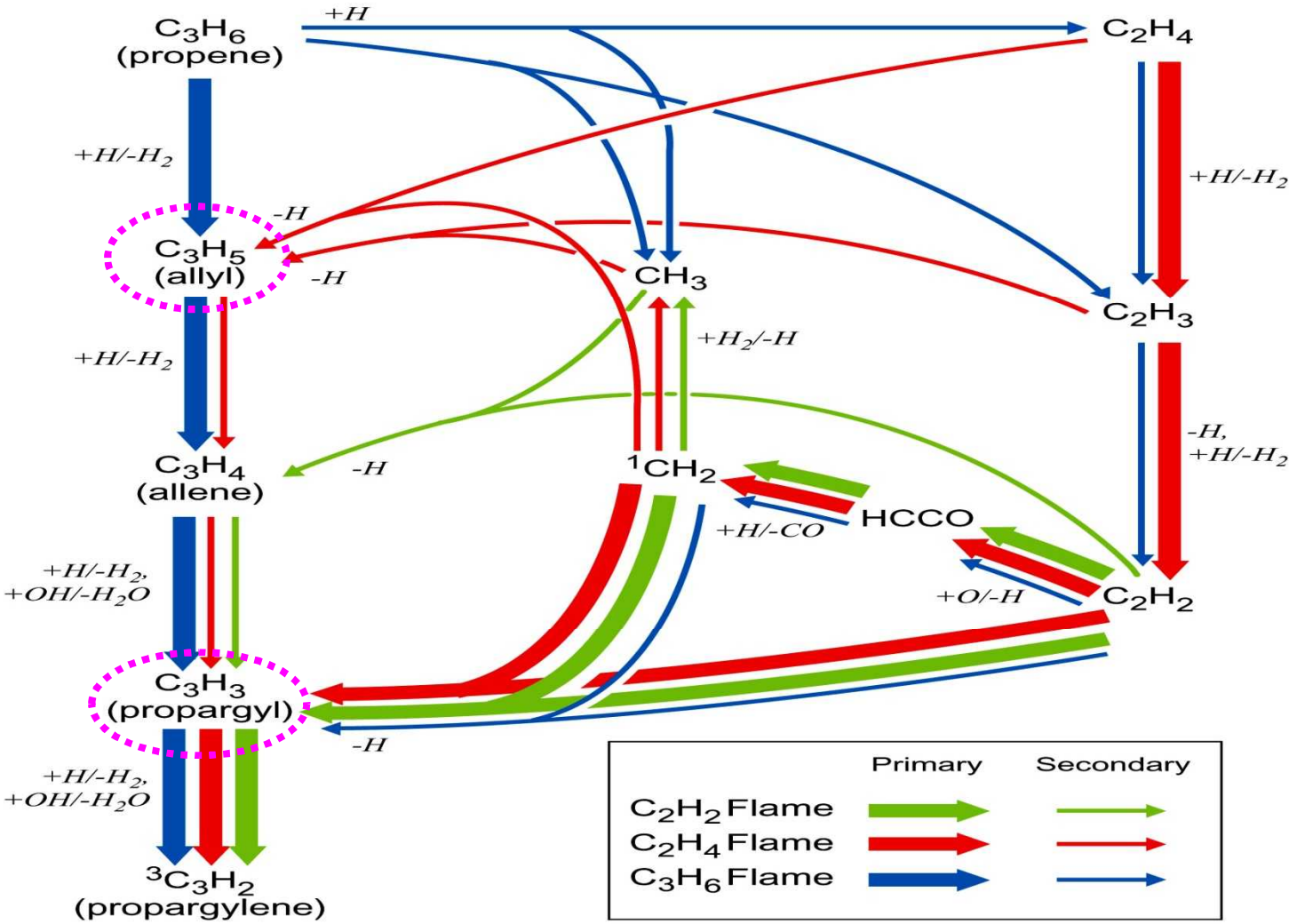
- *c*-C_5H_5 is a 5-member resonance-stabilized radical
- Melius and coworkers have calculated the self reaction as a route to napthalene ($C_{10}H_8$).



- Kislov and Mebel calculate pathways to other $C_{10}H_8$ isomers, such as fulvalene.

- What isomerizations occur as 2 H atoms are lost?
- Will this reaction lead to flat or curved PAHs?

Pathways to Allyl & Propargyl



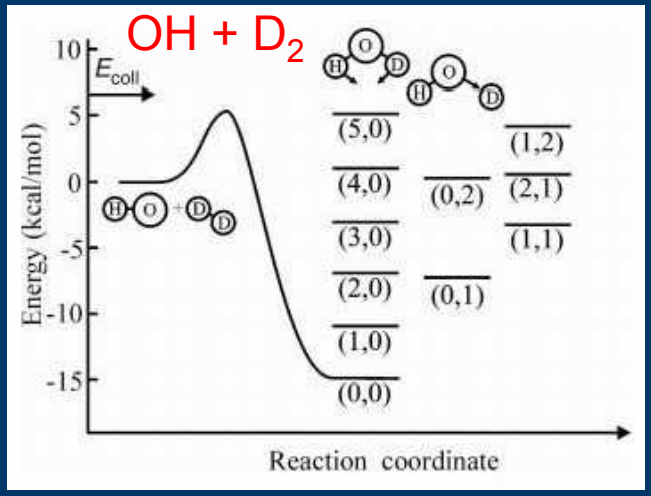
C. J. Pope & J. A. Miller, Proc. Comb. Inst. **28**, 1519 (2000).

Single vs. Multiple Collisions

Single Collision Expts. (crossed beams)

- Quantum numbers reflect reaction dynamics
- Maximum detail

- Stabilization not possible
- Collisions with bath gas may drastically alter reaction



Strazisar, Lin, Davis, Science 290, 958 (2000)

Multi Collision Expts. (reaction cells)

- Quantum numbers reflect energy transfer
- Thermal average over collision energy blurs some details

- Collisional stabilization possible
- Generally more realistic reaction conditions

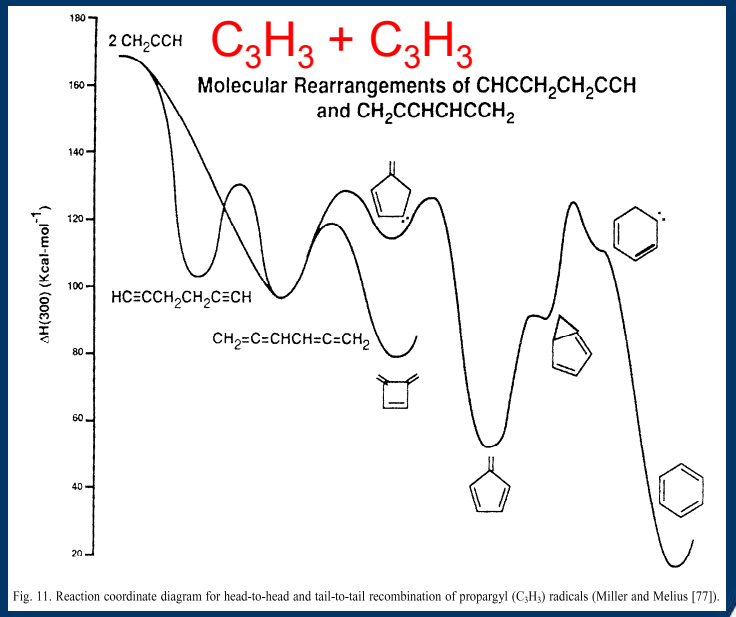


Fig. 11. Reaction coordinate diagram for head-to-head and tail-to-tail recombination of propargyl (C_3H_3) radicals (Miller and Melius [77]).

J. A. Miller, Combust Flame 1992;91:21–39.

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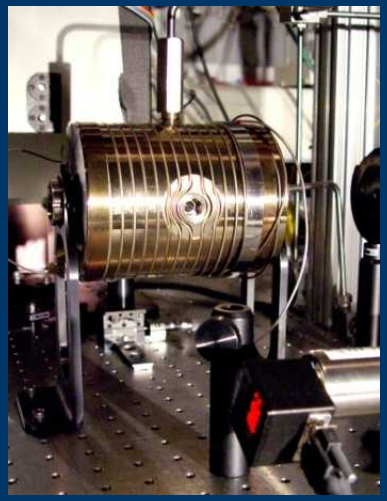
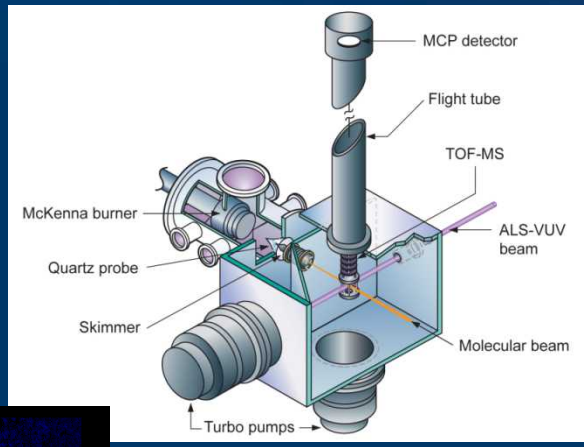
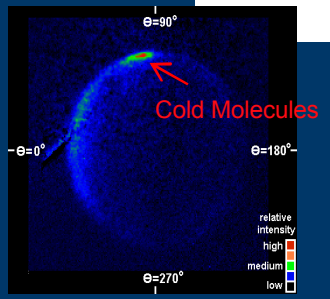
Current job openings

http://sandia.gov/careers/search-openings.html

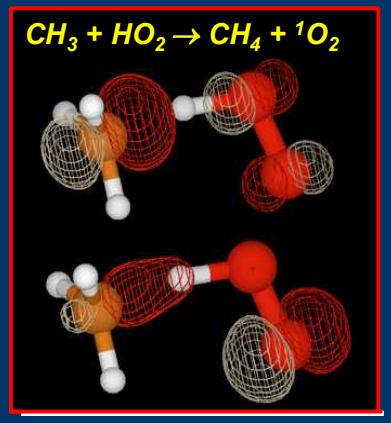


- **Gas Phase Energy Transfer / High Pressure Chemistry**
  - **Job 63305 (PostDoc)**

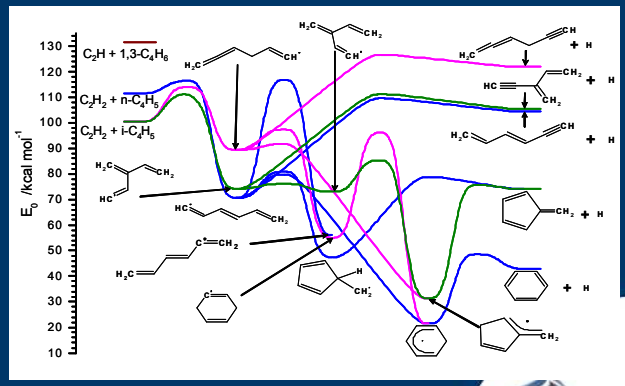




- Low-Pressure Flame Chemistry
  - 2 PostDocs



- Combustion Chemistry Theory and Modeling
  - 1-4 PostDocs



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Molecular Weight Growth Controversy

Which reactions are most important in forming aromatic rings?

lower concentrations, but no entrance barriers ⇨ Radical + Radical (for example, $C_3H_3 + C_3H_3$)

higher concentrations, but entrance barriers ⇨ Radical + Closed Shell (for example, $C_3H_3 + C_2H_2$)

Following reaction sequences with MPIMS

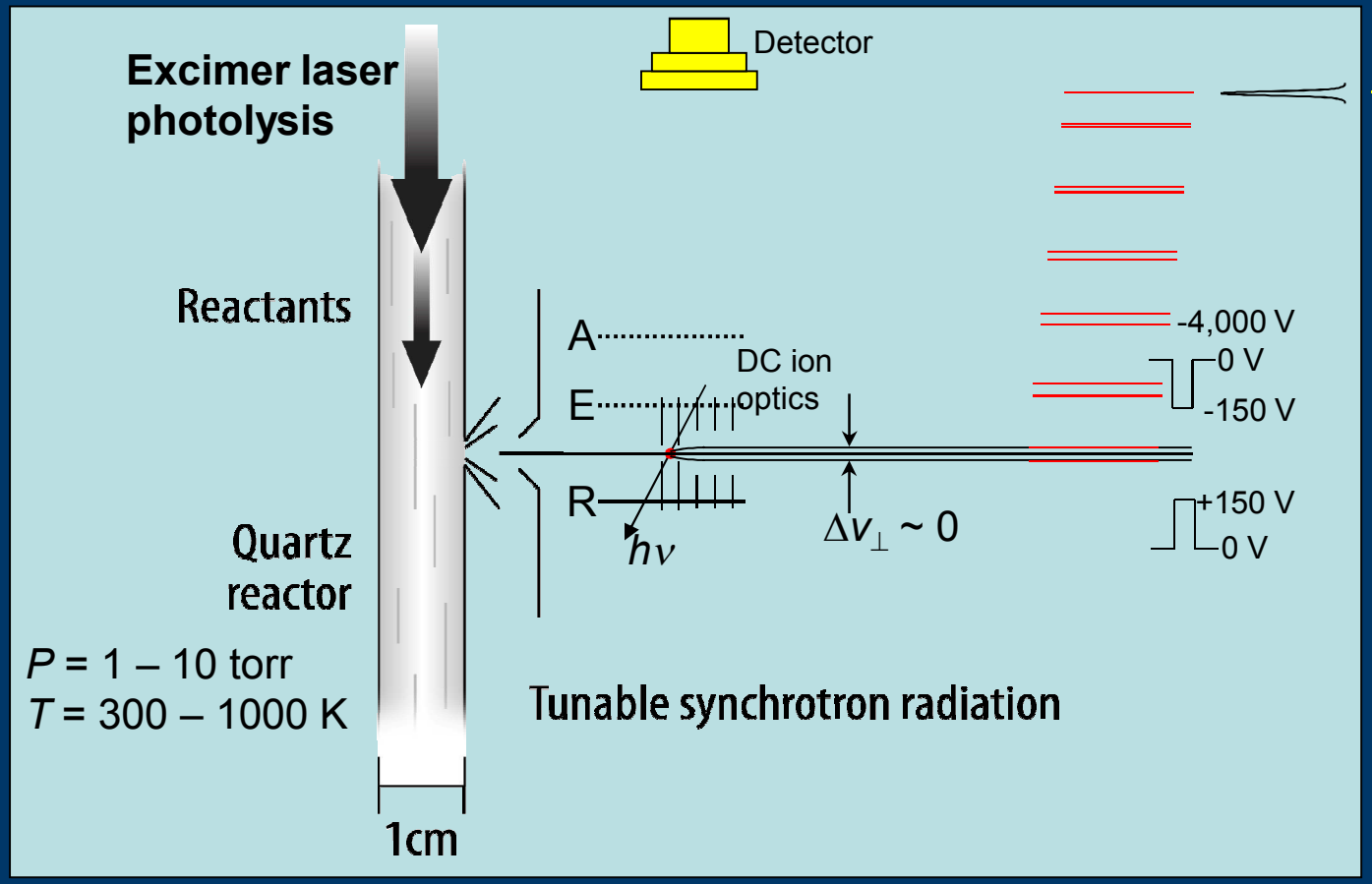
- Most real world chemistry (combustion, atmospheric, etc.) consists of sequences of reactions

  A + B → C1 + C2
  C1 & C2 + B → D
  D + B → E + F

- We can kinetically verify that reaction steps are linked
- We can start the reaction at intermediate points with a single isomer

  C2 + B → D
  D + B → E + F

Laser Photolysis Reactor is Coupled to Time-Resolved Mass Spectrometer



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

50 kHz repetition rate

Reactor, pinhole, and skimmer