Using Tunable VUV Ionization with Molecular Beam Scattering Methods to Study the Dissociation Channels of Organic Radicals

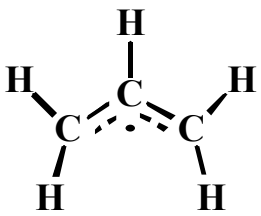
Laurie J. Butler
The University of Chicago

David E. Szpunar
Martin McCullagh
Yi Liu
Julie Mueller
Melita Morton
Johanna Miller
Jinian Shu (ALS)
Fei Qi (ALS)

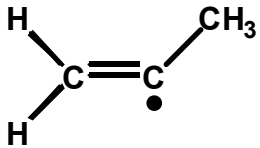
Department of Energy,
Basic Energy Sciences

National Science Foundation,
Chemistry Division

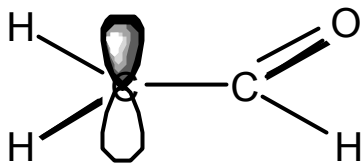
A Method for Studying the Ground State Unimolecular Dissociation Channels of Polyatomic Radicals



allyl radical



2-propenyl radical



vinoxy radical

Chemical Dynamics Beamline

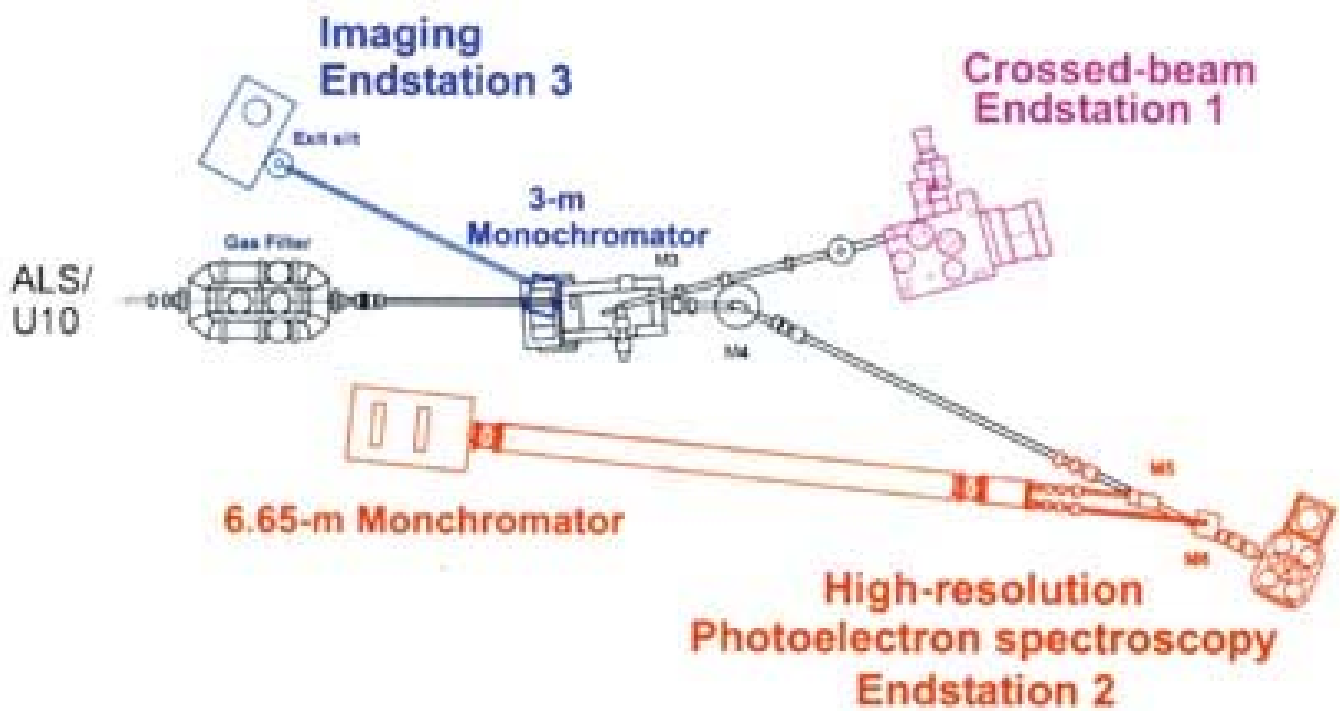
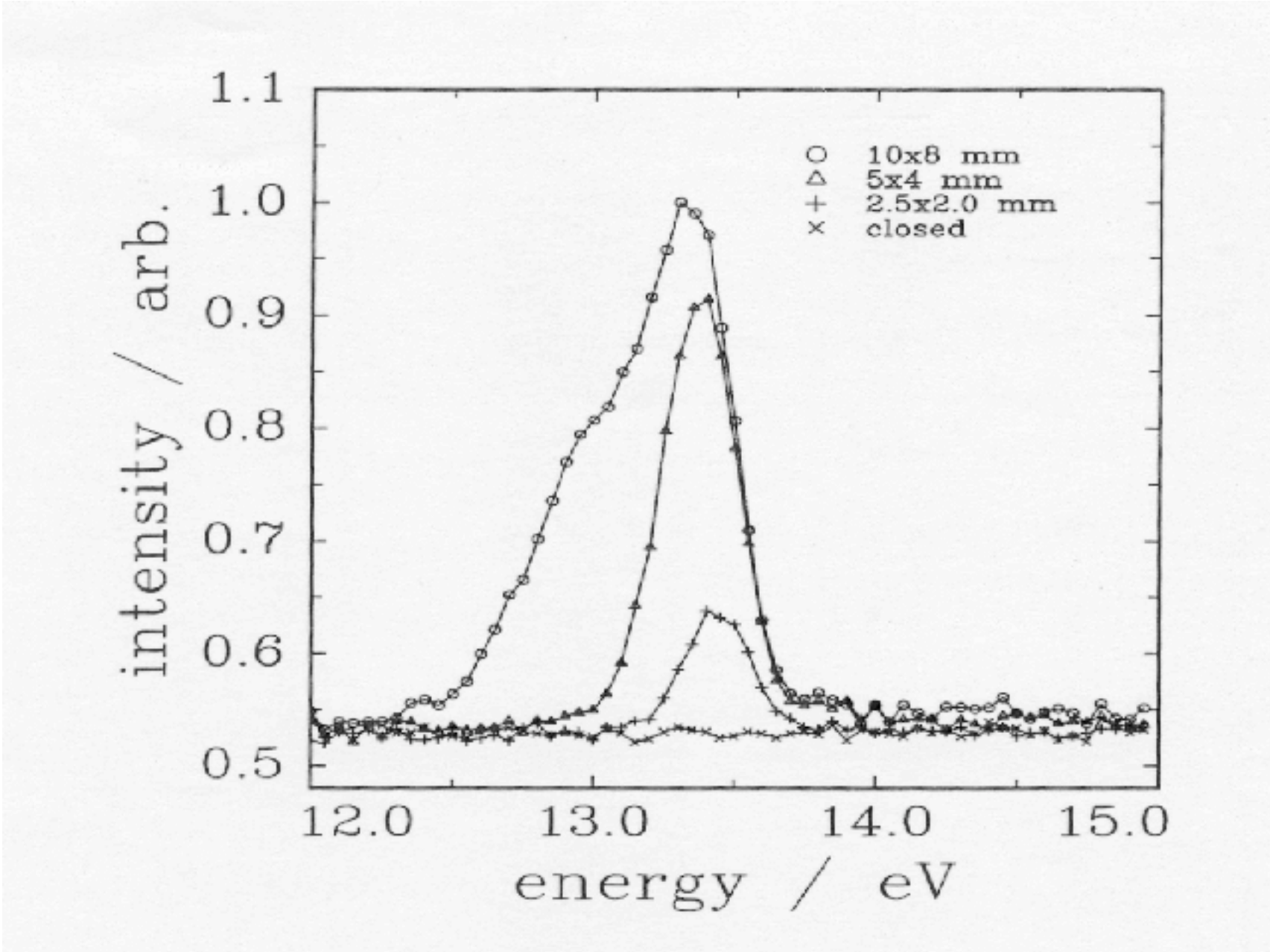
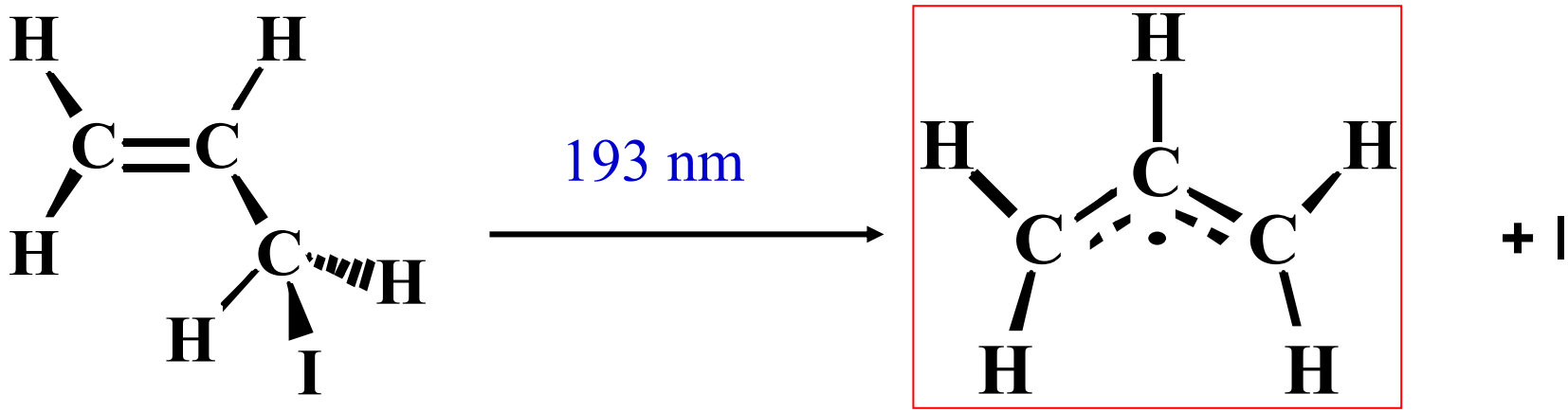


Figure from http://www.chemicaldynamics.lbl.gov/ Beamline 9.0.2

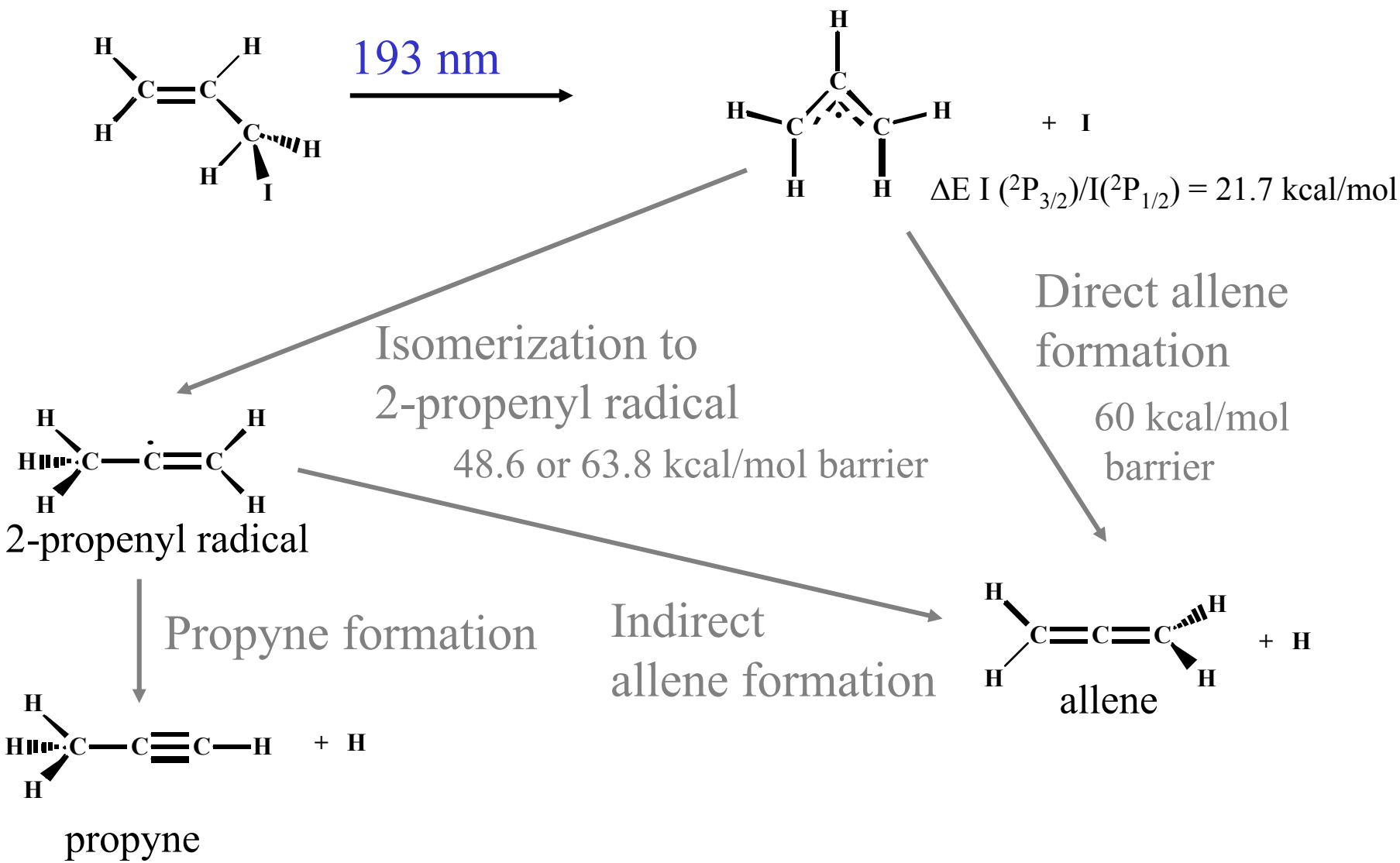


From D. A. Blank, Ph.D. Thesis, University of California, Berkeley, 1997

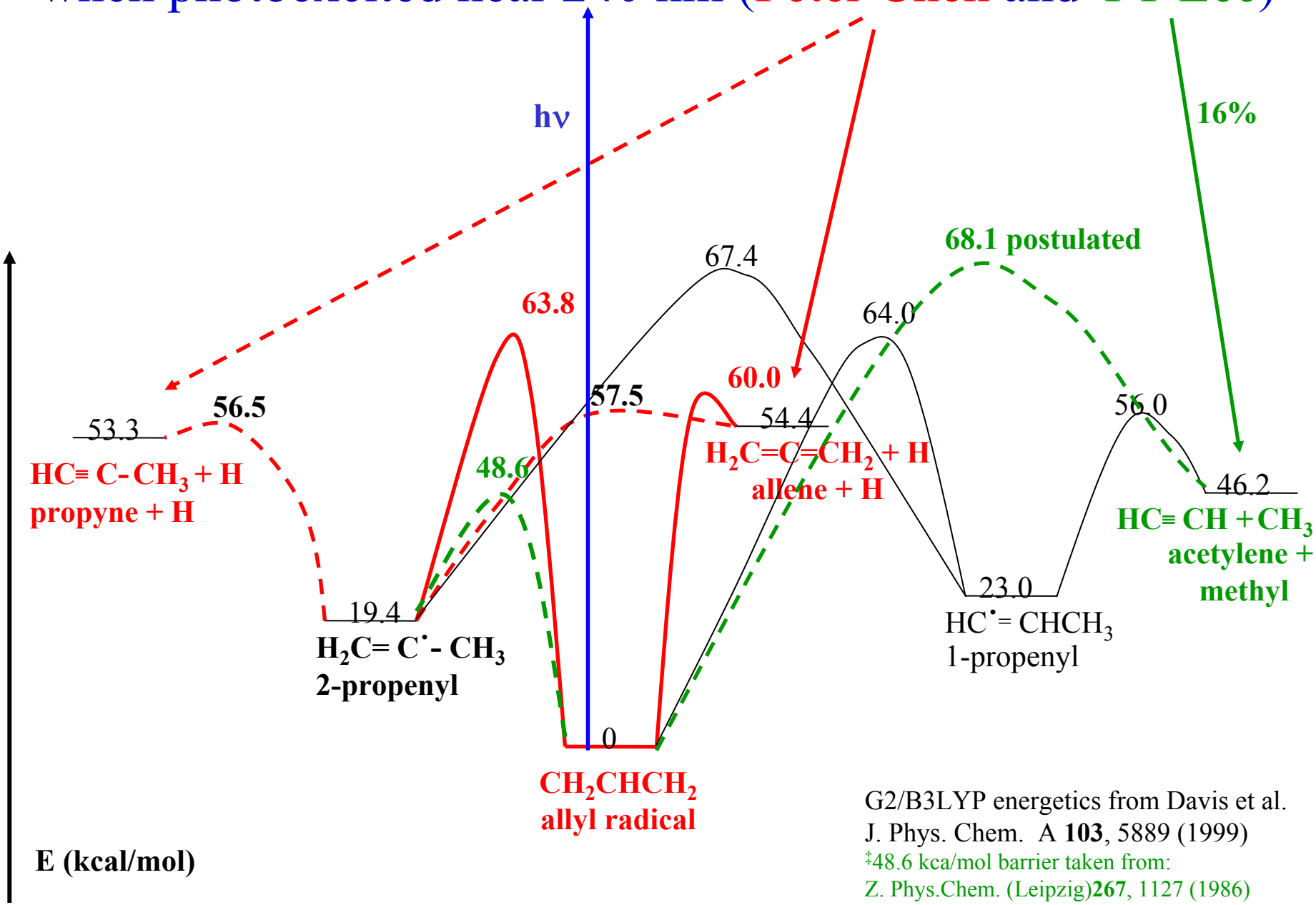


- Allyl Iodide used as photolytic precursor to the allyl radical
- Allyl radical dispersed as a function of translational energy and therefore as a function of internal energy
  - We can study the isomerization and dissociation channels of the allyl radical as a function of internal energy
  - Allyl radical is produced with an internal energy range that spans the barriers of the channels of interest

Allyl Radical Reaction Paths

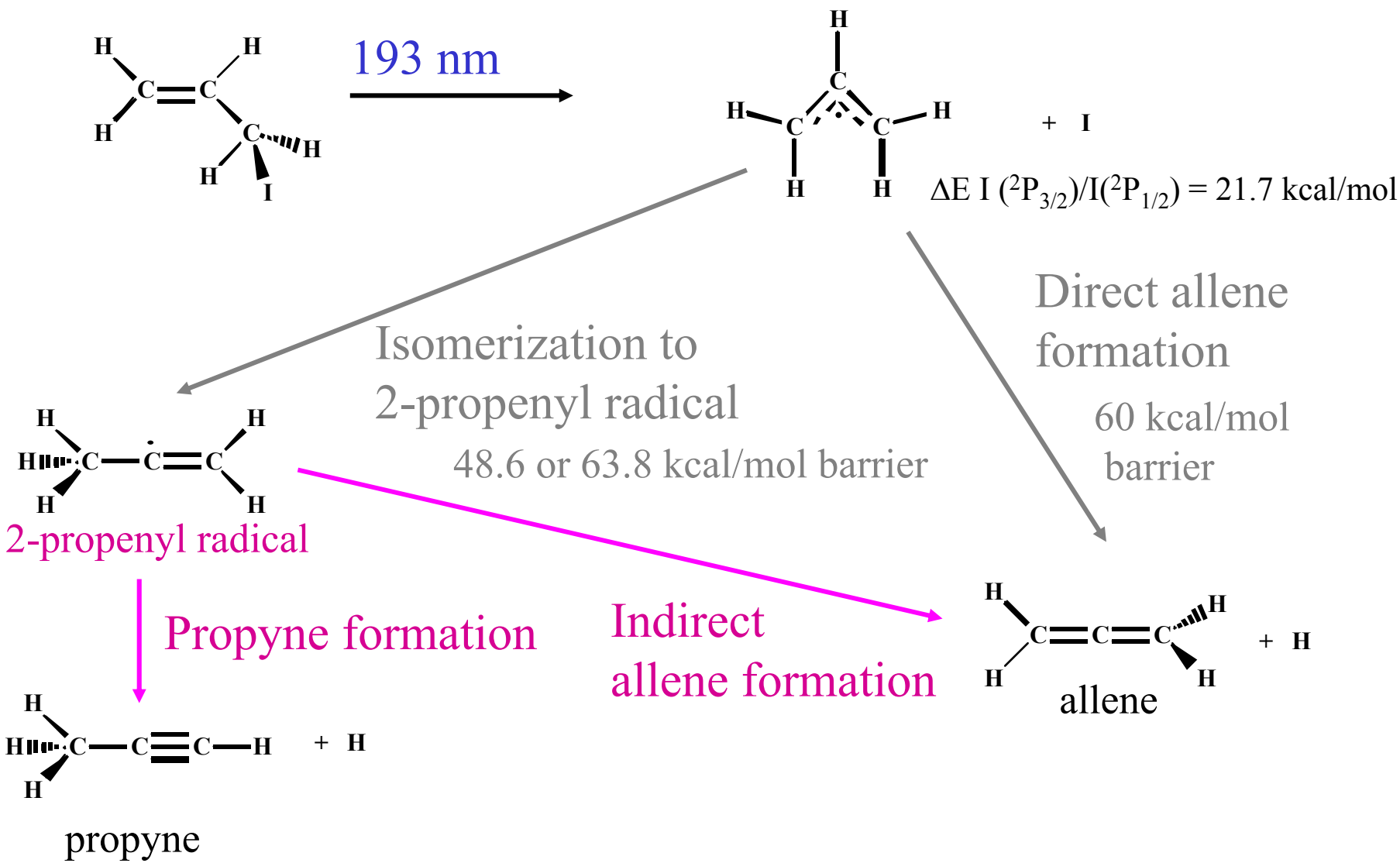


Allyl radical dissociation/isomerization processes when photoexcited near 240 nm (Peter Chen and YT Lee)

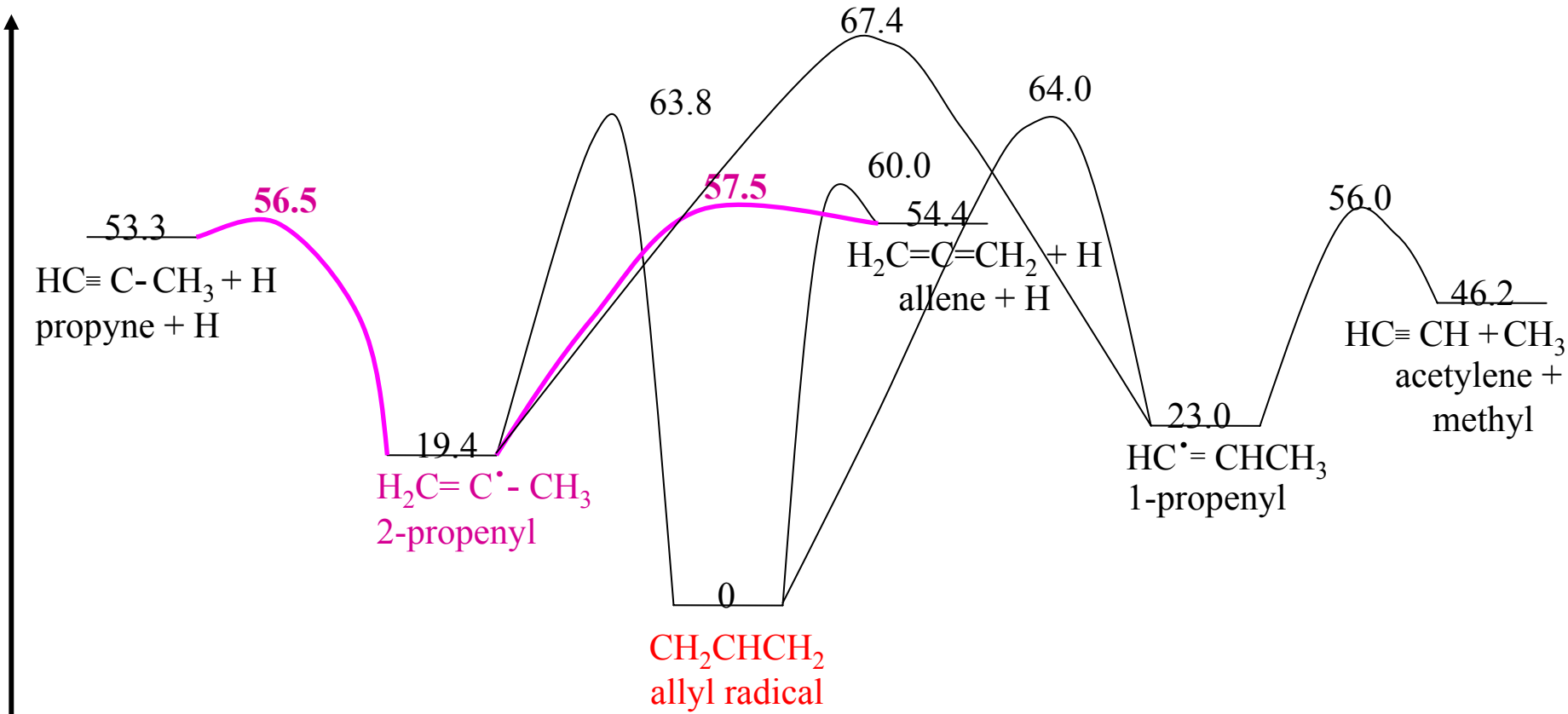


G2/B3LYP energetics from Davis et al.
J. Phys. Chem. A **103**, 5889 (1999)
‡48.6 kca/mol barrier taken from:
Z. Phys.Chem. (Leipzig)**267**, 1127 (1986)

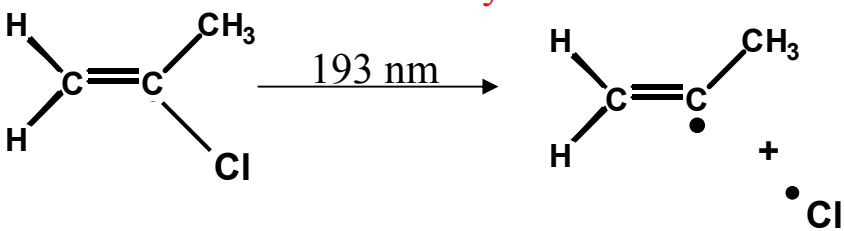
Allyl Radical Reaction Paths



Competing C-H bond fission channels of the 2-propenyl radical

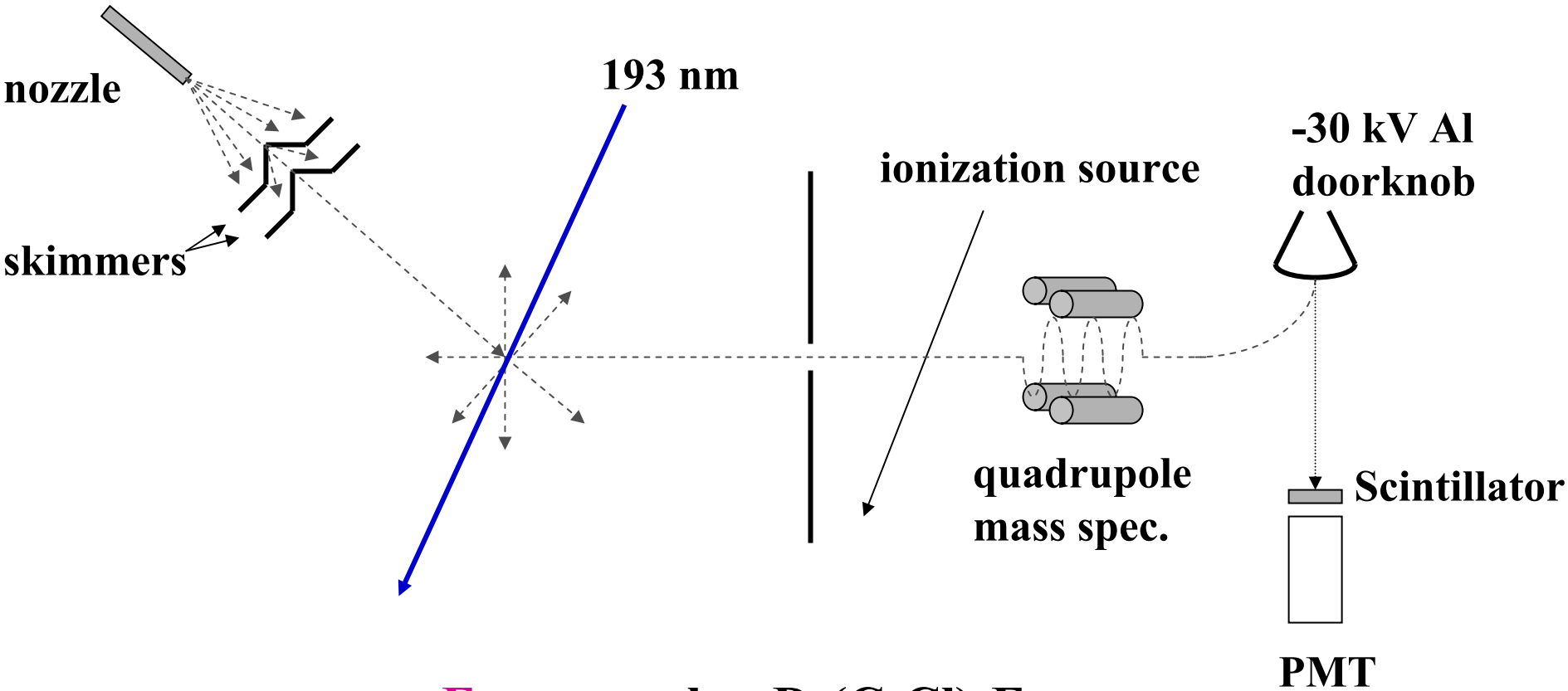


E (kcal/mol)



$$E_{\text{int radical}} = h\nu - D_o(\text{C-Cl}) - E_T$$

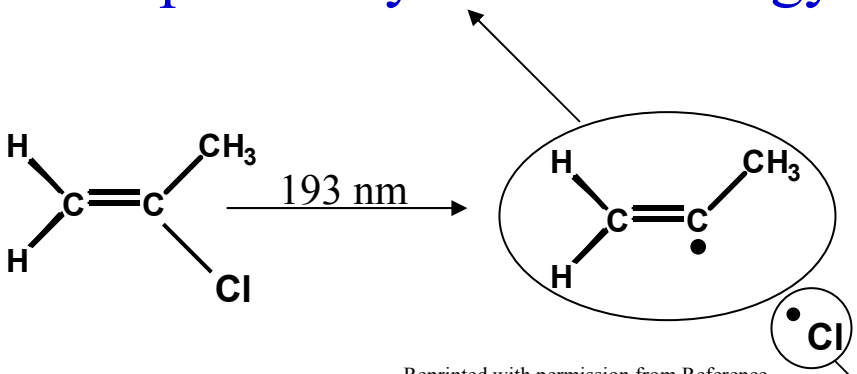
Measure the Kinetic Energy E_T imparted to the Halogen atom + Nascent radical to disperse the radicals by internal energy. Then determine product branching as a function of internal energy in the radical.



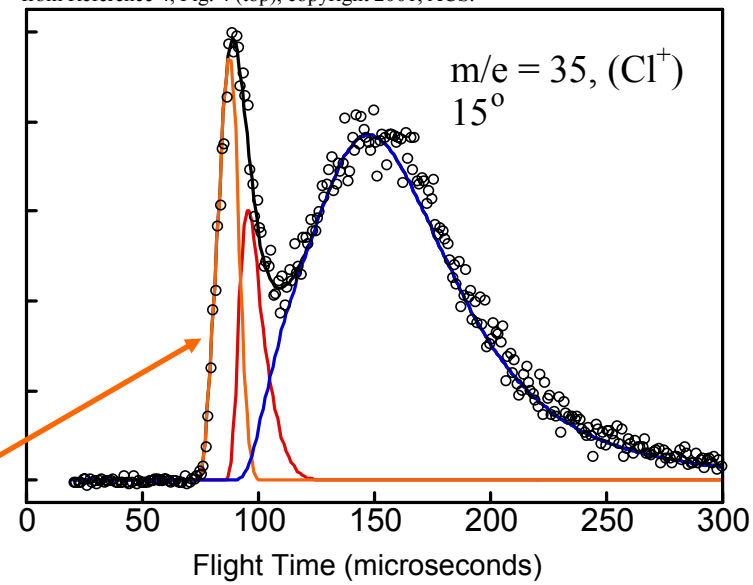
$$E_{int\ radical} = h\nu - D_o(C\text{-}Cl) - E_T$$

Figure from D. E. Szpunar, Ph.D. Thesis, University of Chicago, 2003

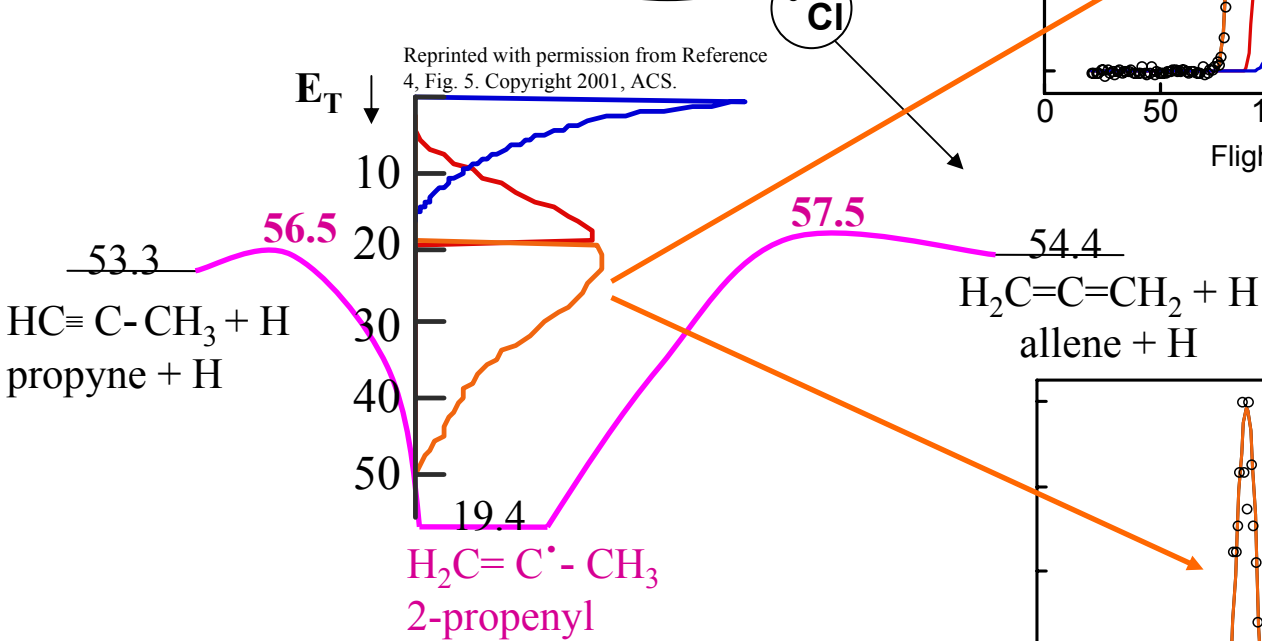
C-Cl fission gives 2-propenyl radicals dispersed by internal energy



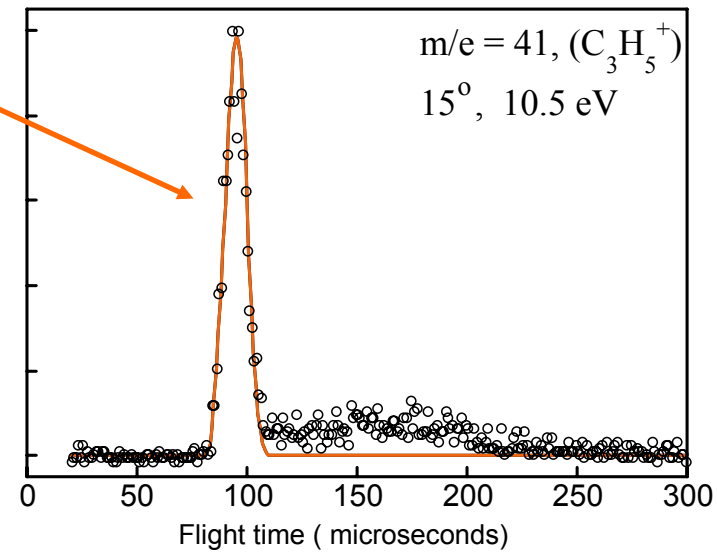
Reprinted with permission from Reference 1, Fig. 1 (top), copyright 2000, AIP and from Reference 4, Fig. 4 (top), copyright 2001, ACS.



Reprinted with permission from Reference 4, Fig. 5. Copyright 2001, ACS.

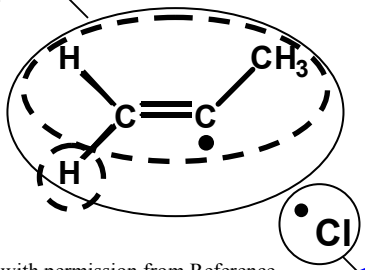


Reprinted with permission from Reference 4, Fig. 6 (top). Copyright 2001, ACS.

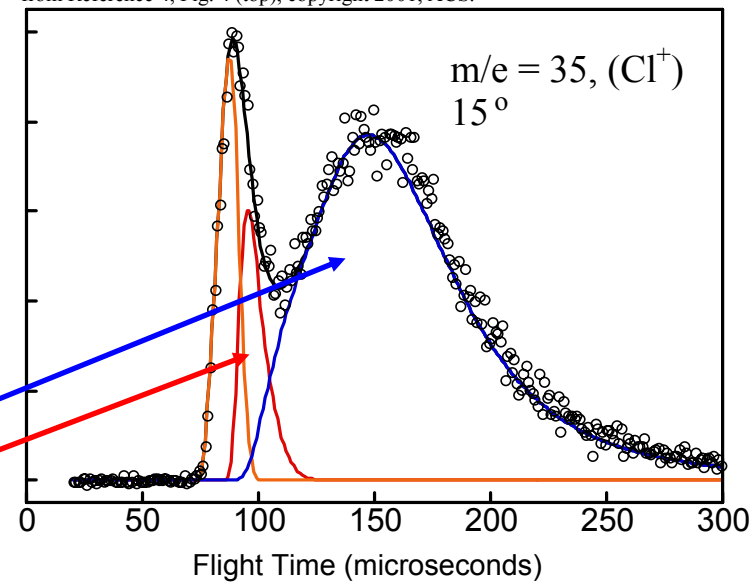


Fast Cl atoms have momentum-matched stable mass 41 radicals

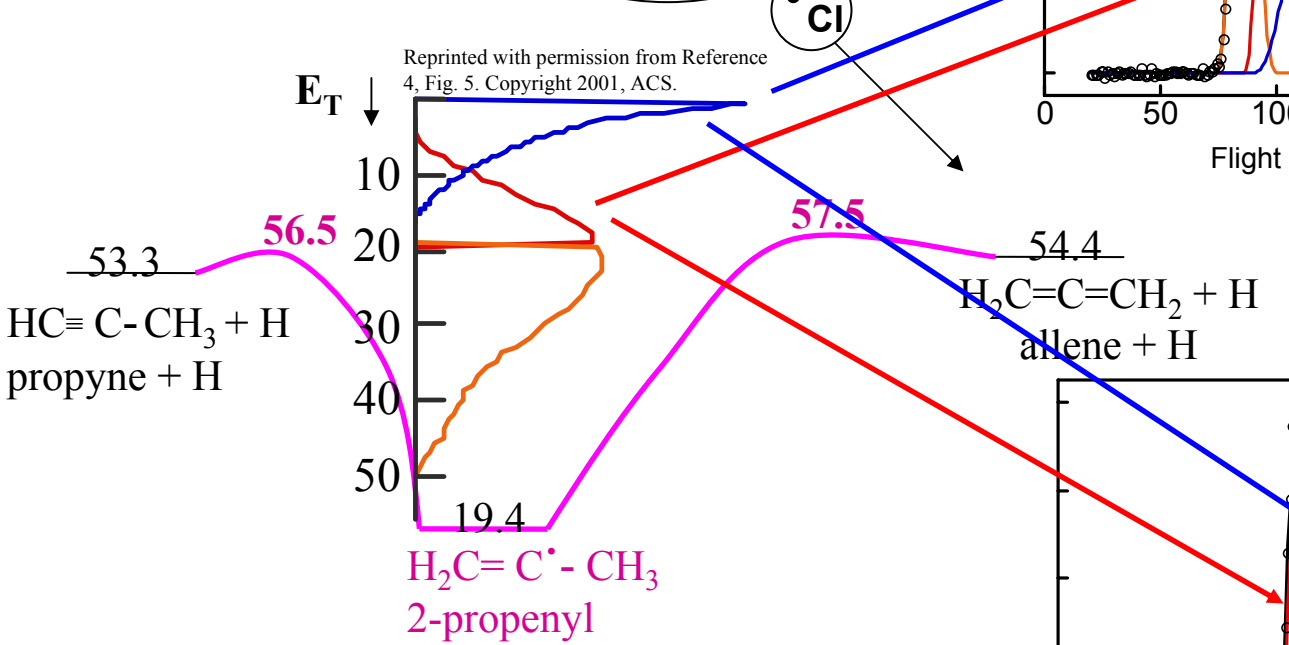
The radical co-fragments of the slower Cl atoms have higher internal energy so dissociate to C_3H_4 (mass 40) + H



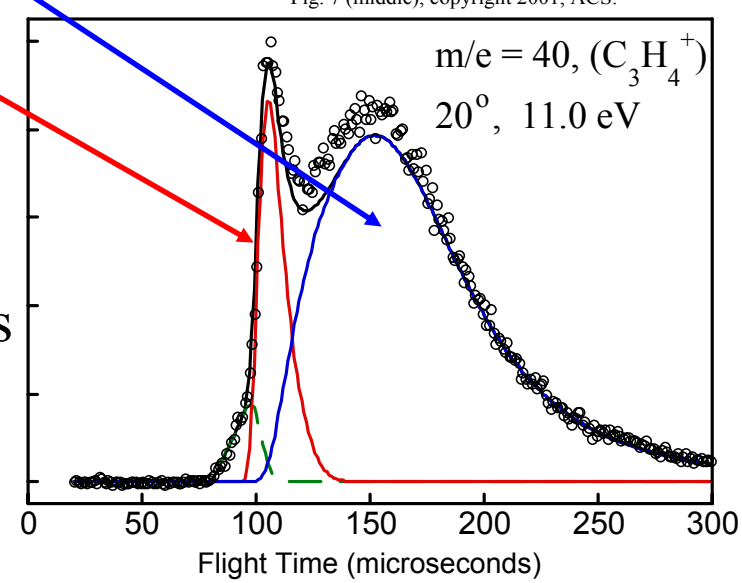
Reprinted with permission from Reference 1, Fig. 1 (top), copyright 2000, AIP and from Reference 4, Fig. 4 (top), copyright 2001, ACS.



Reprinted with permission from Reference 4, Fig. 5. Copyright 2001, ACS.



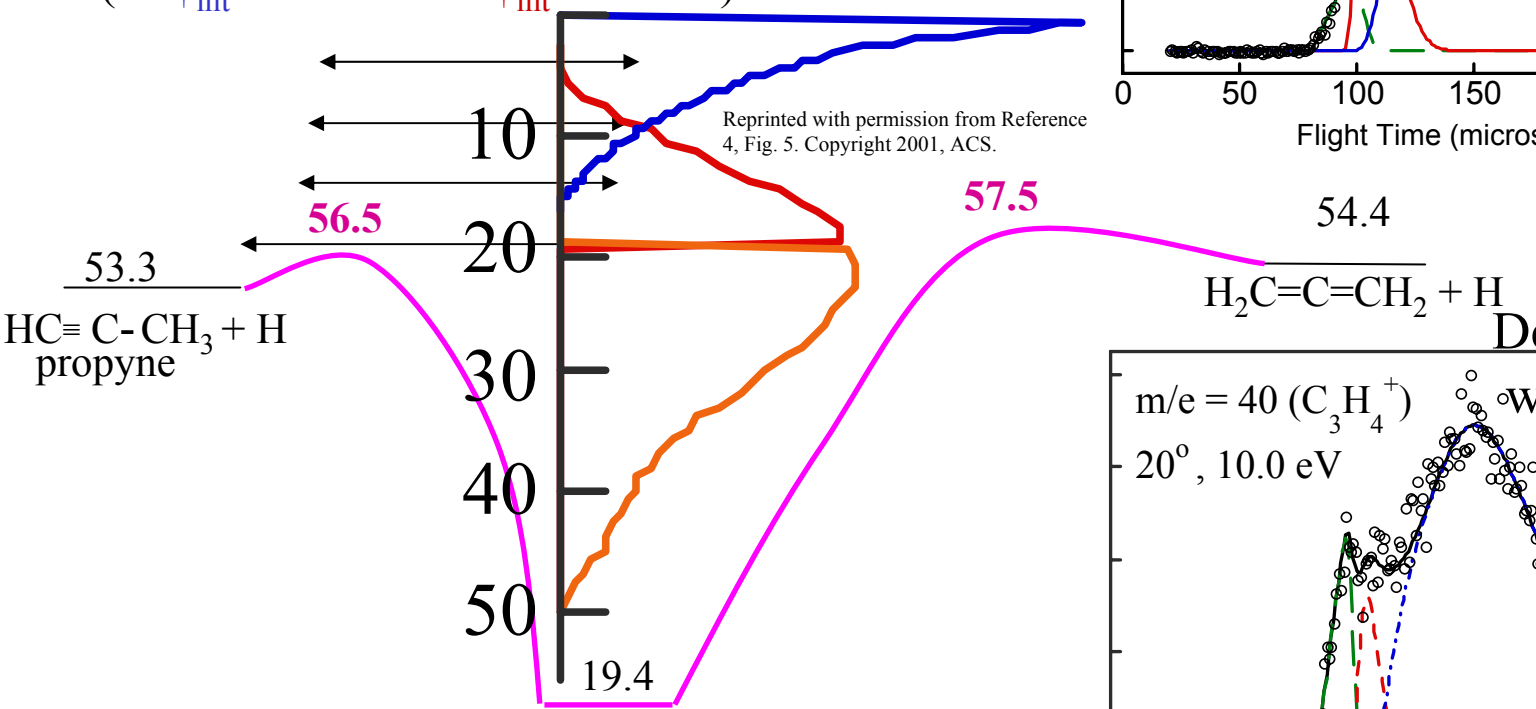
Reprinted with permission from Reference 1, Fig. 1 (middle), copyright 2000, AIP and from Reference 4, Fig. 7 (middle), copyright 2001, ACS.



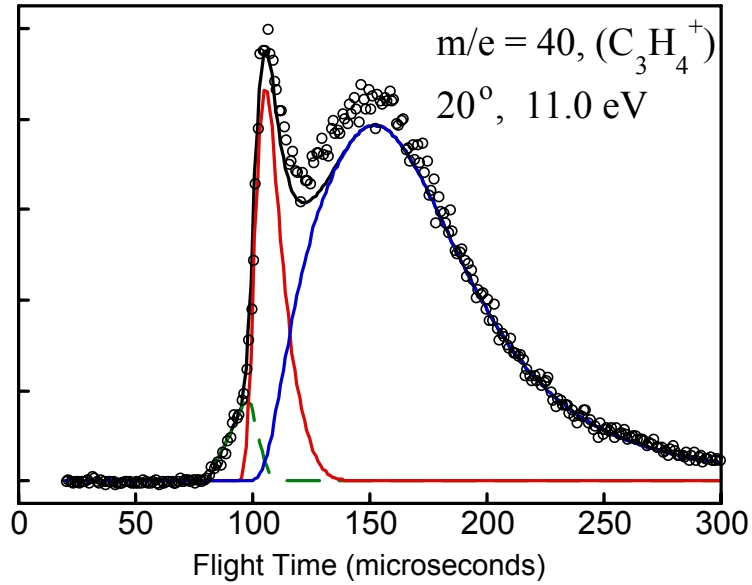
Allene/propyne products from radicals with a given internal energy can be identified by their velocity.

Expt'l vs. RRKM branching ratio as a function of internal energy in the radical

Data show allene yield is 2.0 (+.05/-.15) times higher for the higher internal energy radicals than the lower internal energy ones.
RRKM prediction is 2.2 times higher.
(<E†$_{int}$>=15 kcal <E†$_{int}$>=3 kcal)



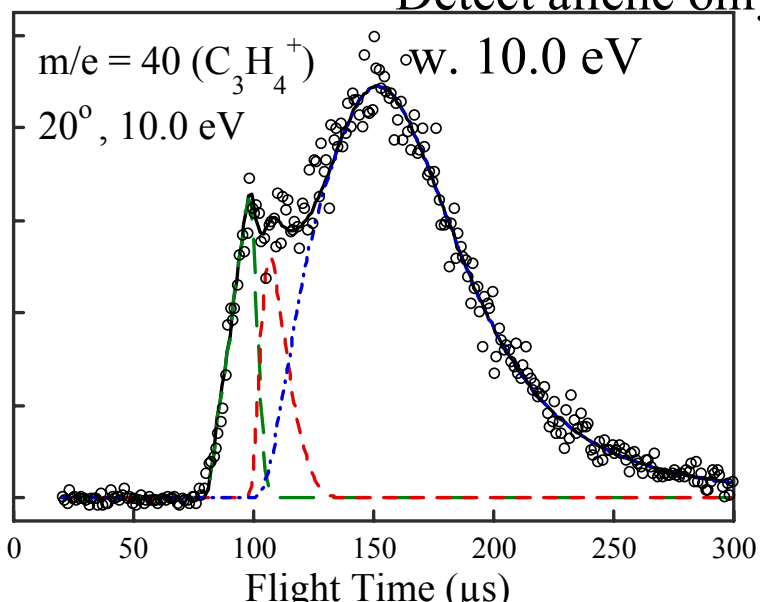
Reprinted with permission from Reference 4, Fig. 5. Copyright 2001, ACS.



Reprinted with permission from Reference 1, Fig. 1 (mddle), copyright 2000, AIP and from Reference 4, Fig. 7 (middle), copyright 2001, ACS.

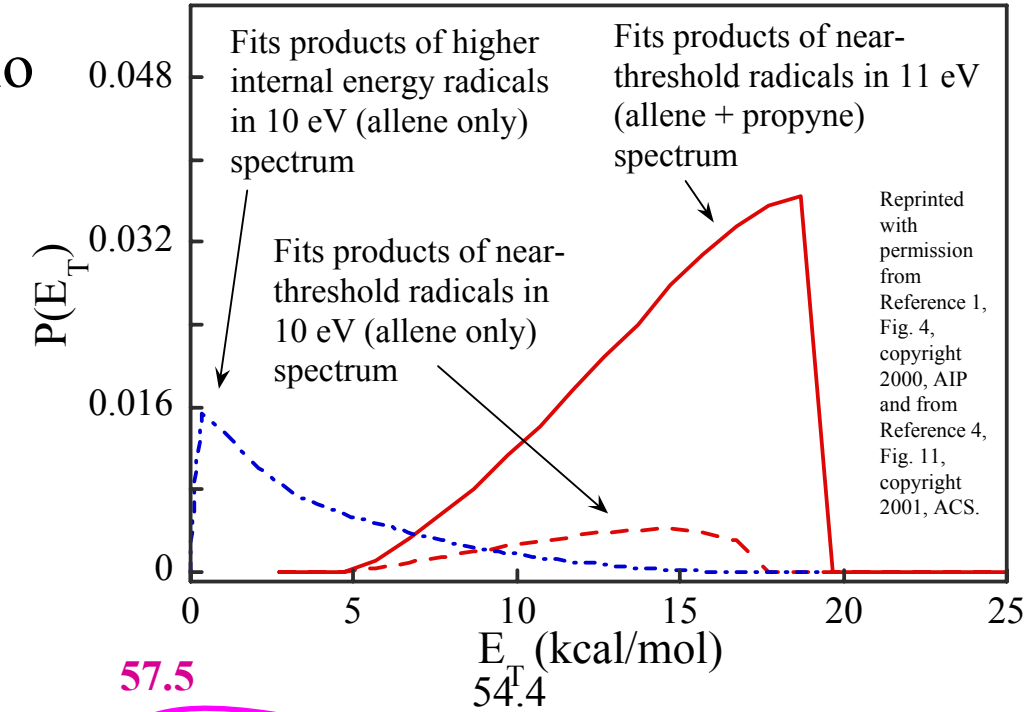
Reprinted with permission from Reference 1, Fig. 3, copyright 2000, AIP and from Reference 4, Fig. 10, copyright 2001, ACS.

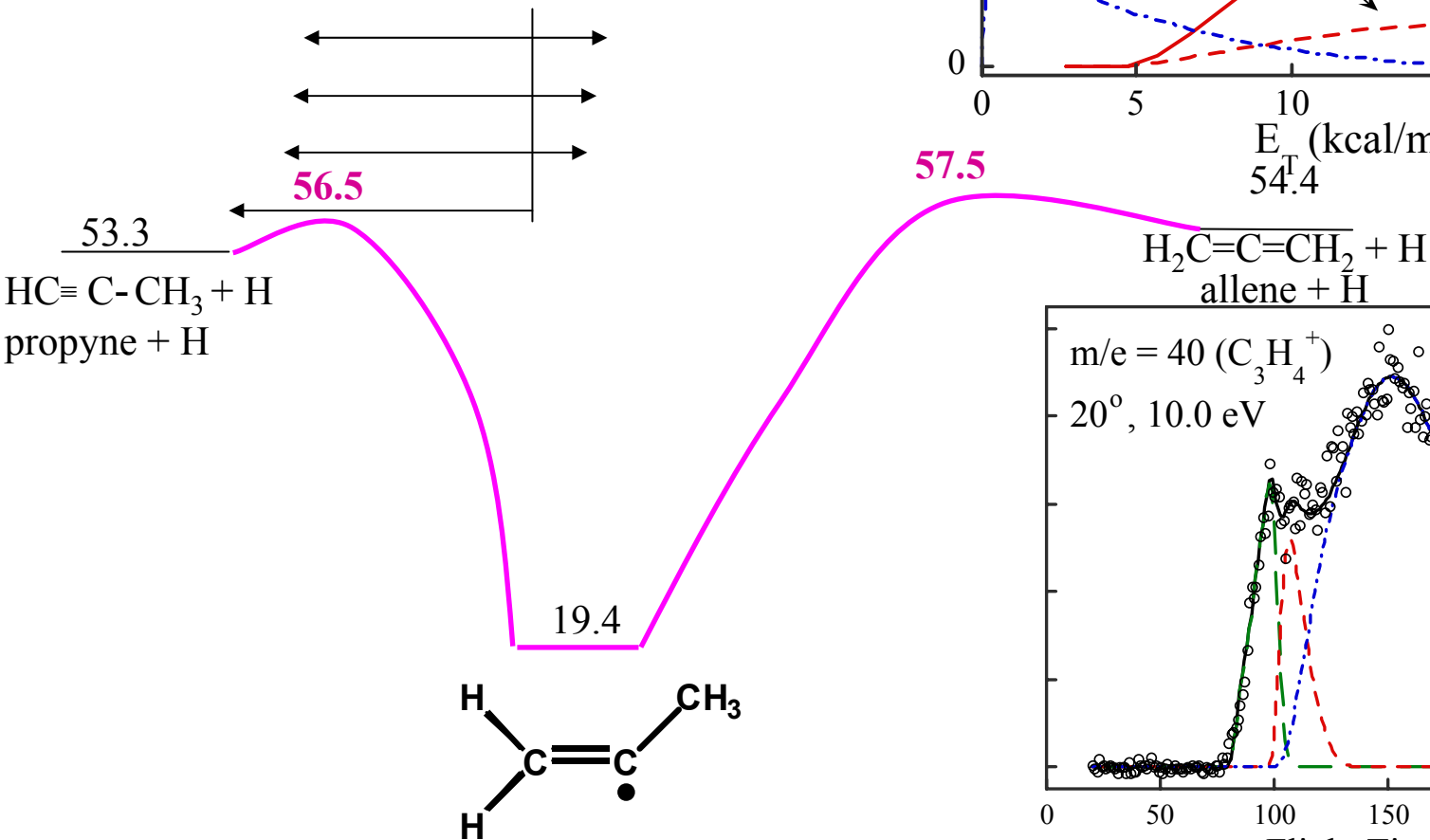
Detect allene only



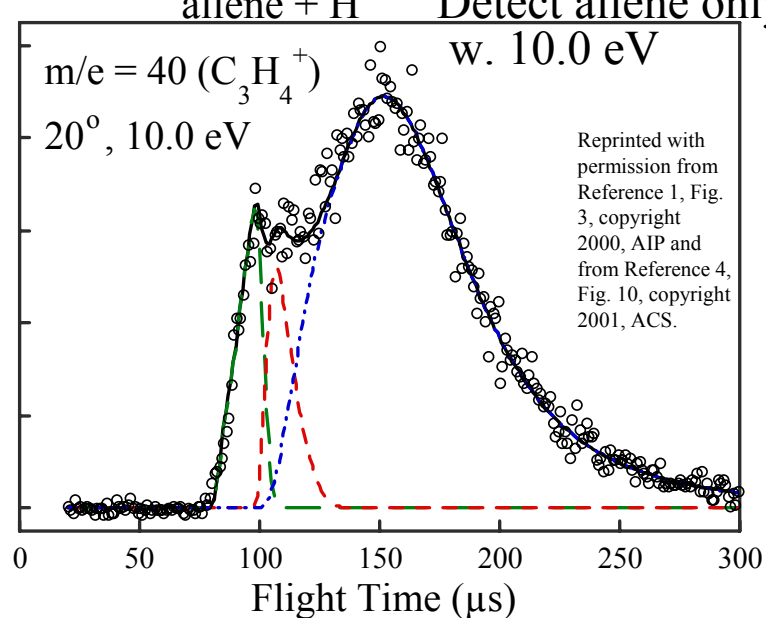
Expt'l vs. RRKM branching ratio

Data shows higher internal energy onset for allene + H and is fit well using RRKM prediction $k_a(E)/(k_a(E)+k_p(E))$

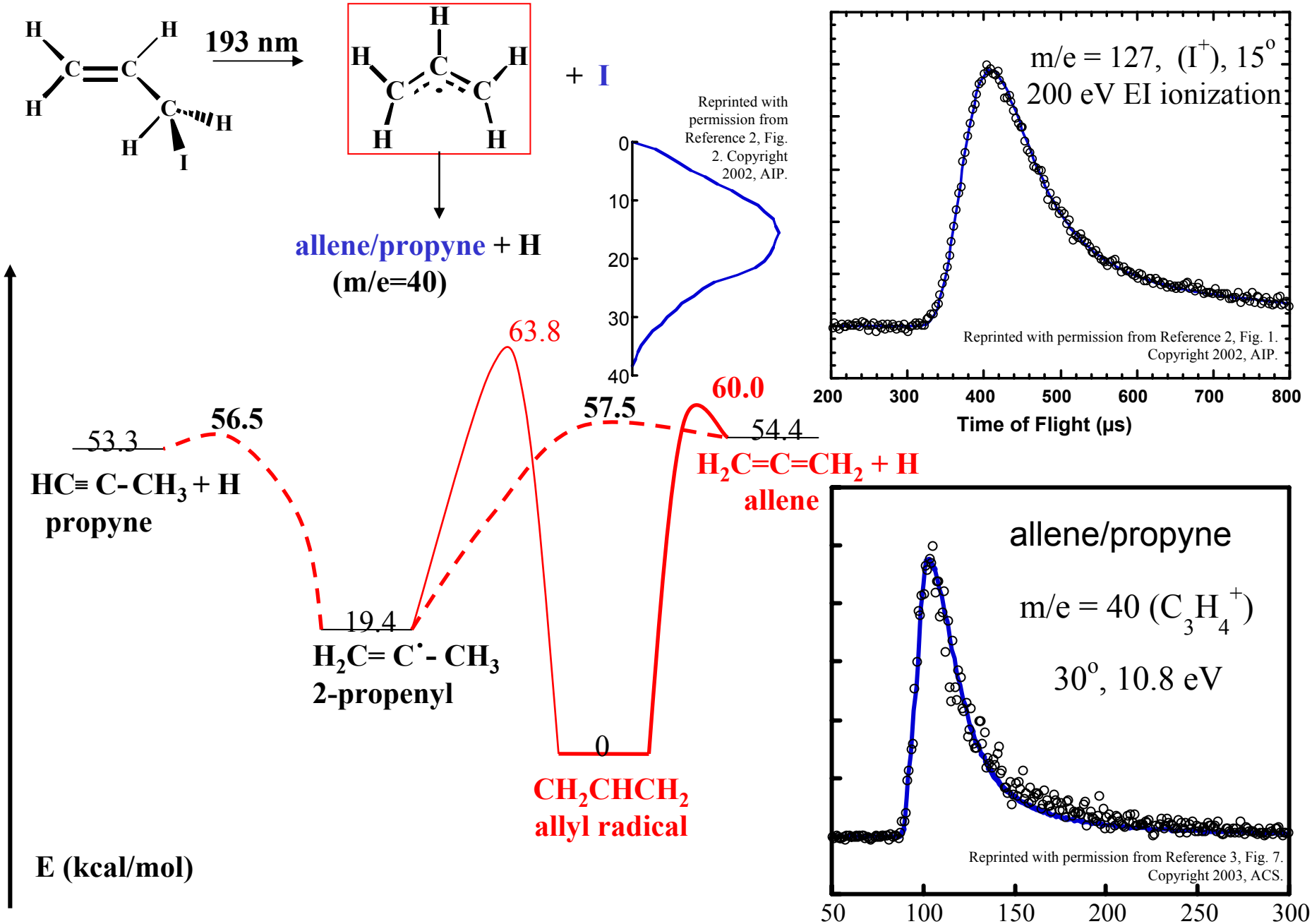




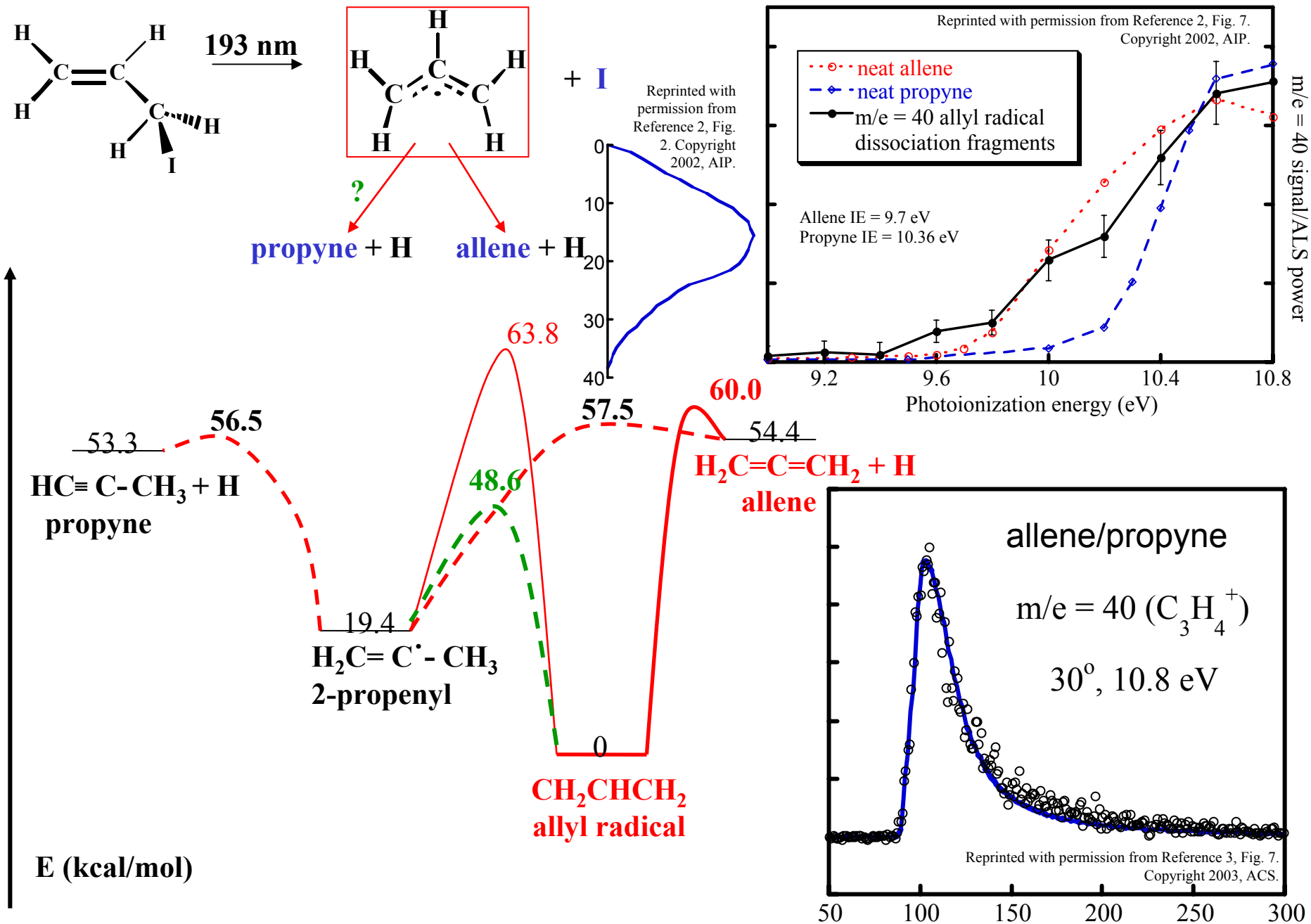
Detect allene only w. 10.0 eV



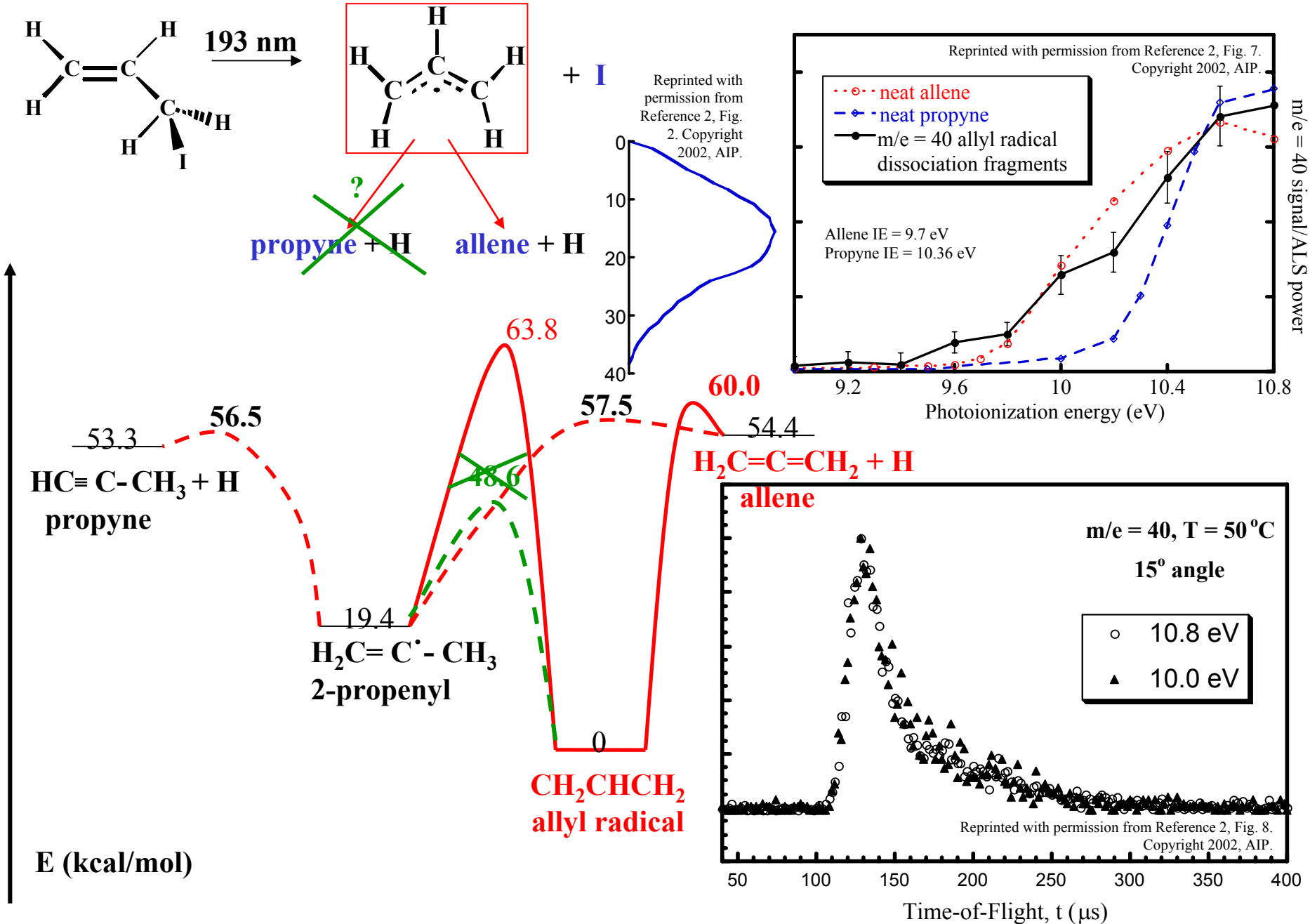
Allyl radical dissociation/isomerization (allyl iodide precursor)



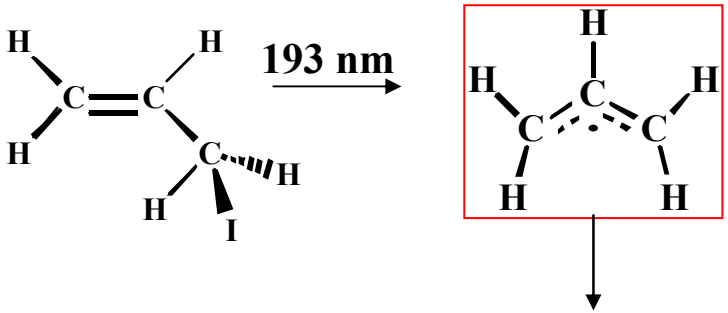
Allyl radical dissociation/isomerization (allyl iodide precursor)



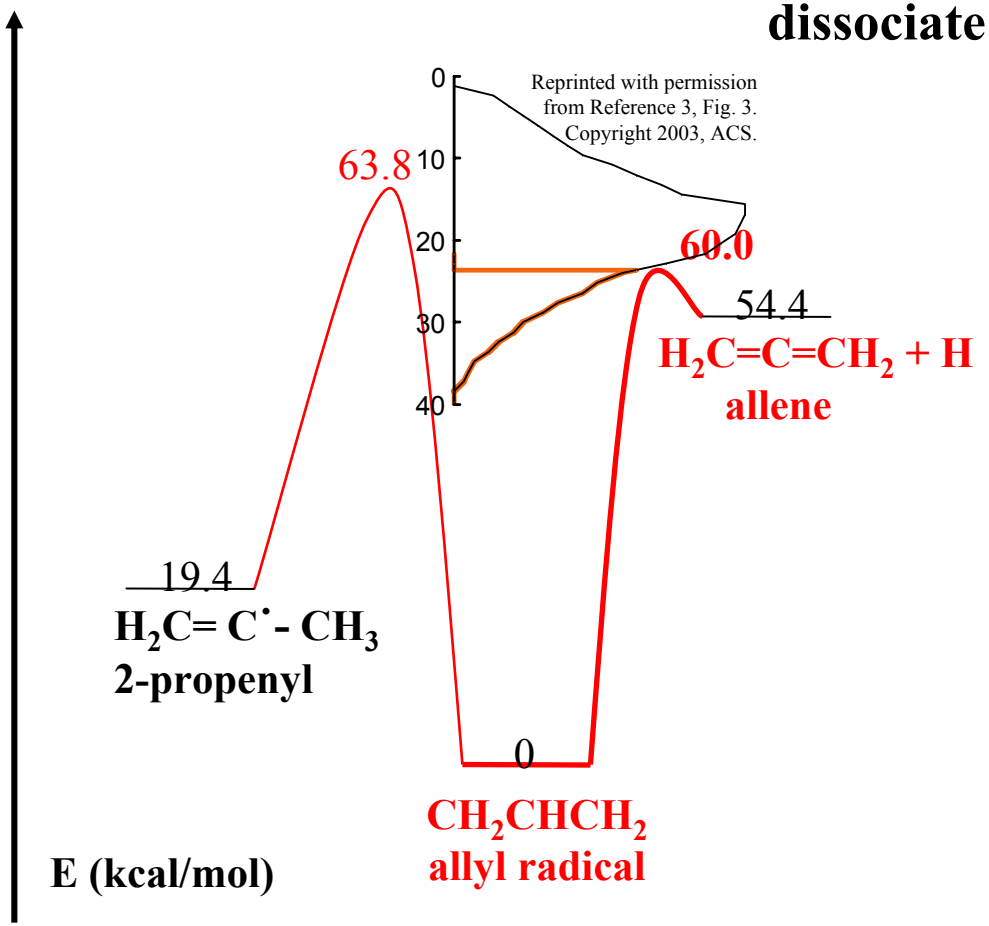
Allyl radical dissociation/isomerization (allyl iodide precursor)

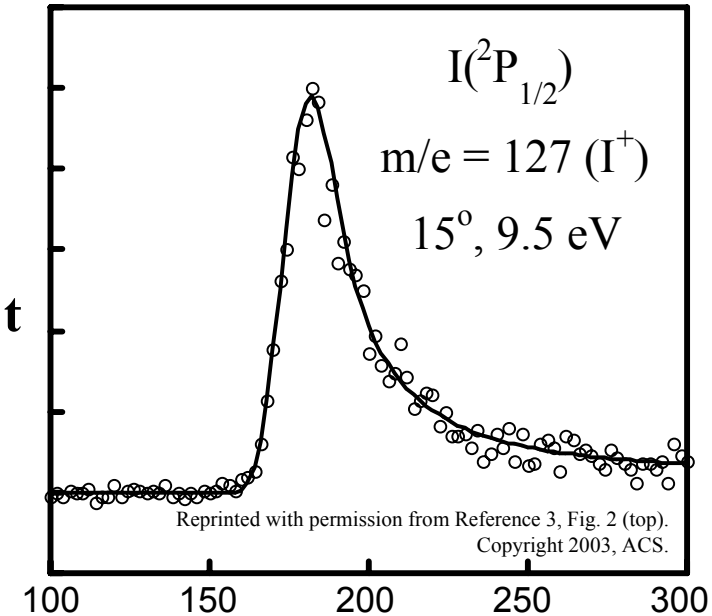


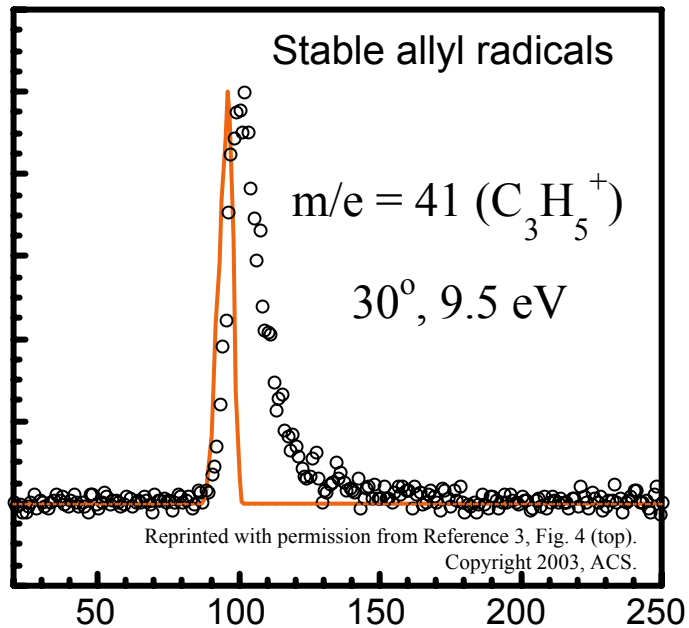
A minor $I(^2P_{1/2})$ channel produces near-threshold allyl radicals



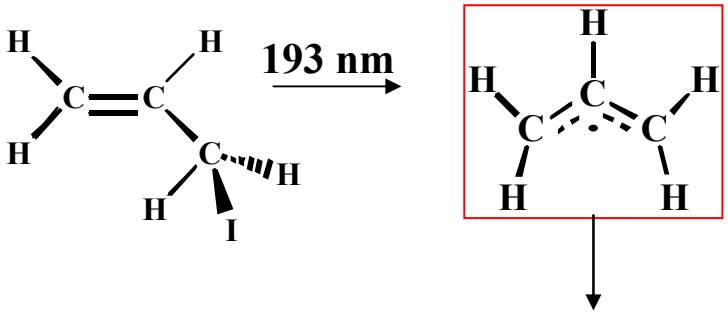
Which allyl radicals don't dissociate?







A minor $I(^2P_{1/2})$ channel produces near-threshold allyl radicals

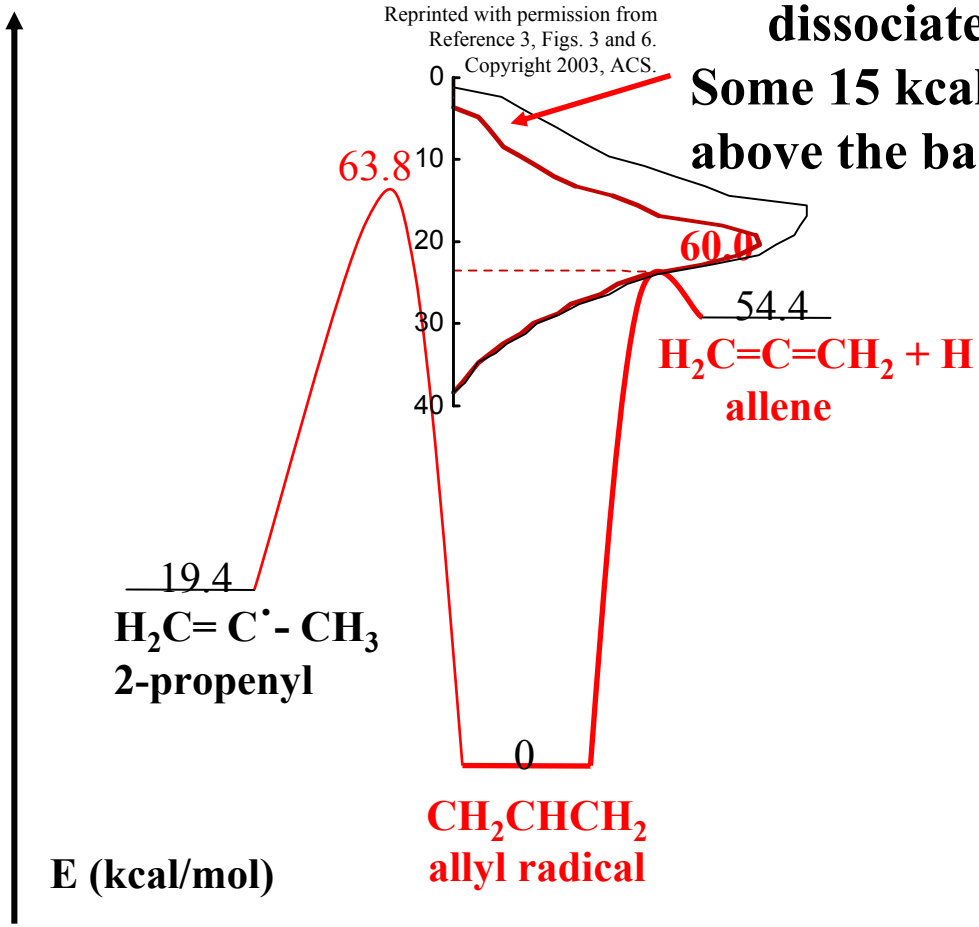


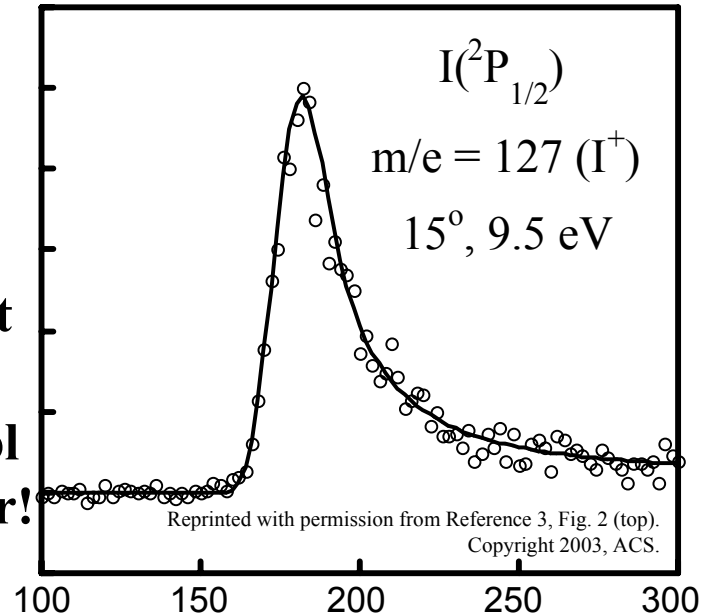
allene + H

Reprinted with permission from Reference 3, Figs. 3 and 6. Copyright 2003, ACS.

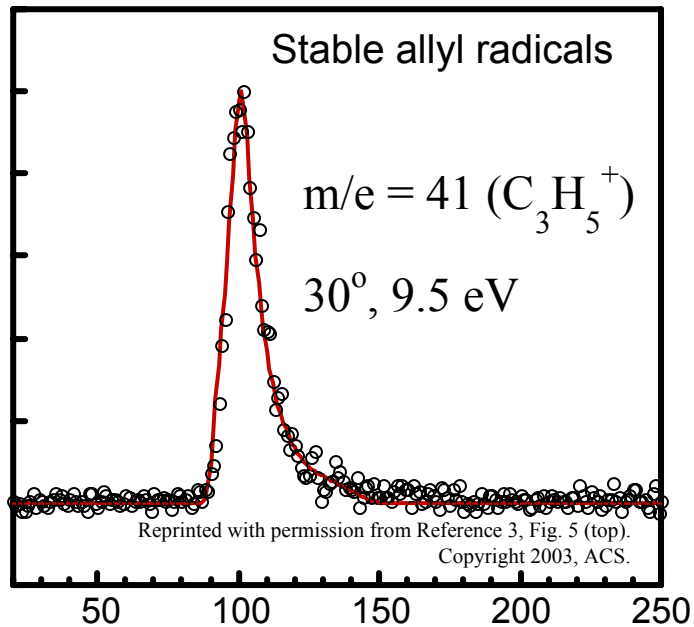
Which allyl radicals don't dissociate?

Some 15 kcal/mol above the barrier!



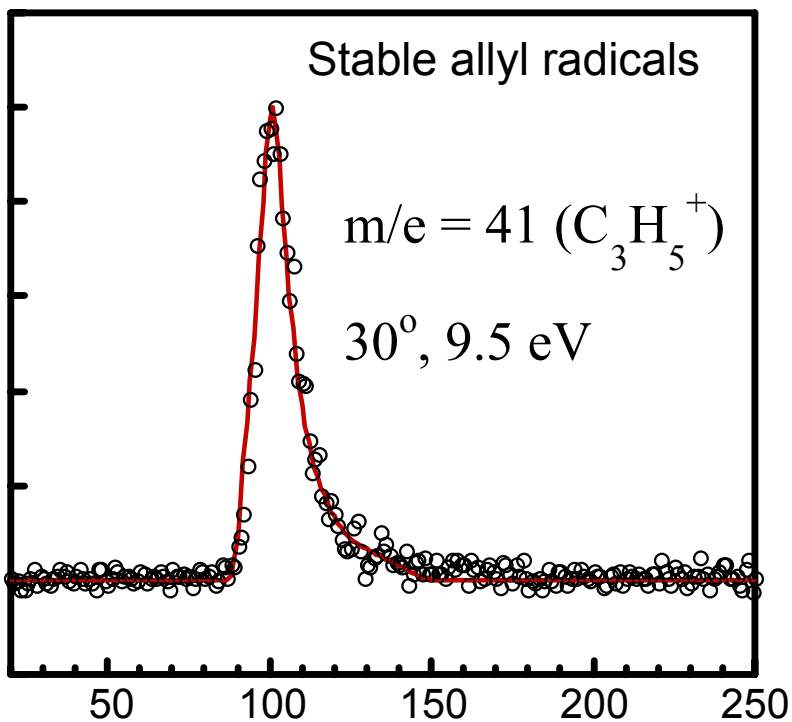


Reprinted with permission from Reference 3, Fig. 2 (top). Copyright 2003, ACS.

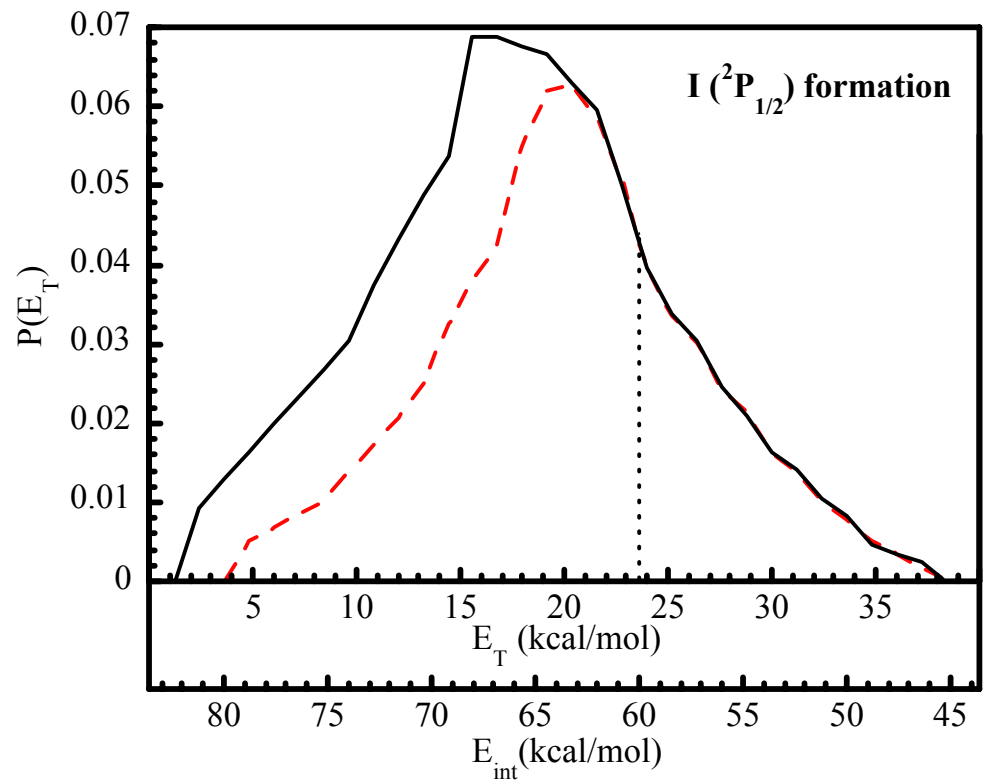


Reprinted with permission from Reference 3, Fig. 5 (top). Copyright 2003, ACS.

How can allyl radicals be stable with internal energies over 15 kcal/mol in excess of the C-H bond fission barrier?

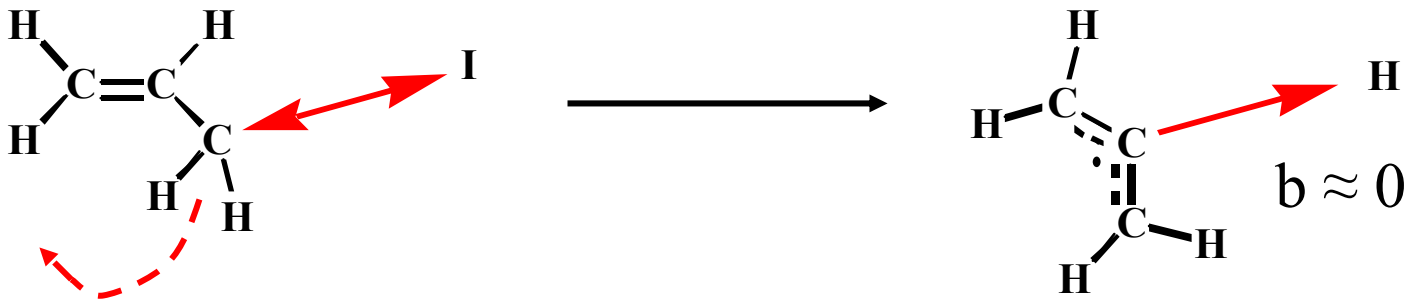


Reprinted with permission from Reference 3, Fig. 5 (top). Copyright 2003, ACS.



Reprinted with permission from Reference 3, Figs. 3 and 6. Copyright 2003, ACS.

Nascent allyl radicals stable due to a centrifugal barrier to loss of an H atom from the central carbon atom



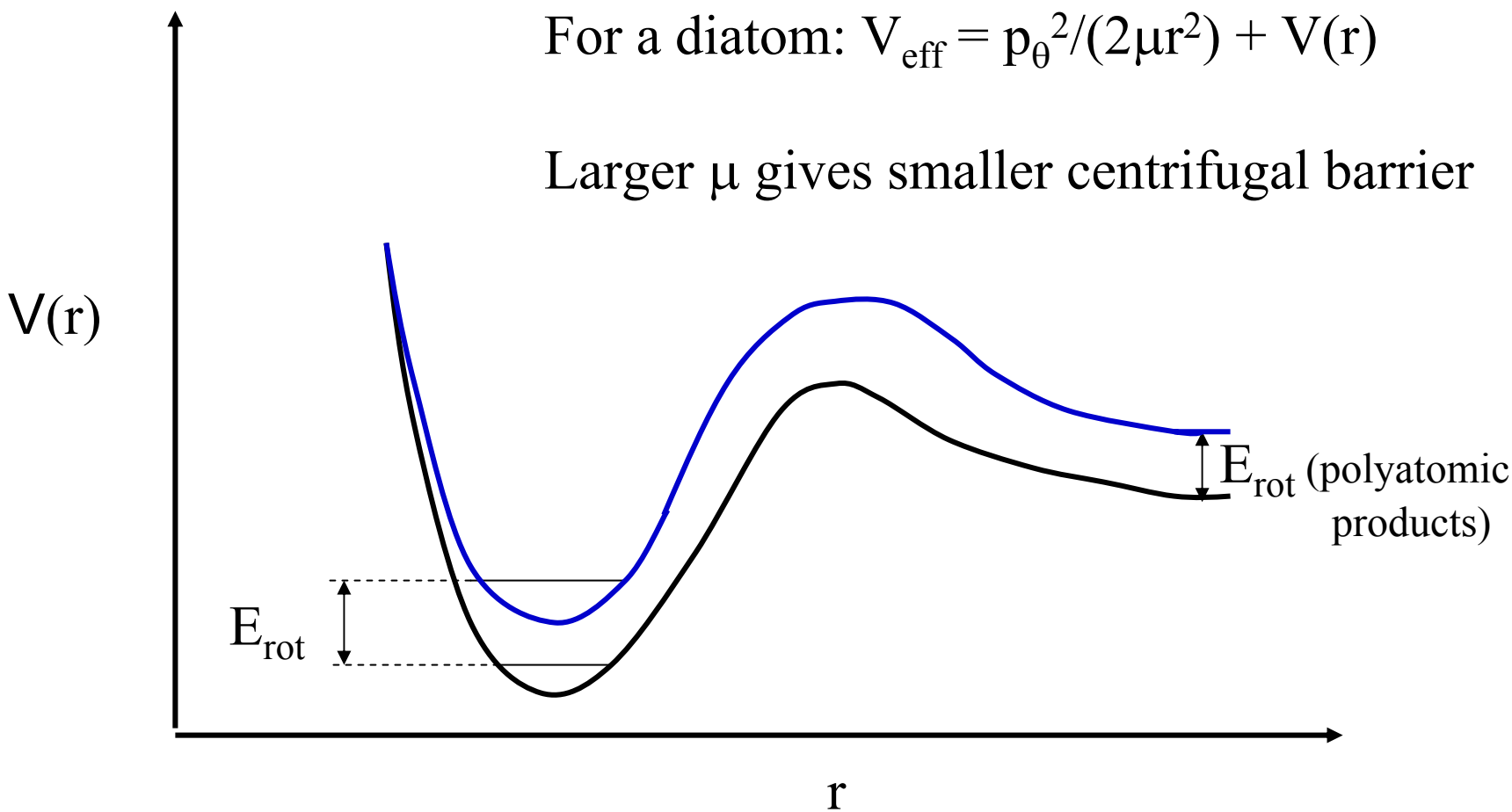
- High translational recoil and long lever arm to the C_3H_5 center of mass results in significant partitioning of energy to rotation in the nascent allyl radical (19 kcal/mol when E_T(C-I fission) = 24 kcal)
- Much of this rotational energy must appear in rotational energy of allene because the orbital angular momentum of the H + allene product recoil, $|\mathbf{L}| = \mu |\mathbf{v_{rel}}| b$, is small due to the near zero impact parameter, b and the small reduced mass, μ
- Thus the barrier to unimolecular dissociation is higher than expected

Centrifugal Barrier

$$L_{allyl} = \mu \left| \mathbf{v_{rel}} \right| b + L_{allene}$$

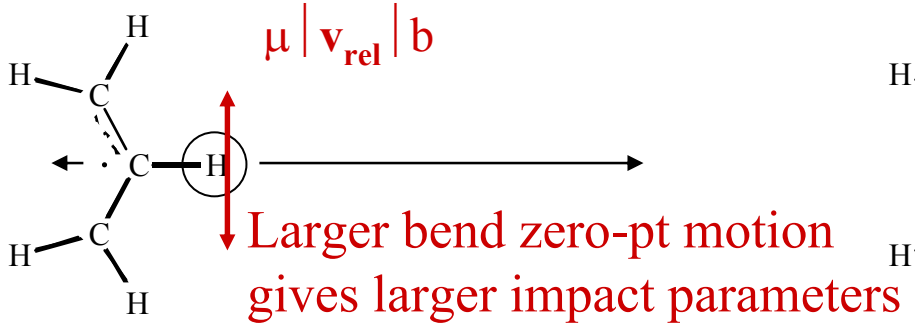
For a diatom: $V_{eff} = p_\theta^2/(2\mu r^2) + V(r)$

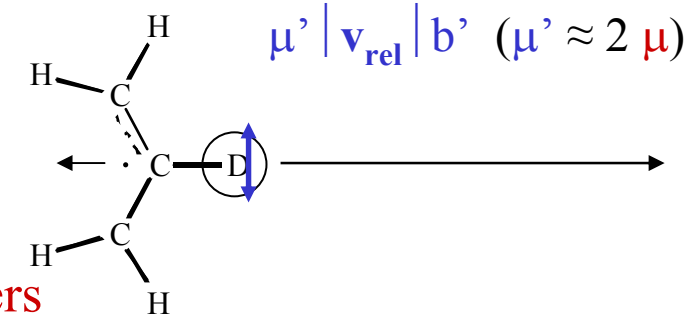
Larger μ gives smaller centrifugal barrier



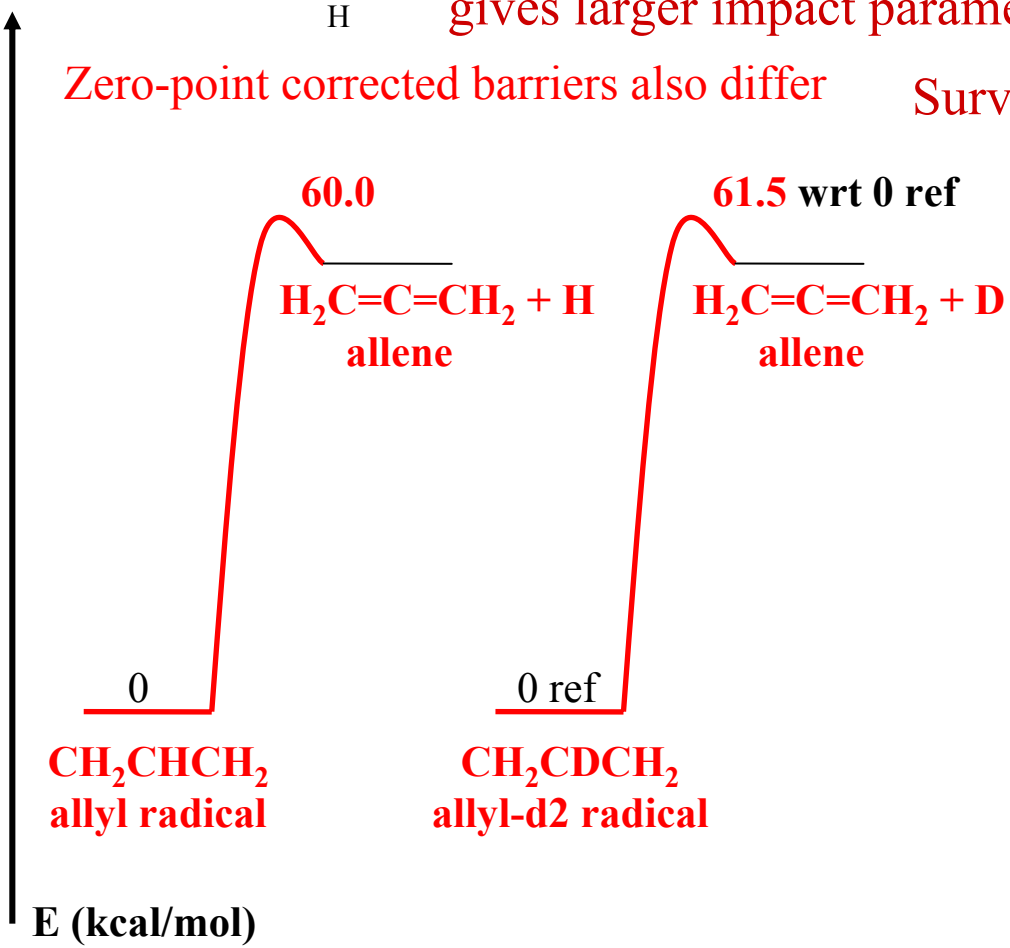
Alter the centrifugal barrier by using allyl-d2 radicals

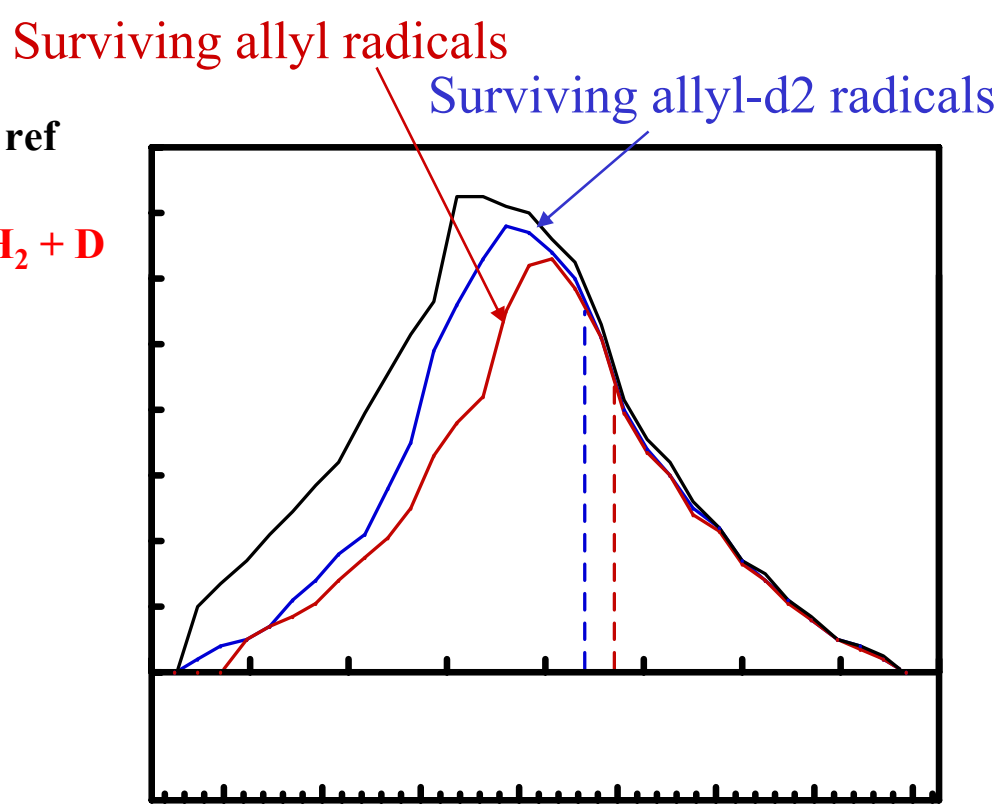
Larger μ gives smaller centrifugal barrier, but what about b vs. b'?





Zero-point corrected barriers also differ





Reprinted with permission from Reference 3, Figs. 3 and 6.
Copyright 2003, ACS.

References

The figures presented here are reproduced with copyright permission from:

1. "Internal Energy Dependence of the H + Allene / H + Propyne Product Branching from the Unimolecular Dissociation of 2-Propenyl Radicals," J. A. Mueller, J. L. Miller, L. J. Butler, F. Qi, O. Sorkhabi, and A. G. Suits, J. Phys. Chem. A 104, 11261-4 (2000).

2. "Primary and Secondary Dissociation from Allyl Iodide Excited at 193 nm: Centrifugal Effects in the Unimolecular Dissociation of the Allyl Radical," D. E. Szpunar, M. L. Morton, L. J. Butler, and P. M. Regan, J. Phys. Chem. B 106, 8086-8095 (2002).

3. "Photodissociation of allyl-d_2 iodide excited at 193 nm: Stability of highly rotationally excited H_2CDCH_2 radicals to C-D fission," D. E. Szpunar, Y. Liu, M. J. McCullagh, L. J. Butler, and J. Shu, J. Chem. Phys. 119, 5078-5084 (2003).

4. "Competing isomeric product channels in the 193 nm photodissociation of 2-chloropropene and in the unimolecular dissociation of the 2-propenyl radical," J. A. Mueller, B. F. Parsons, L. J. Butler, F. Qi, O. Sorkhabi, and A. G. Suits J. Chem. Phys. 114, 4505-4521 (2001).