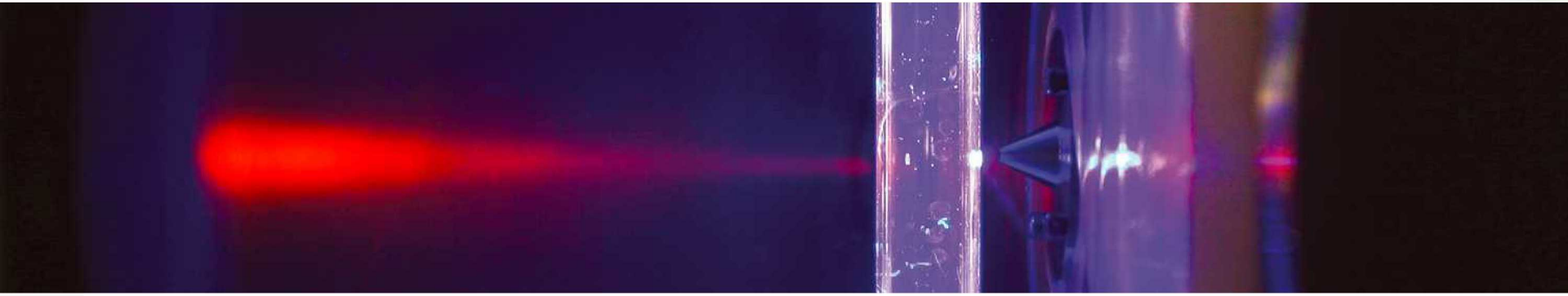
SAND2019-0028C

COMBUSTION RESEARCH FACILITY

Photodissociation of Acetylacetone: Photoionization and Threshold Photoelectron Spectroscopy Reveal Much More than OH Radicals



David L. Osborn

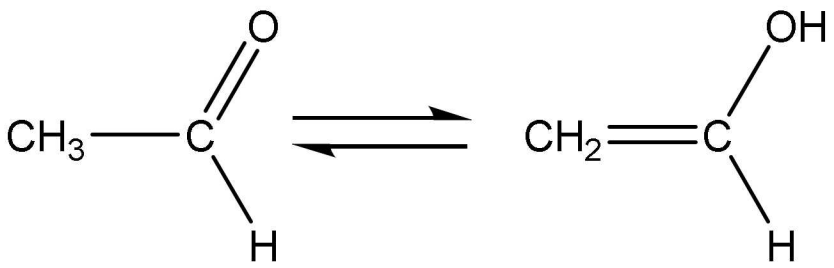
Combustion Research Facility, Sandia National Laboratories

Photon Tools for Physical Chemistry 2019

January 8 – 11, 2019

Sandia National Laboratories

Keto – Enol Tautomerization



$$K(300K) = \frac{[\text{vinyl alcohol}]}{[\text{acetaldehyde}]} \sim 3 \times 10^{-7}$$

acetaldehyde
E = 0

vinyl alcohol
E = +10.3 kcal/mol

Enols Are Commo
in Hydrocarbo

Craig A. Taatjes,[1,2*] Nils Ha
James A. Miller,[1] Juan P. Senosia
Fei Qi,[1,3] Liusi Sheng,[3] Yunwu
Juan Wang,[4] Phillip R. Westmo
Tina Kasper,[6] Katharina

SCIENCE VOL 308 2

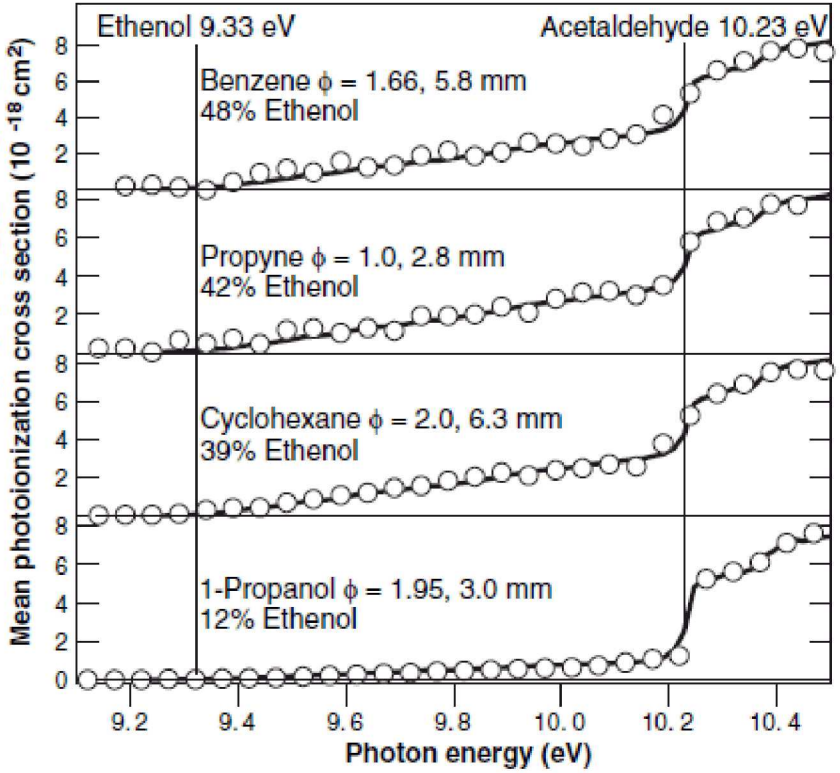
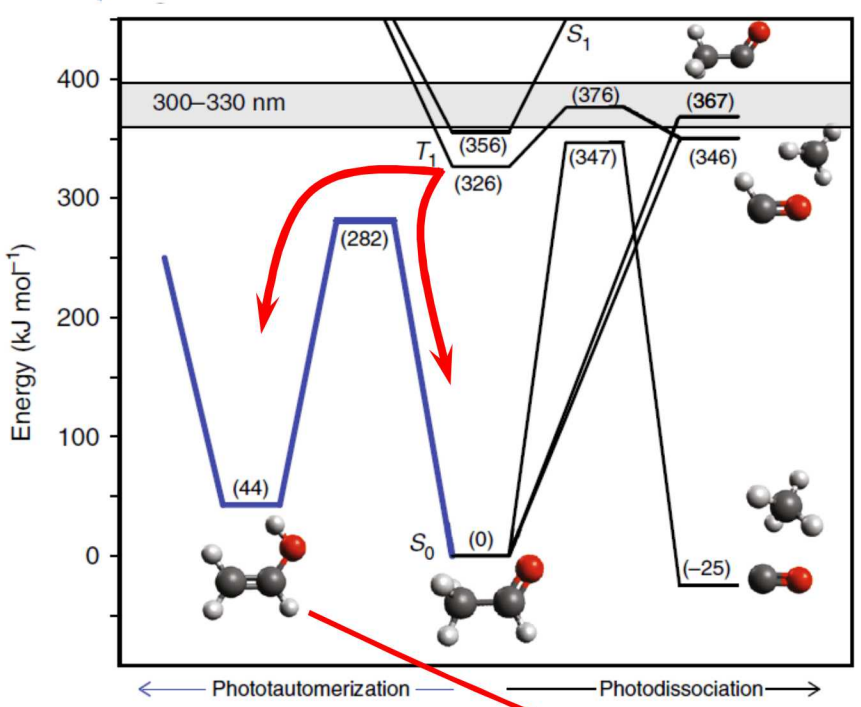


Photo-tautomerization by Sunlight?

Photoisomerization of aldehydes to enols



Dylan Millet

Scott Kable

Meredith Jordan

Shaw et al., Nat. Comm. **9**, 2584 (2018)

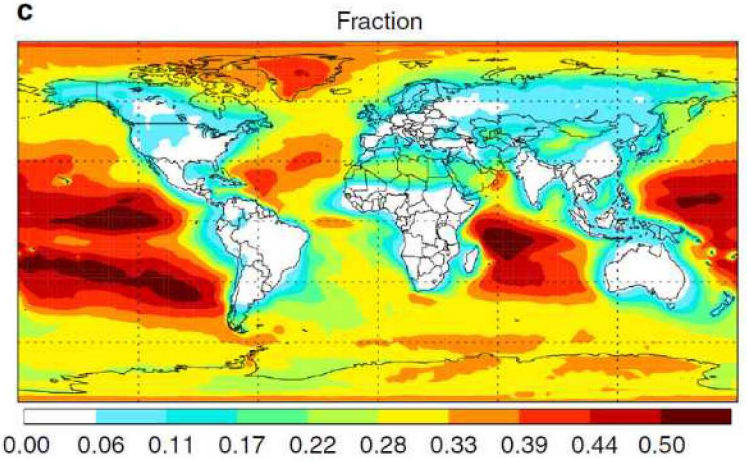


Fig. 5 Column-integrated formic acid (FA) production rates as simulated by the GEOS-Chem 3D chemical transport model as a function of latitude and

Clubb et al., *JPC Lett* **3**, 3522 (2012)

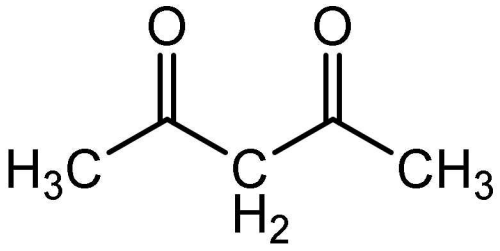
Shaw et al., *Nature Communications* **9**, 2584 (2018)

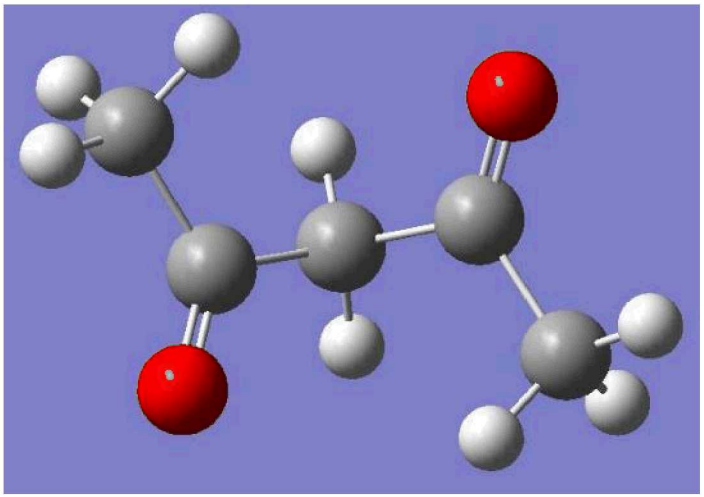
+ OH (+O_2) → HCOOH

So, Wille, da Silva, *Environ. Sci. Technol.* **48**, 6694 (2014)

What's Unusual About Acetyl Acetone?

- CO chromophore
- CC chromophore
- Conjugation
- Hydrogen bond



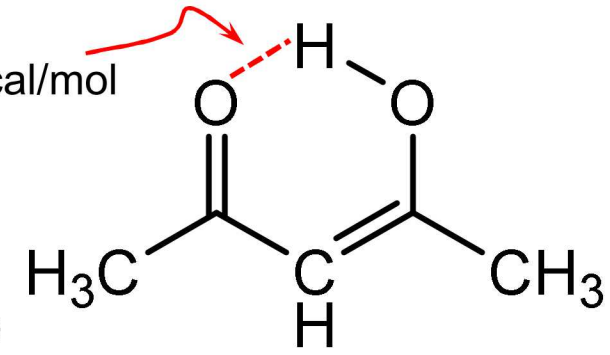


diketo-AcAc

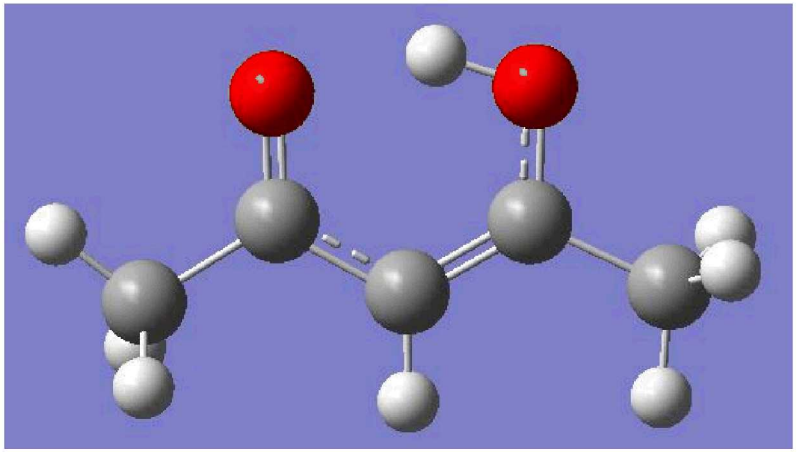
4%
At 300K, gas phase
96%

Nakanishi, Bull Chem. Soc. Jap. **50**, 2255 (1977)

12 kcal/mol



~ 4 kcal/mol more stable than diketone

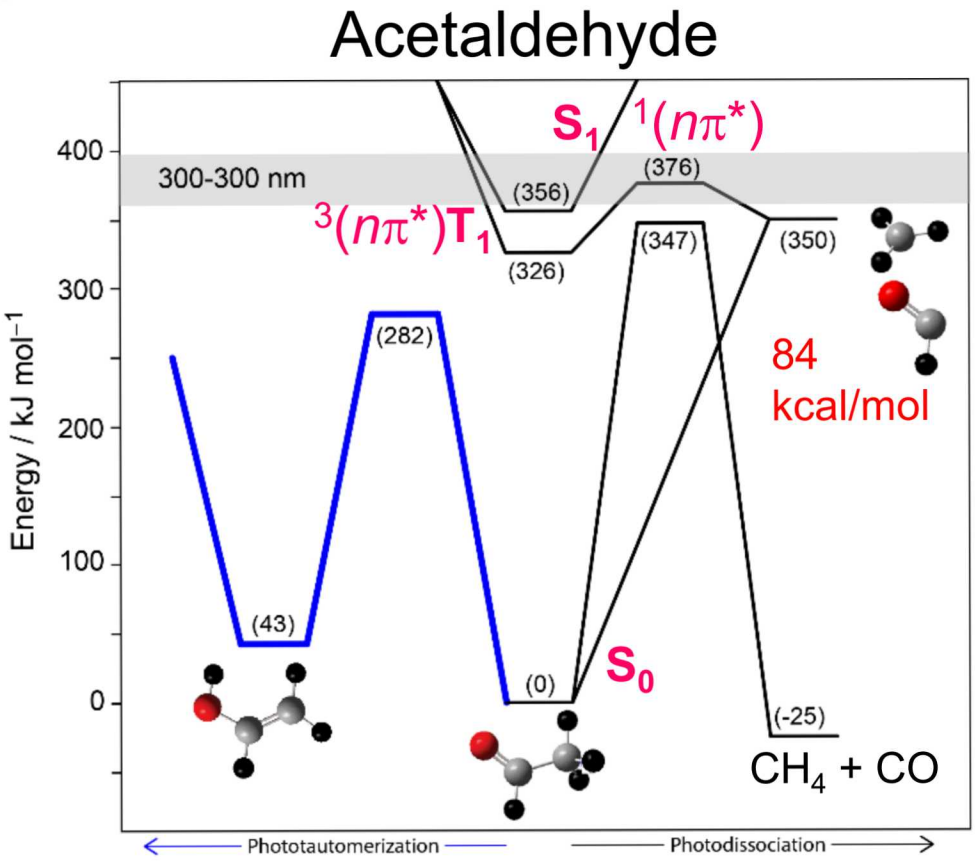


enolone-AcAc

Barrier to H atom transfer ~2.5 kcal/mol

Howard, Kjaergaard, Huang, Meuwly, J. Phys. Chem. A **119**, 7980 (2015)

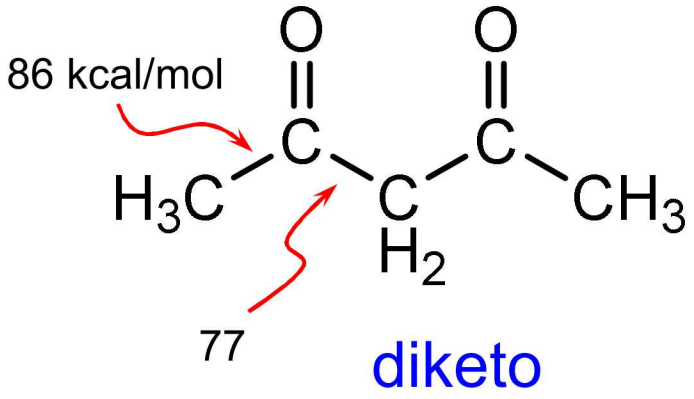
Background of Carbonyl Photochemistry

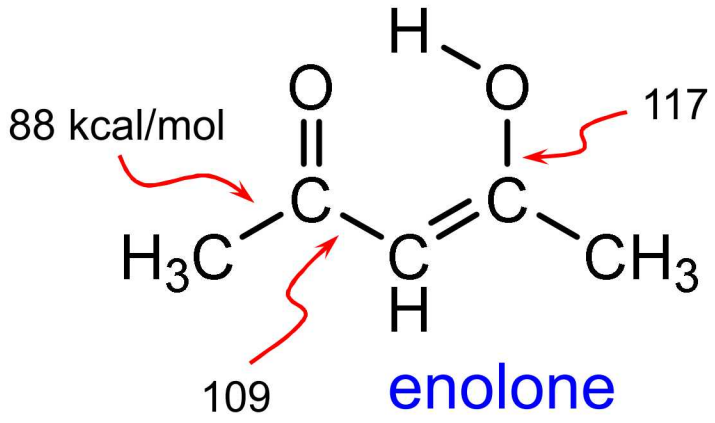


Courtesy of Scott Kable Group

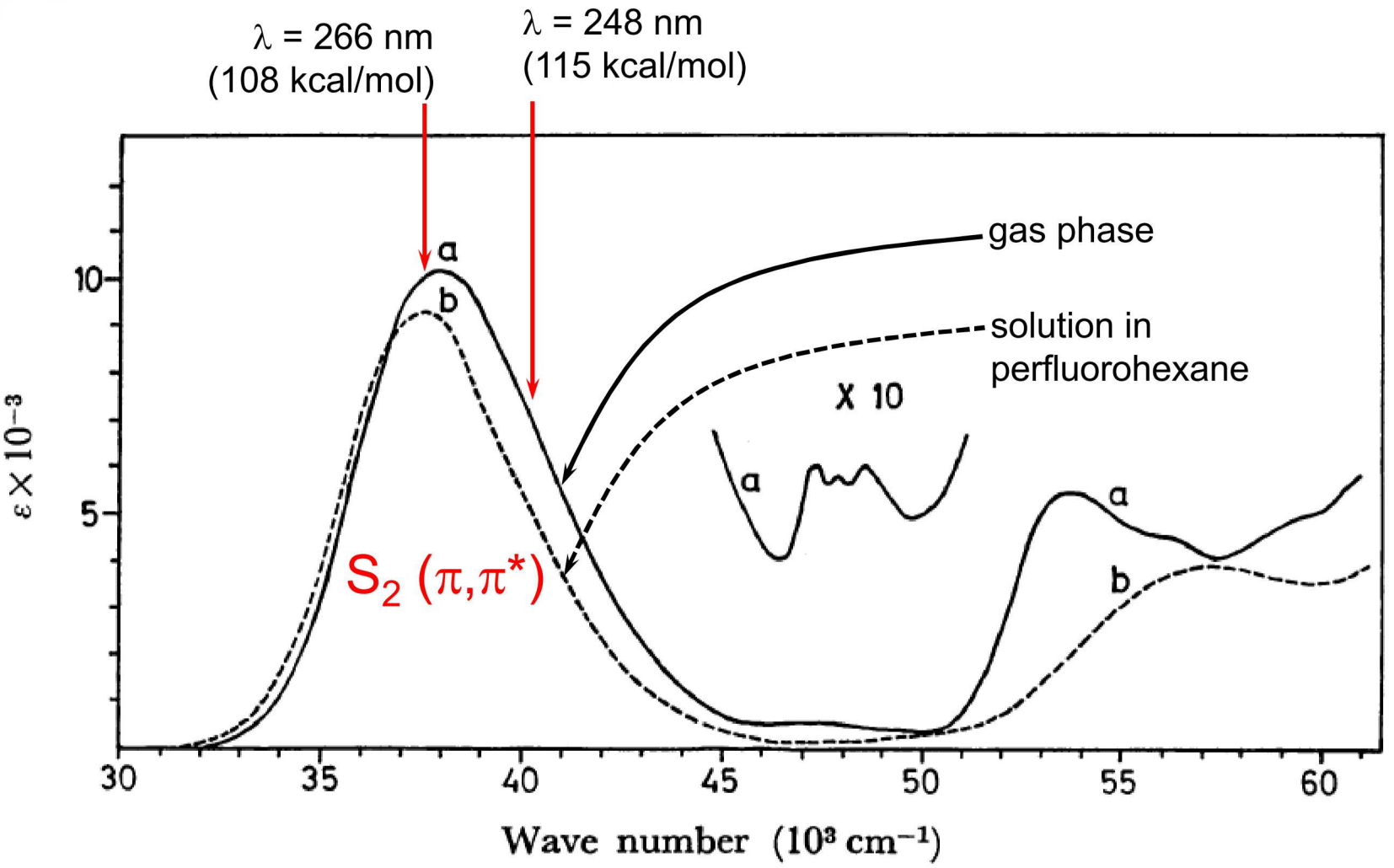
What Should We Expect From Acetyl Acetone Photochemistry?

- E-$S_2(\pi\pi^*)$ ← E-S_0 (266 nm)
- Yoon et al. (1999)
  - OH detected as product
  - Vibrationally cold
  - No fluorescence
- Nagashima (2001)
  - UV-induced enolone → diketo in cold matrix ; No photoproducts
- Upadhaya (2003)
  - Fast and slow OH production
- Xu & Zewail (2004)
  - Ultrafast electron diffraction
  - OH dominant, S_1 → T_1 with 247 ps lifetime
- Chen (2006)
  - Theory: S_2 → S_1 → T_2 → T_1 → OH product
  - No H_2O, no photo-tautomerization
- Poisson (2007), ultrafast valence photoionization
  - S_2 → S_1 in 1.4 ps, S_1 → T_1 ~ 250 ps
- Bhattacherjee & Leone (2017)
  - UV pump, soft x-ray probe
  - S_2/S_1 → T_1 with 1.5 ps time constant





UV Absorption of AcetylAcetone



H. Nakanishi, Bulletin of the Chemical Society of Japan, **50**, 2255 (1977)

Multiplexed Photoionization

Advanced Light Source LBNL

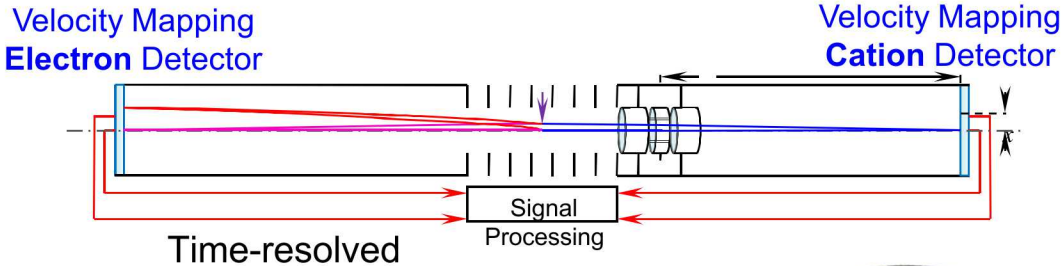
Swiss Light Source
Paul Scherrer Institut

λ = 248 or 266 nm

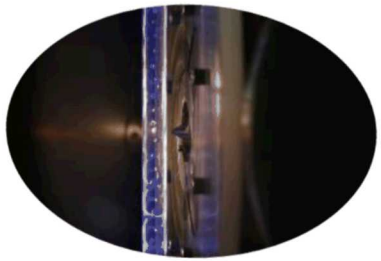
AcAc ⟶ Products

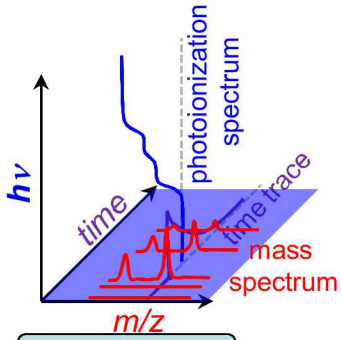
T = 300 - 600 K, P = 1 - 8 Torr

f_{rep} (TOF) = 50 kHz



Time-resolved
Photo-electron
Photo-ion
Coincidence (TR-PEPICO)





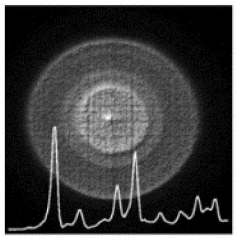
3-D Data

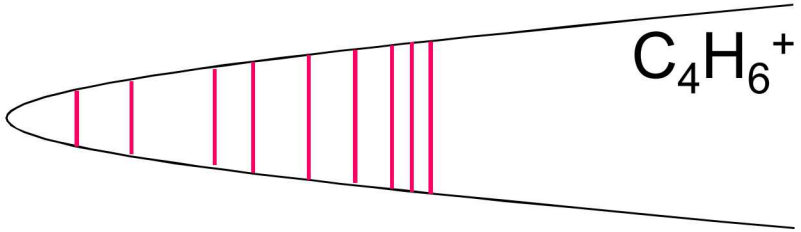
- Universal
- Multiplexed
- Sensitive
- Selective

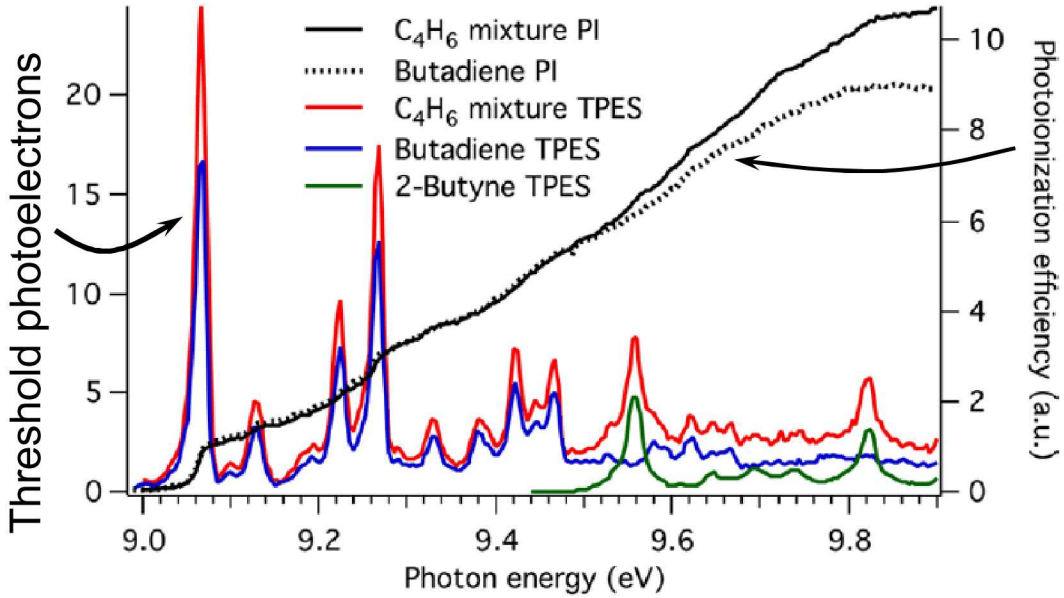
Photoelectron vs. Photoionization Spectroscopy

$$PI = \int [\text{cation vibrational levels}]\, dE$$

PE = [cation vibrational levels]

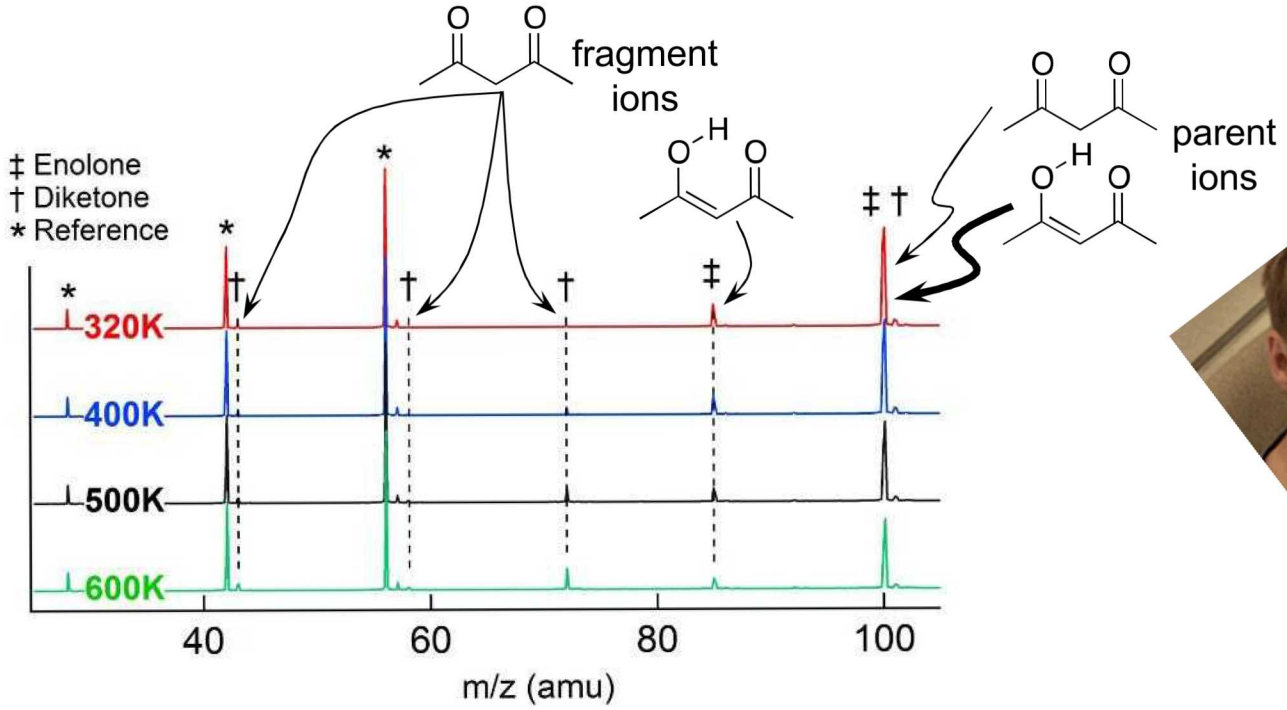






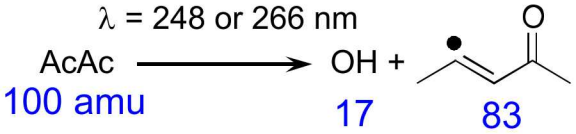
Swiss Light Source, Paul Scherrer Institut

Static Mass Spectrum of Acetyl Acetone

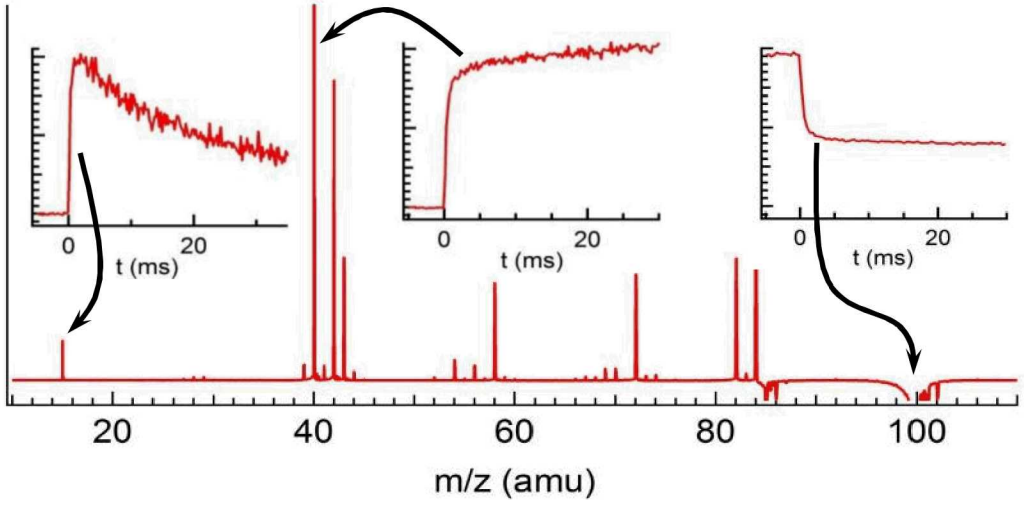


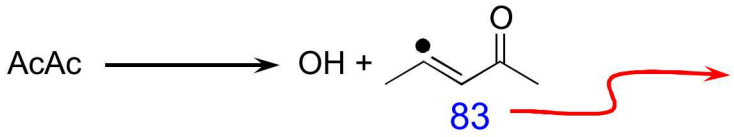
Ivan Antonov

What are the Photoproducts?



T = 300 - 600 K, P = 1 - 8 Torr





Summary

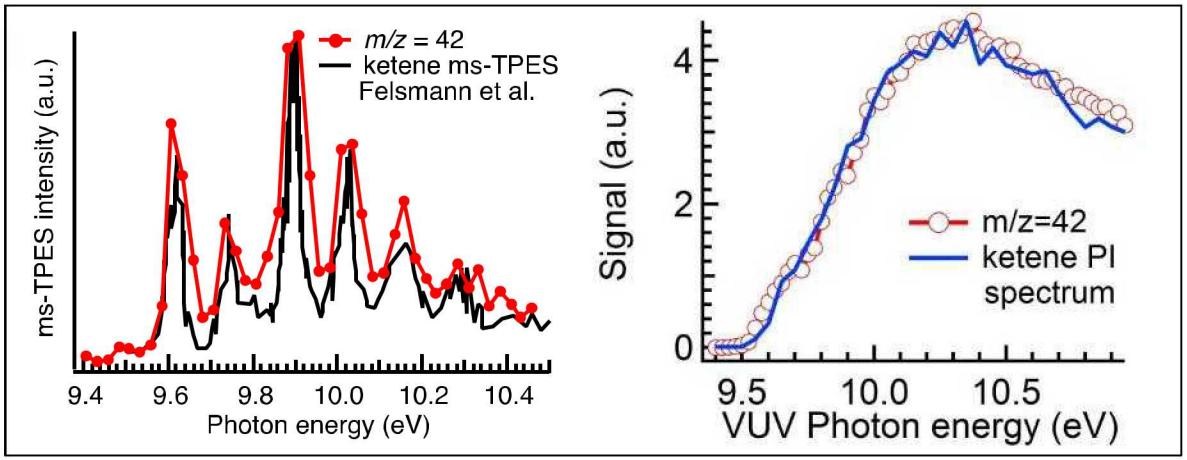
14 mass peaks, representing
15 species

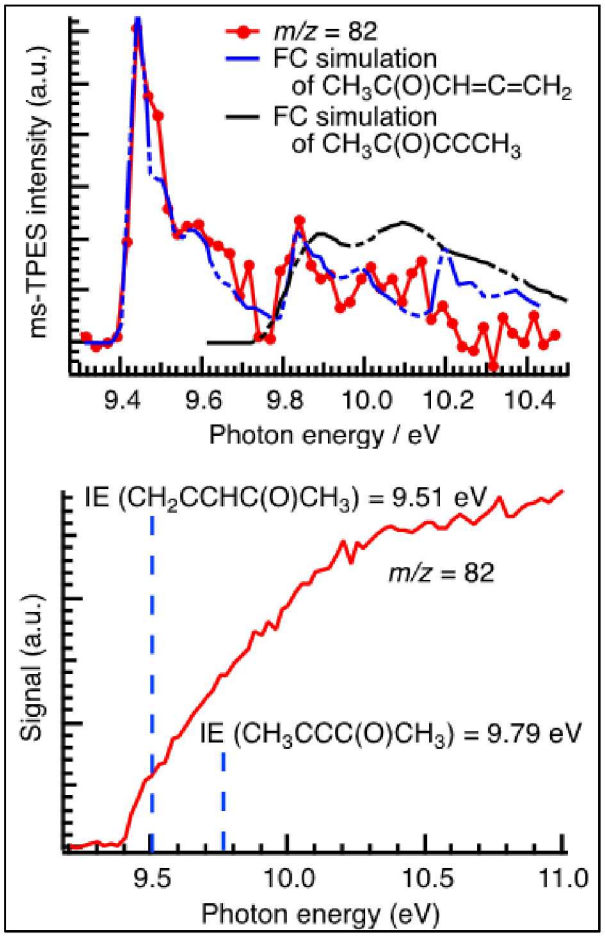
m/z	Species
15	CH3 (methyl radical)
16	CH4 (methane)
18	H2O (water)
29	Fragment ion of acetonyl radical [H2C-C(O)-CH3]
39	C3H3 (propargyl radical)
40	H3C-C≡C-H (propyne)
	H2C=C=CH2 (allene)
42	H2C=C=O (ketene)
43	CH3CO (acetyl radical)
	Fragment ion of diketo-Acetyl Acetone
58	H3C-C(O)-CH3 (acetone)
	H2C=C(OH)-CH3 (propen-2-ol)
	Fragment ion of diketo-Acetyl Acetone
72	Fragment ion of diketo-Acetyl Acetone
82	H2C=C=CH-C(O)-CH3 (1,2 pentadien-4-one)
84	O=C=CH-C(O)-CH3 (acetyl ketene)
85	Fragment ion of enolone-Acetyl Acetone
100	Parent ion, enolone-Acetyl Acetone
	Parent ion, diketo-Acetyl Acetone

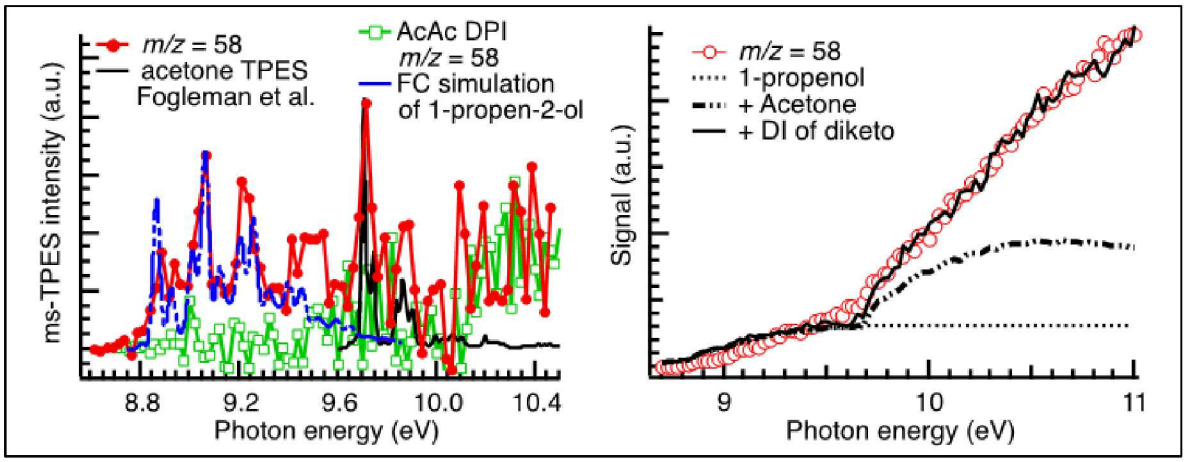
Sample Photoionization & Photoelectron Spectra

Time-resolved

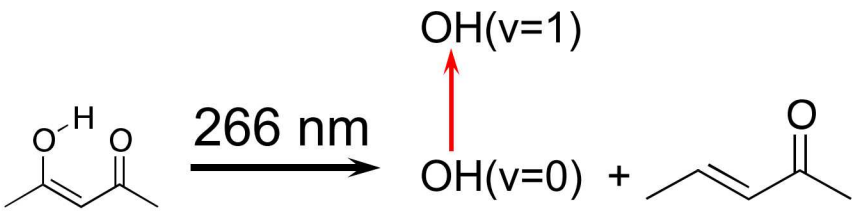
● Photoelectron ○ Photoionization

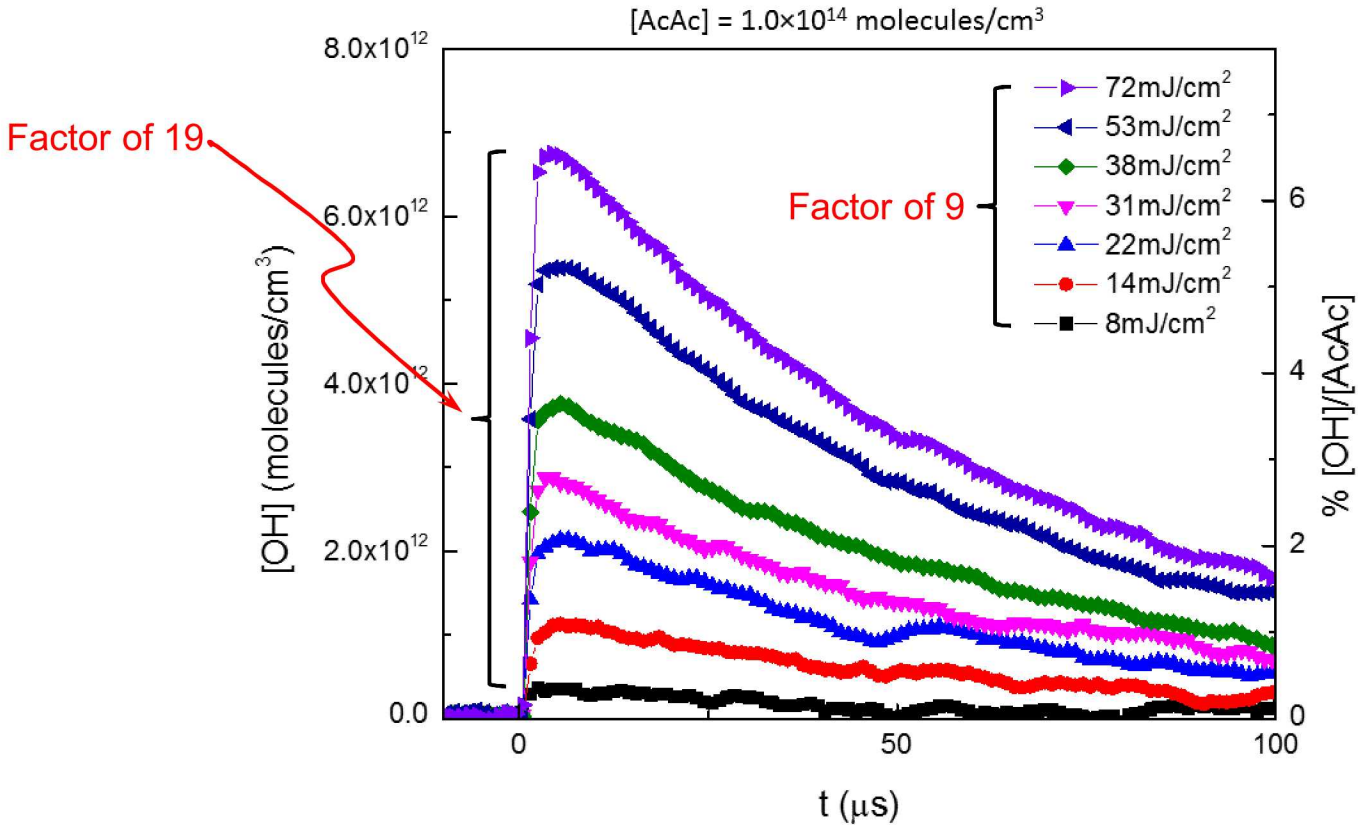




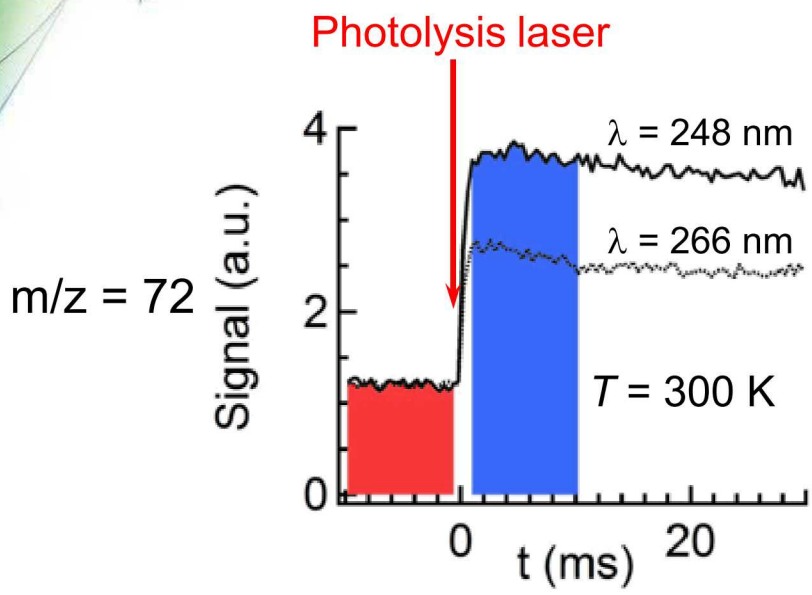


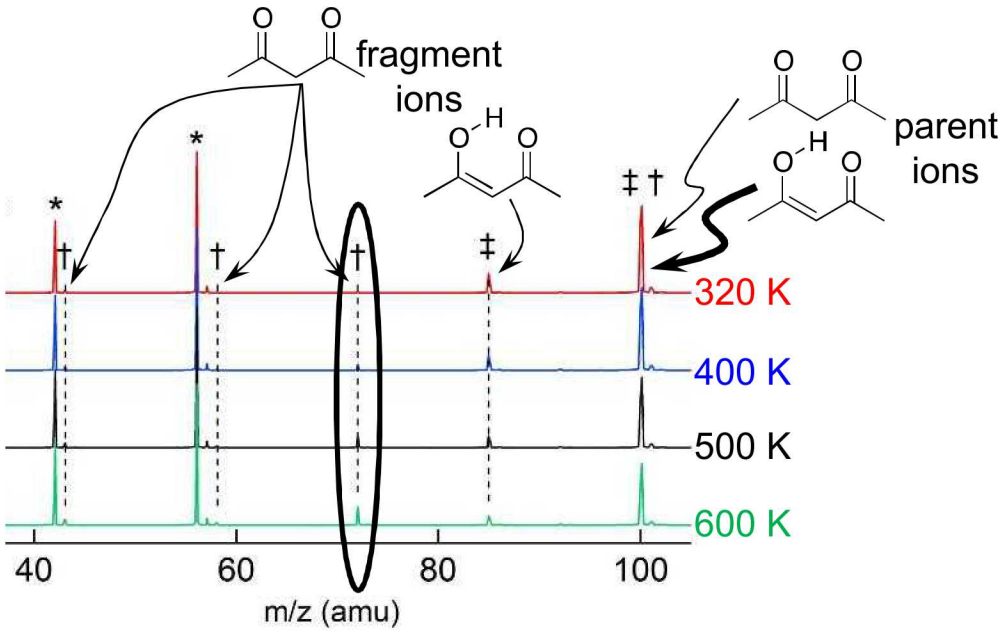
OH Detection by Optical Spectroscopy

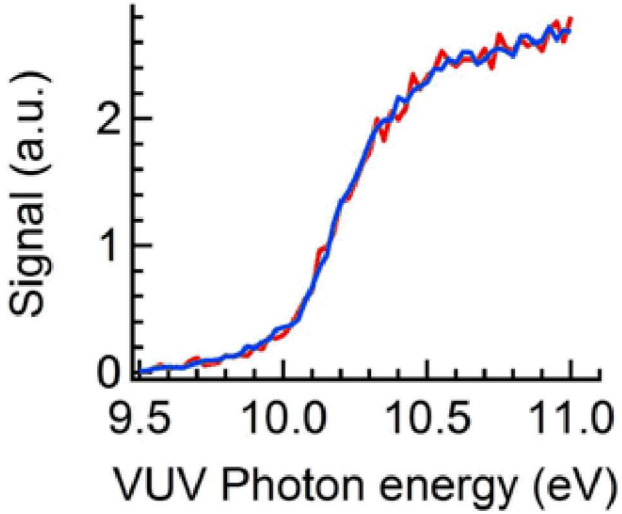




What Dynamics are Consistent with our Data?







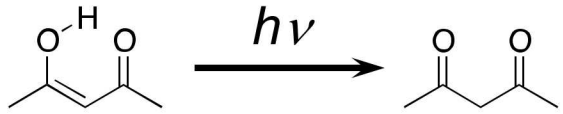
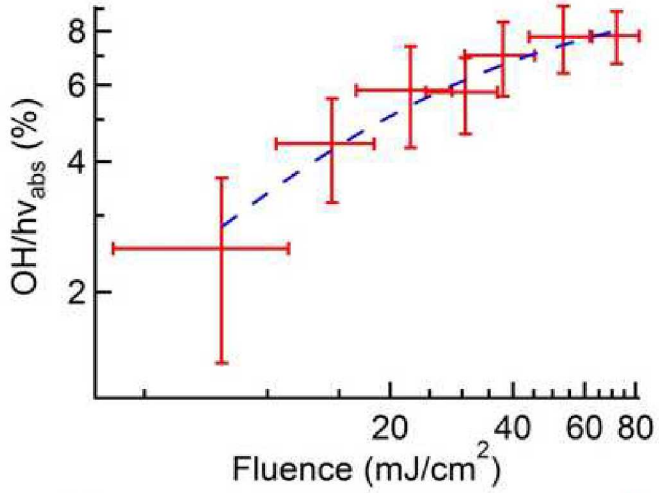
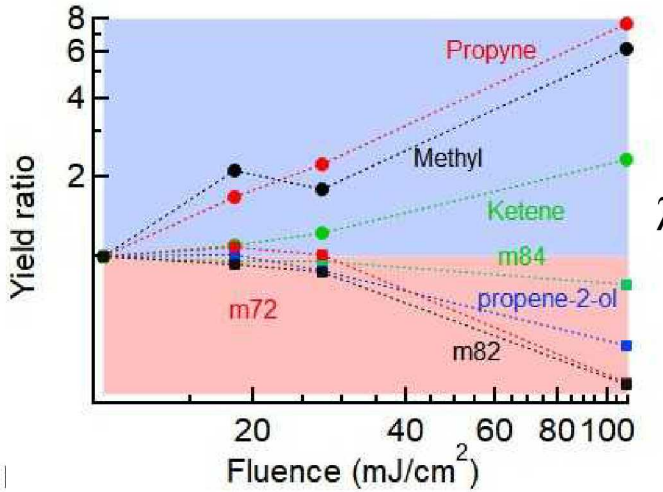


Photo-tautomerization

Fluence Dependence



λ = 266 nm



λ = 248 nm

Observed 1-Photon Product Channels

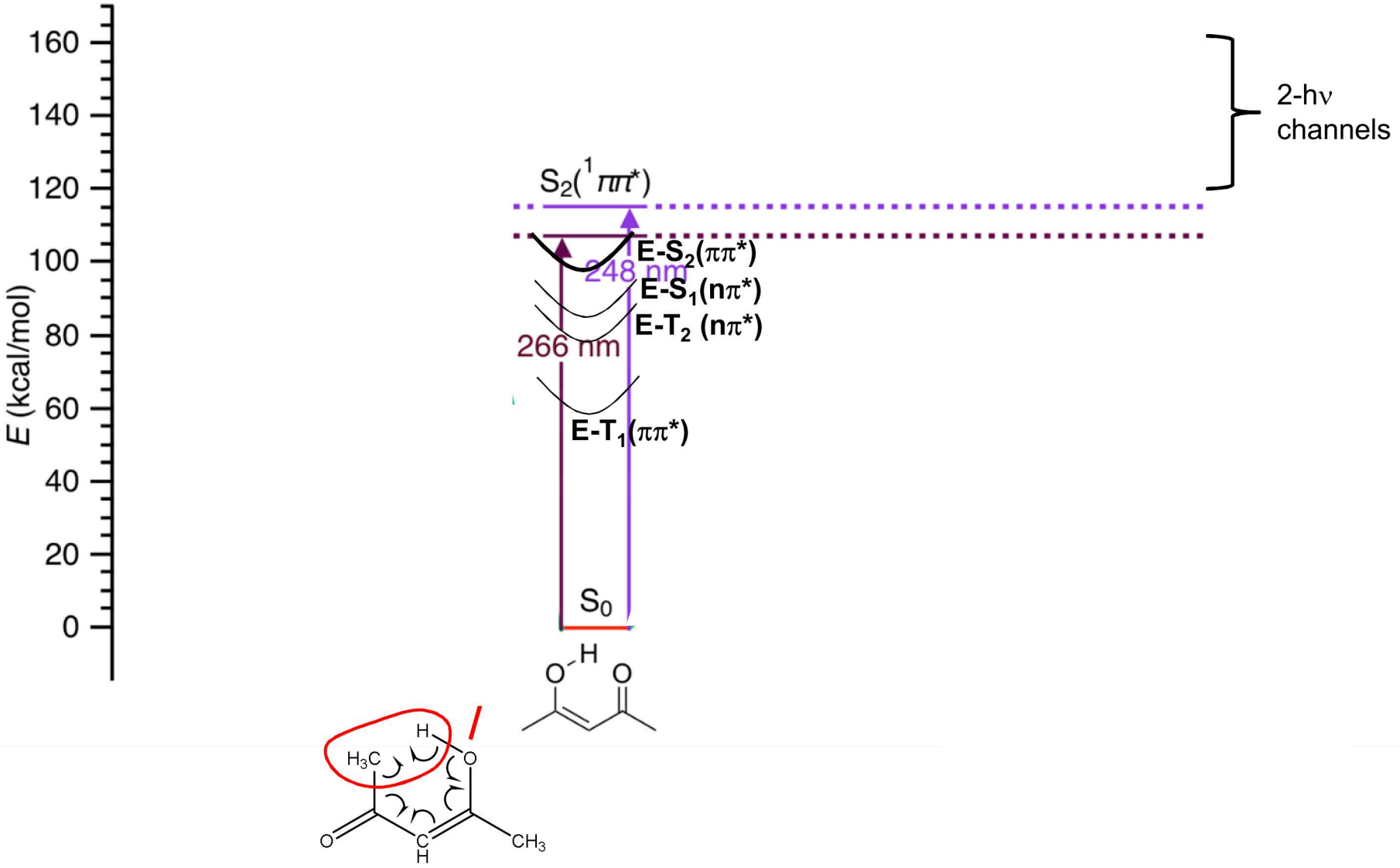
detected parent ion (mass)

detected daughter ion (mass)

Channel	Products	Arises from:	Surface

Photodissociation Pathways

Excited state energies from Chen *et al*. *J. Phys. Chem. A, Vol. 110, No. 13, 2006*



CASSCF(10,8) Model of Dynamics

Chen *et al*. *J. Phys. Chem. A, Vol. 110, No. 13, 2006*

- 5-state problem
- 39 dimensions
- Conical intersection
- Coupling to S_0?

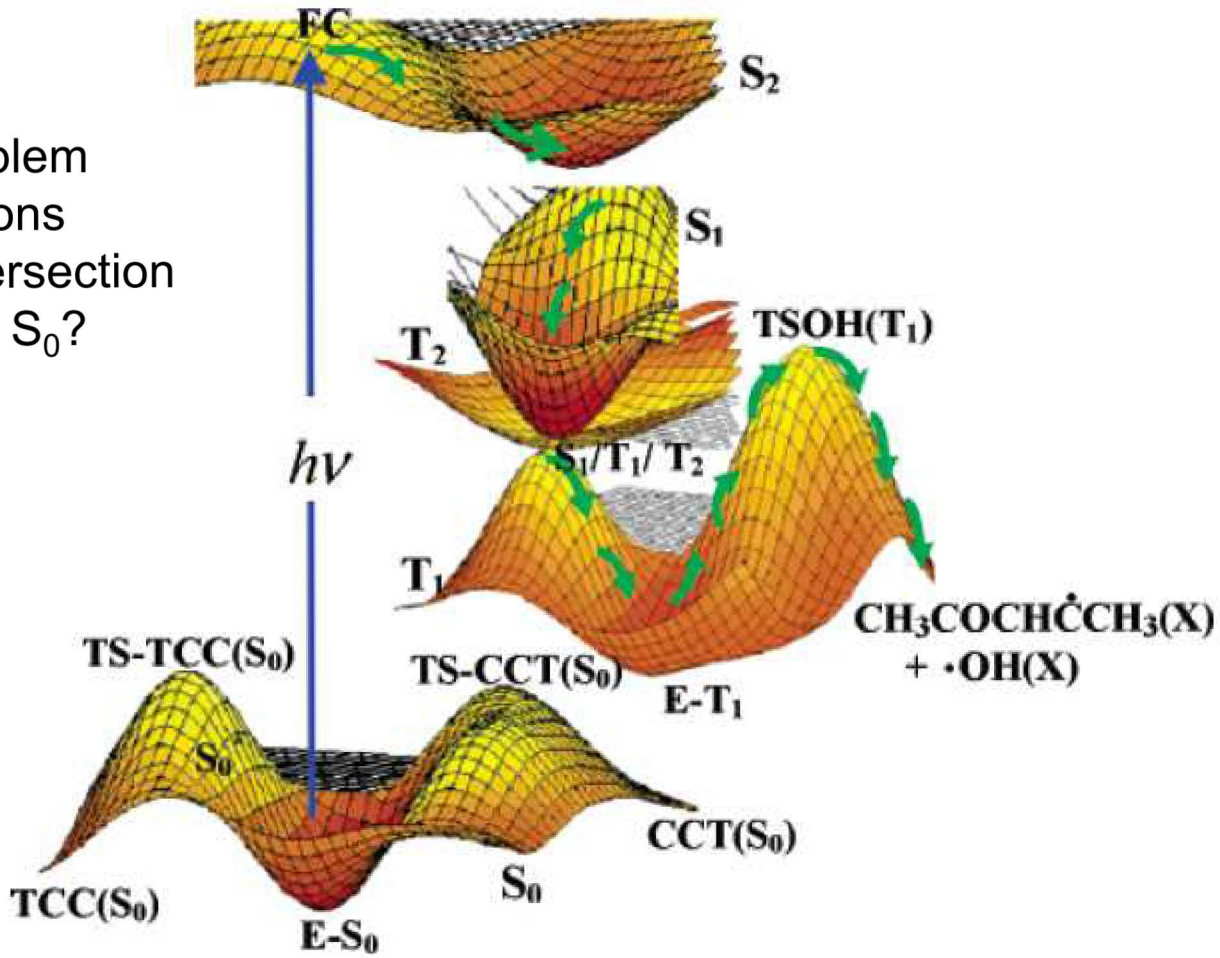
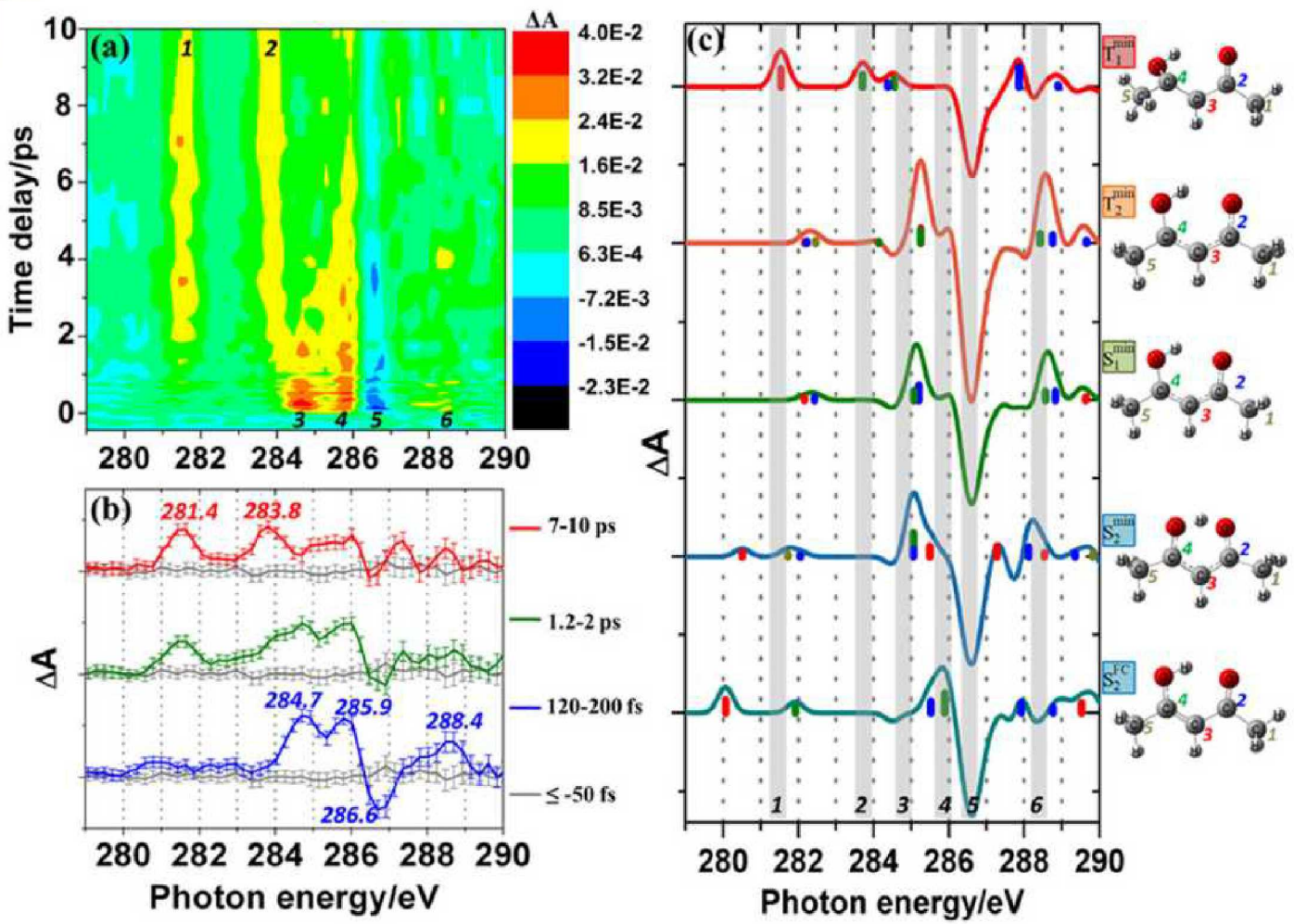


Figure 4. Schematic diagram of the most possible pathways upon photoexcitation of AcAc in the UV regions.

Recent Ultrafast Soft X-ray Absorption

A. Bhattecherjee, S. R. Leone, J. Am. Chem. Soc. **139**, 16576 (2017)



$S_2 \rightarrow S_1$ (very fast) $S_1 \rightarrow T_1$, 1.5 ± 0.2 ps

Conclusions

- Multiplexed Photoion / Photoelectron Spectroscopy can provide a global picture of mutli-well, complex chemical reactions
- Clear evidence of photo-tautomerization: enol → keto
- Reactivity on both the S_0 surface, and possible on T_1.
- Unlike ketones, initial excitation is $^1(\pi\pi^*)$, and T_1 reaction $^3(\pi\pi^*)$
- Many more reactive channels than OH production.

- Future Work:
  - Electronic structure of T_1 surface
  - Internal conversion pathways unknown
  - Theoretical dynamics / kinetics?

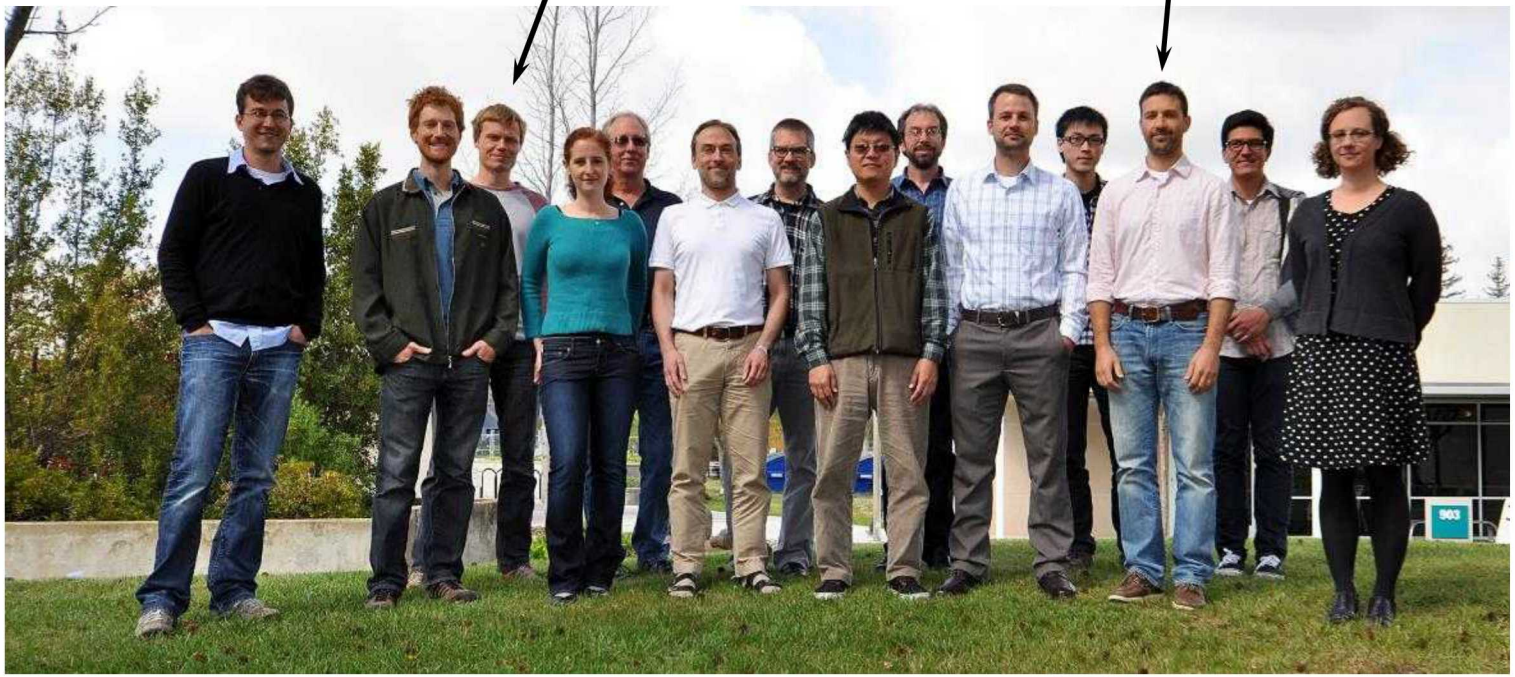
Acknowledgements

Bálint Sztáray

Ivan Antonov

Lenny Sheps

Patrick Hemberger



Andras Bodi

Krisztina Voronova

Sandia National Laboratories

PAUL SCHERRER INSTITUT PSI

DOE Gas Phase Chemical Physics

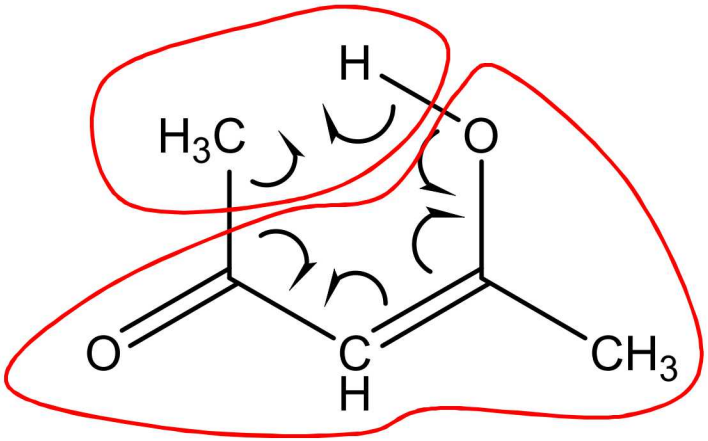
UNIVERSITY OF THE PACIFIC 1851

ALS ADVANCED LIGHT SOURCE

Chemical Dynamics Beamline 9.0.2

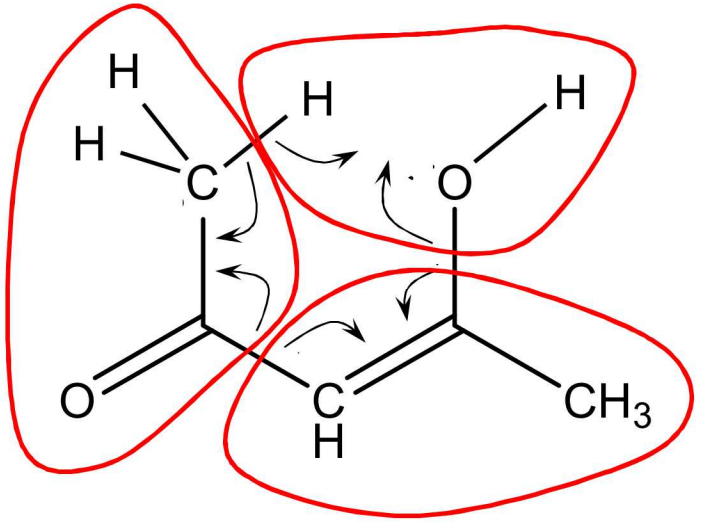
This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U.S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration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

I showed this :



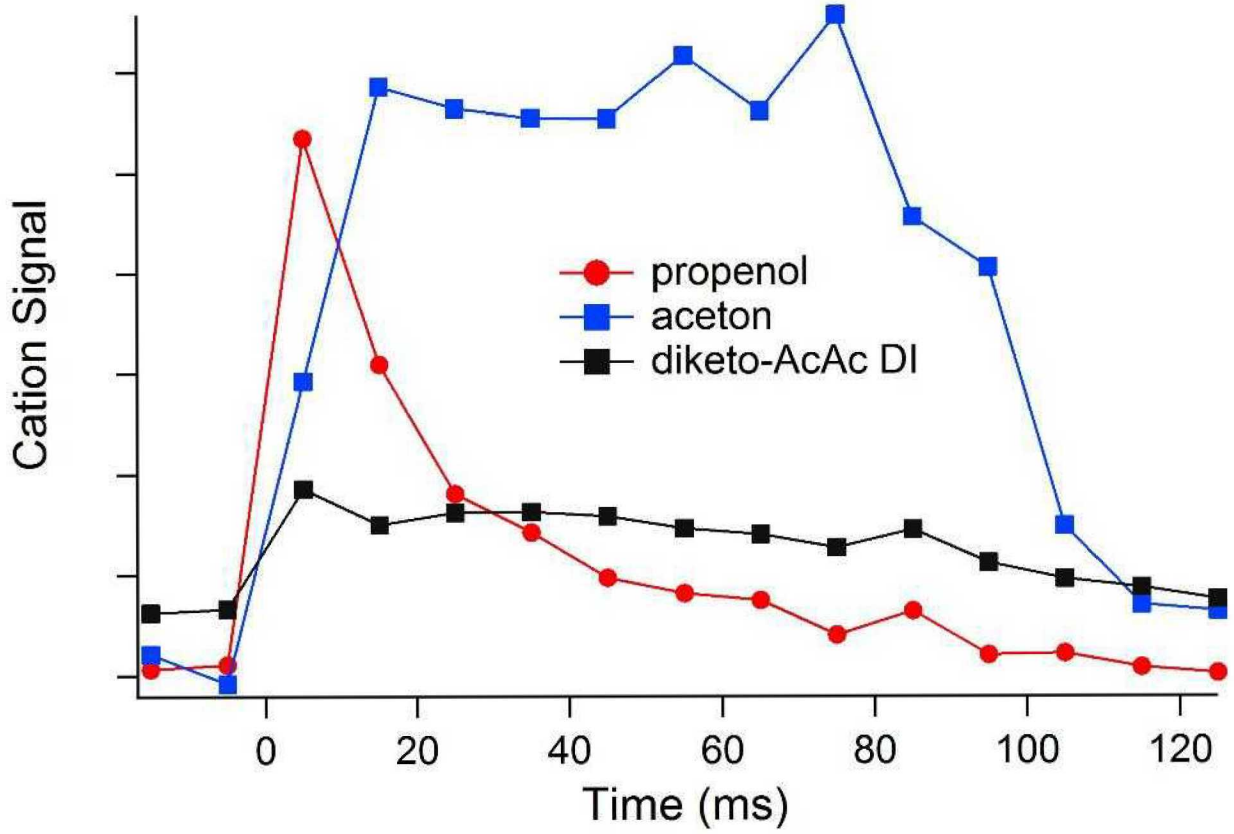
Cope rearrangement to make
CH4 + acetylketene

Scott Kable suggested this:



Cope rearrangement to make
$H_2O + H_2C{=}C{=}O + HC{\equiv}CCH_3$

Tautomerization of 2-propenol



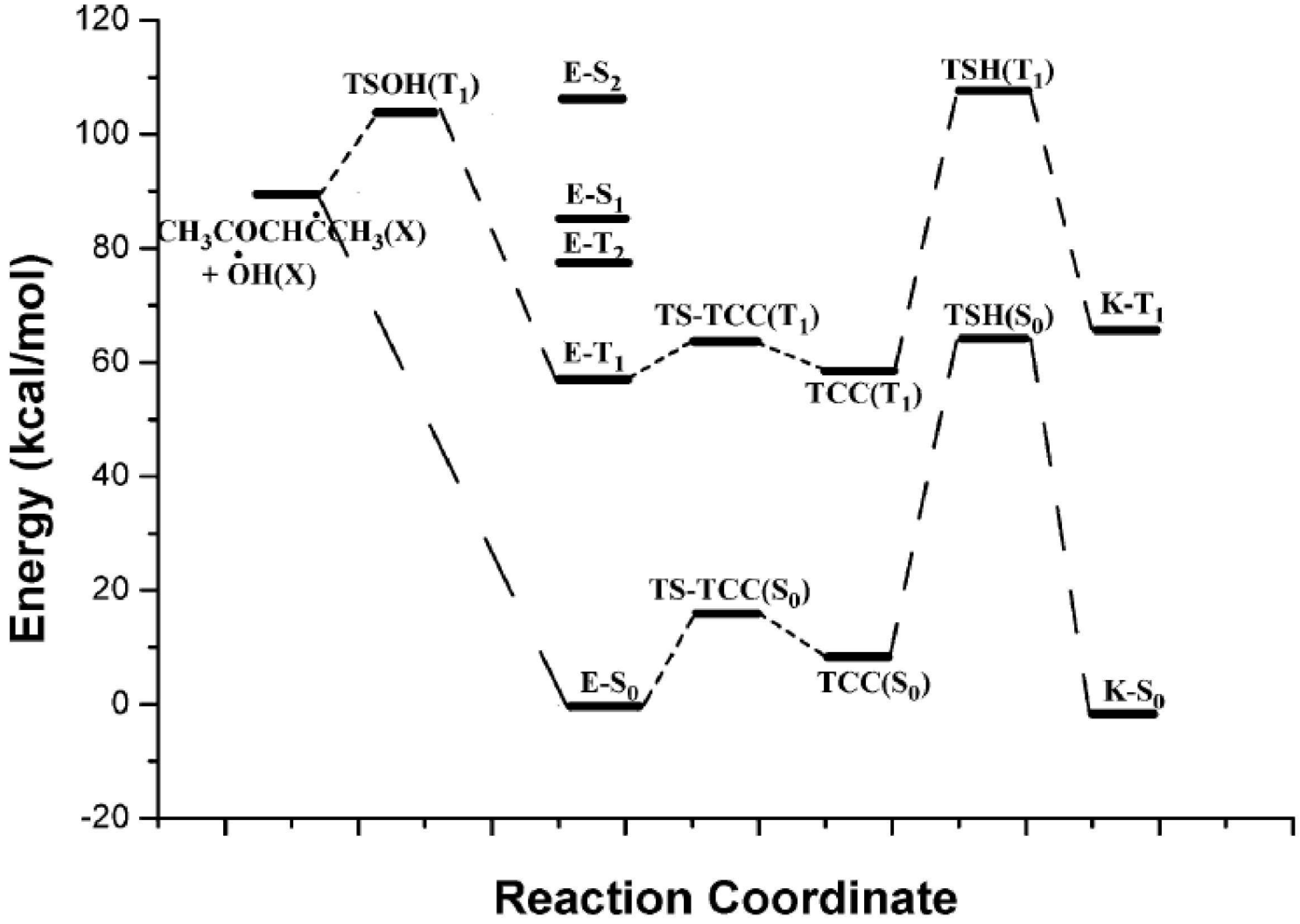
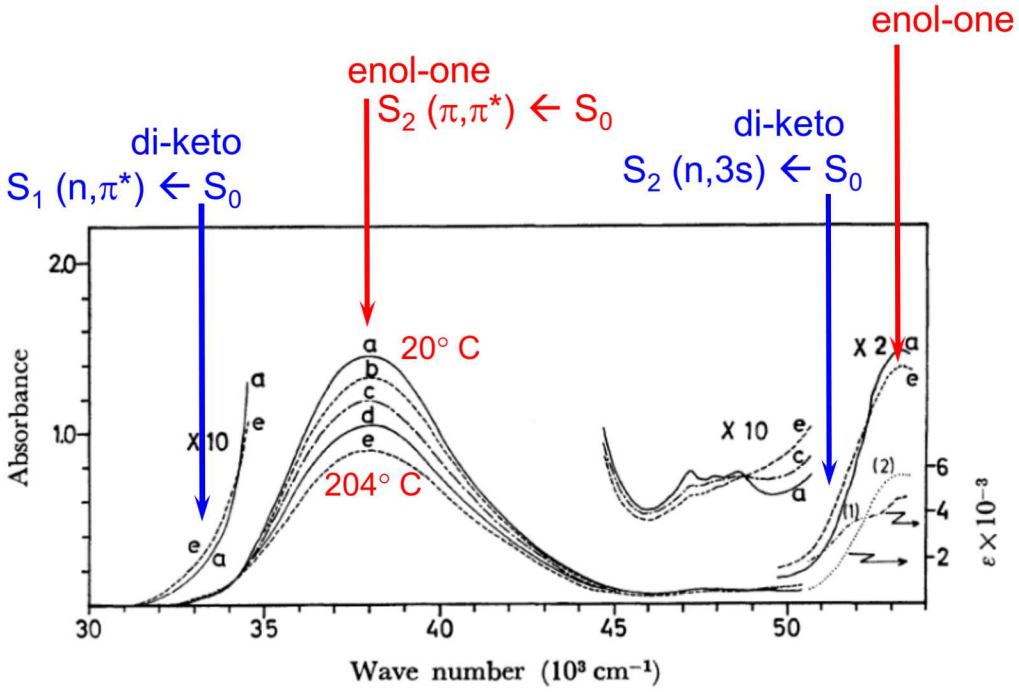
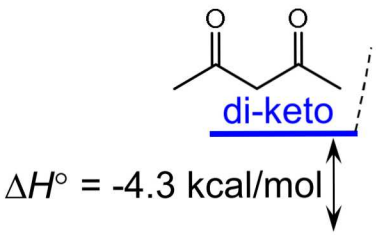


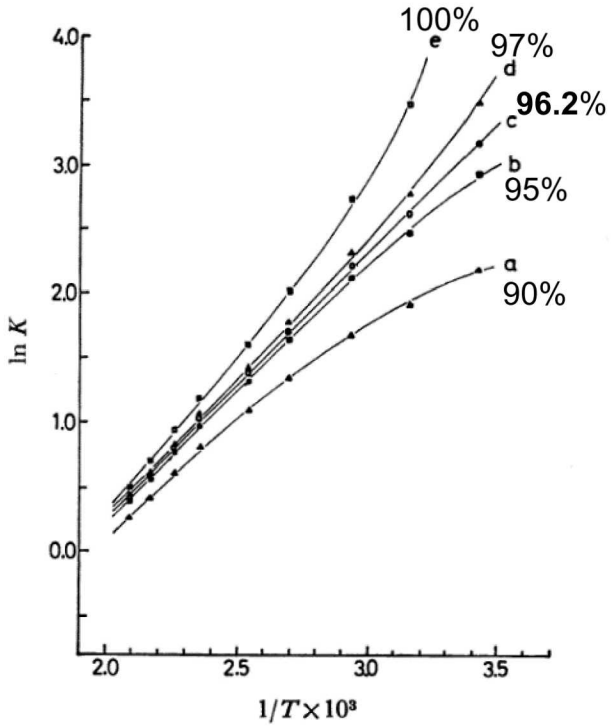
Figure 2. Schematic potential energy surfaces for the C2−O3 fission and keto−enolic tautomerization reactions in the S_0 and the T_1 ($^3\pi\pi^*$) states along with the CAS(10,8)/cc-pVDZ-computed relative energies (kcal/mol).

Enolone is ~96% at 293K in Gas Phase

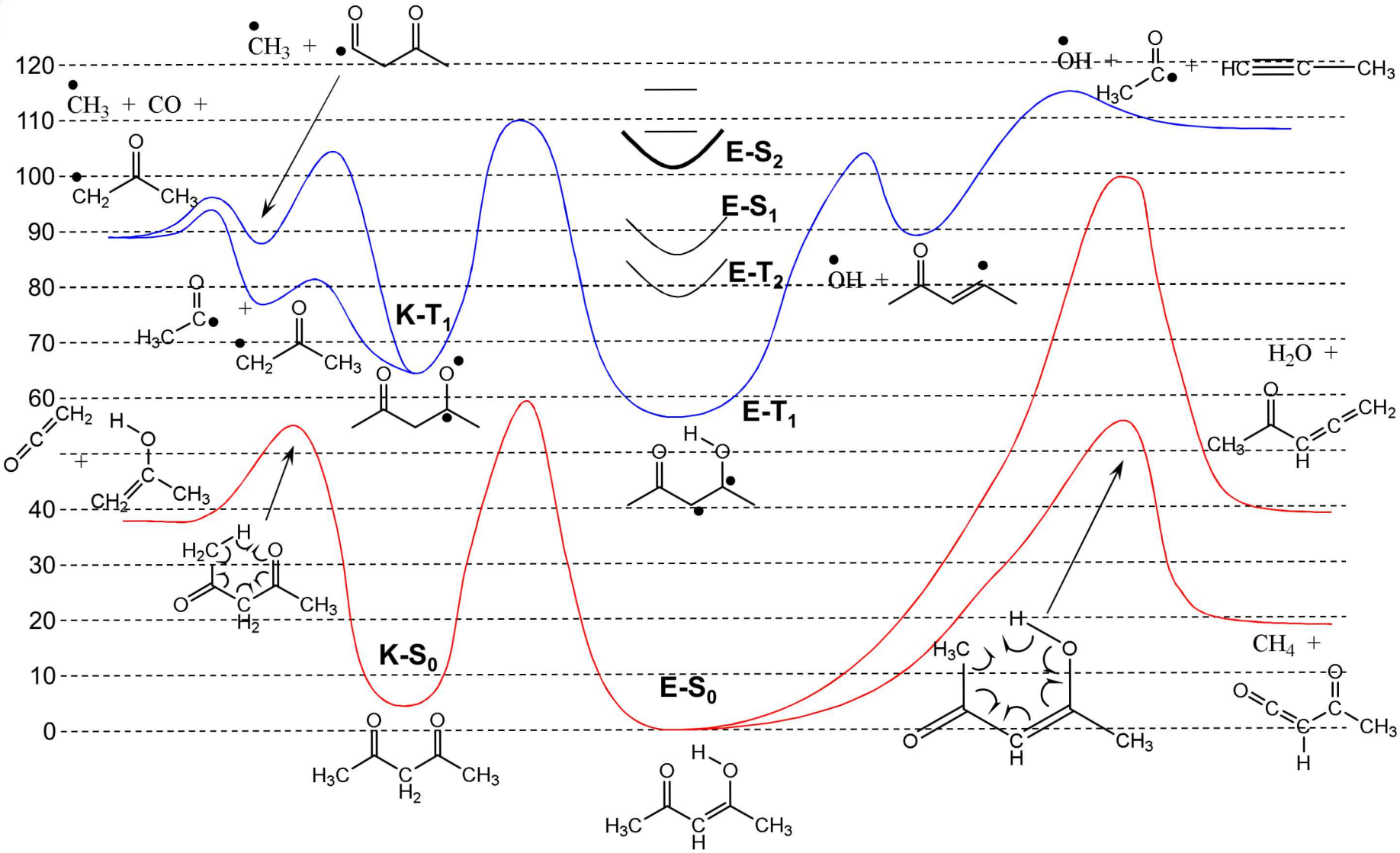


$$K = \frac{[\text{enol-one}]}{[\text{di-keto}]}$$





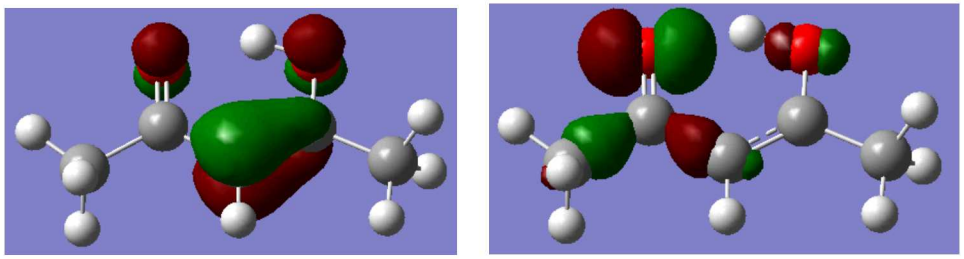
Potential Energy Surface

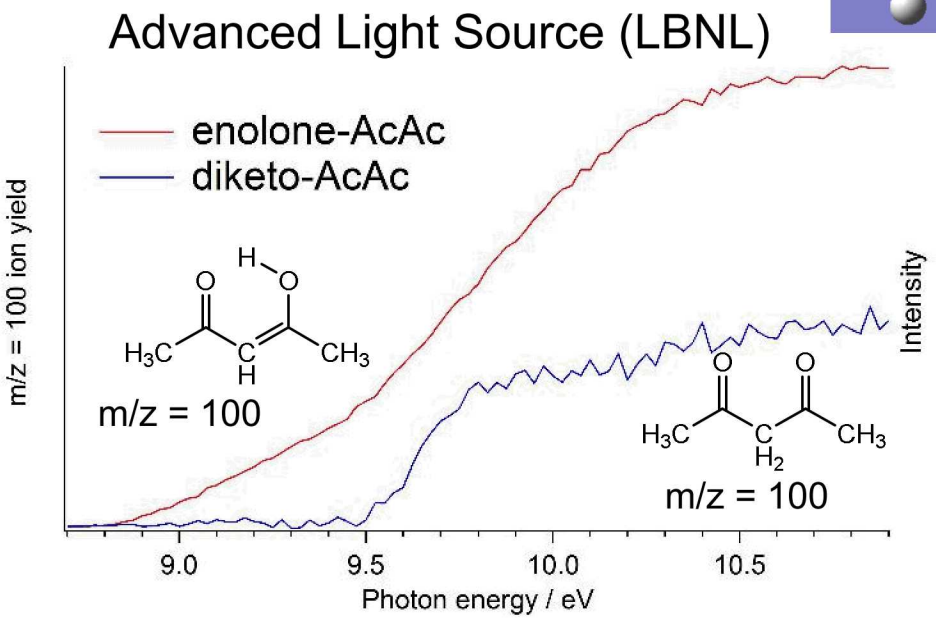


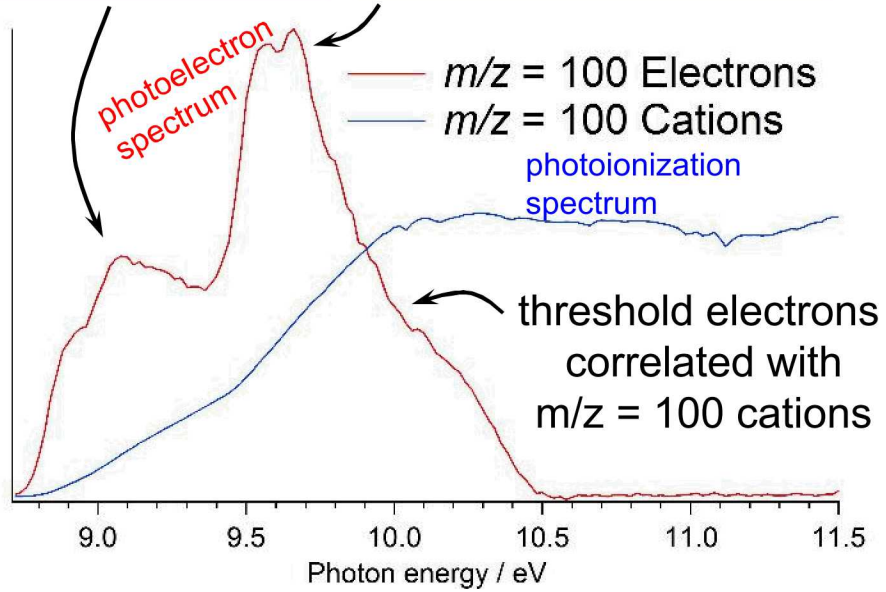
Equilibrium is heavily shifted by solvent polarity. Photochemistry also appears very different in gas phase vs. matricies, and would probably be still different in solvents.

- Yoon 1999, There is no fluorescence from Acetyl Acetone, even at the origin region. And upper limit of 90.3 kcal/mol of C-OH bond strength. They also say they've done the first photochemistry in 1999.
- Example of acetaldehyde vs VA PES. Enol almost always less stable.
- Multiple authors have concluded that the only, or the dominant, gas phase pathway is OH loss after excitation to S2.
- Irradiation at 248 nm in solid p-H2 matricies causes phototautomerization, but same environment leads to no observable OH. Why?
- S2 (π - π^*), to S1(n - π^*) in under 2 ps (B. Soep), then T1 (π - π^*) in 250 ps. In matricies the idea is that phonons cool the T1 state (which has a broken H bond) which then doesn't dissociate, and gets back on S0 slowly.
- Lozada-Garcia says 248 clearly induces fragmentation, whereas 266 nm does not (in matricies). We see lots of fragmentation at boht wavelengths, so I would say it is energy removal that is causing this difference, not an insufficient amount of energy at 266 nm.
- Lozada-Garcia concludes that the major process at 266 nm (in matricies) is isomerization on T1 to the CTC conformer.
- Yoon 1999, Upadhaya 2003, and Zewail all (I think) conclude that OH is the only fragmentation channel.
- Upadhaya 2003 and Chen 2006 say that in S2 the H atom is shared equally between the two O atoms. Big geometry change upon excitation.
- Soep gets his eneretics from Chen & Phillips 2006.
- Trivella 2010 says at 248 nm, "stereoisomerism" is the main reaction observed, contrary to gas phase.
- Trivella 2010 also says that small barriers on T1 (< 0.5 eV) lead to many different conformations, and hence the isomerizations they see probably happen on T1 (in matricies). Why do they not happen in the gas phase? ET that sucks energy out to get below exit barrier?
- Trivella 2010 says fragmentation probably results from Norrish I processes, making CH3CO. They see much more CO produced if O2 is present, and attribute this to O2 scavenging radicals and inhibiting recombination.
- Trivella 2010 says S1, S3, and T2 are all (n pi*) states, and maybe the fragmentation comes from direct excitation to them using their broadband UV source. But we can definitively say you don't need a broad band source, and S2 is a fine starting place.
- Chen says barrier on T1 is 46.8 kcal/mol, with exit barrier of 16 kcal/mol from Upadhaya 2003.
- Chen also says T1 state is 3(pi pi*), with the minimum rotated about the former C=C double bond.
- Chen also says rotational isomerization hard on S0, easy on T1.
- Chen also says C-O bond cleavage the dominant process on T1 (why not CC cleavage)?
- Chen says tautomerization on S0 is 62 kcal/mol barrier, on T1 is 31 kcal/mol above T1 min. So difficult always.
- Chen: rotational isomerization on S0 difficult because of C=C double bond. But on T1 all the rotational isomerization barriers are pretty facile. So it flops around on T1.
- Chen: T1 is 57 kcal/mol above So, much lower than in Acetaldehyde (78) and Acetone (81).
- Chen says dehydration makes the acetyl propyne molecule, but the barrier is too high for this to be feasible. We see H2O + acetylallene!
- Chen says E-S1 minimum is very similar in structure to T1 and T2 at this energy, and hence ISC is expected to be facile.
- Hydrogen bond calculated to be 12.5 kcal/mol (Rios), much larger than normal 5 kcal/mol.

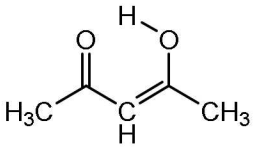
Photoionization / Photoelectron Spectra of Acetyl Acetone



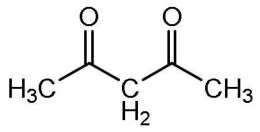




Swiss Light Source (PSI)



96%



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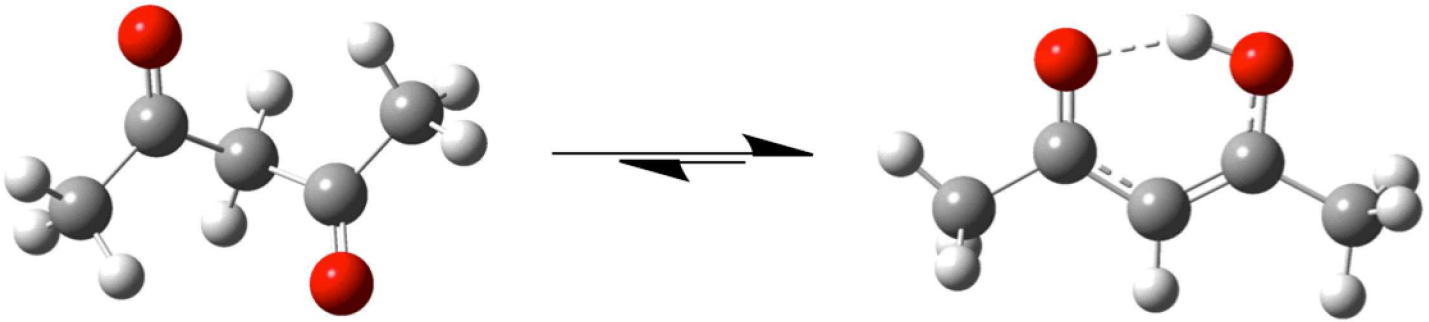
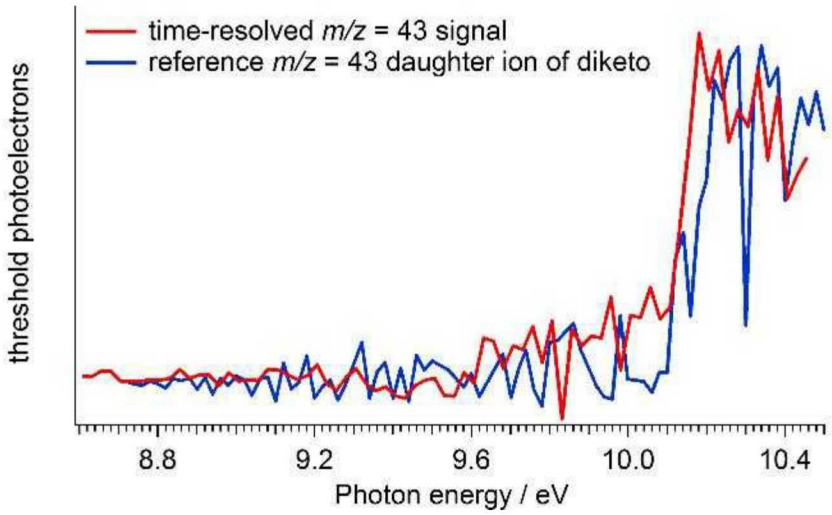


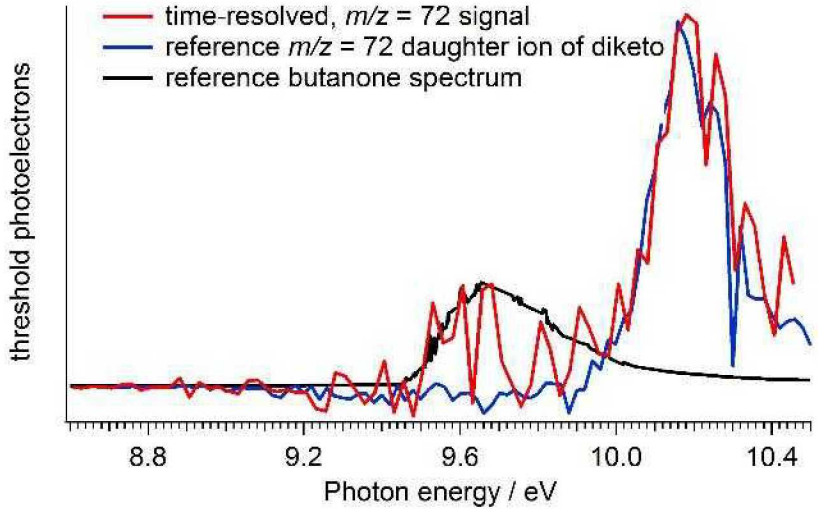
diketo-AcAc

enolone-AcAc

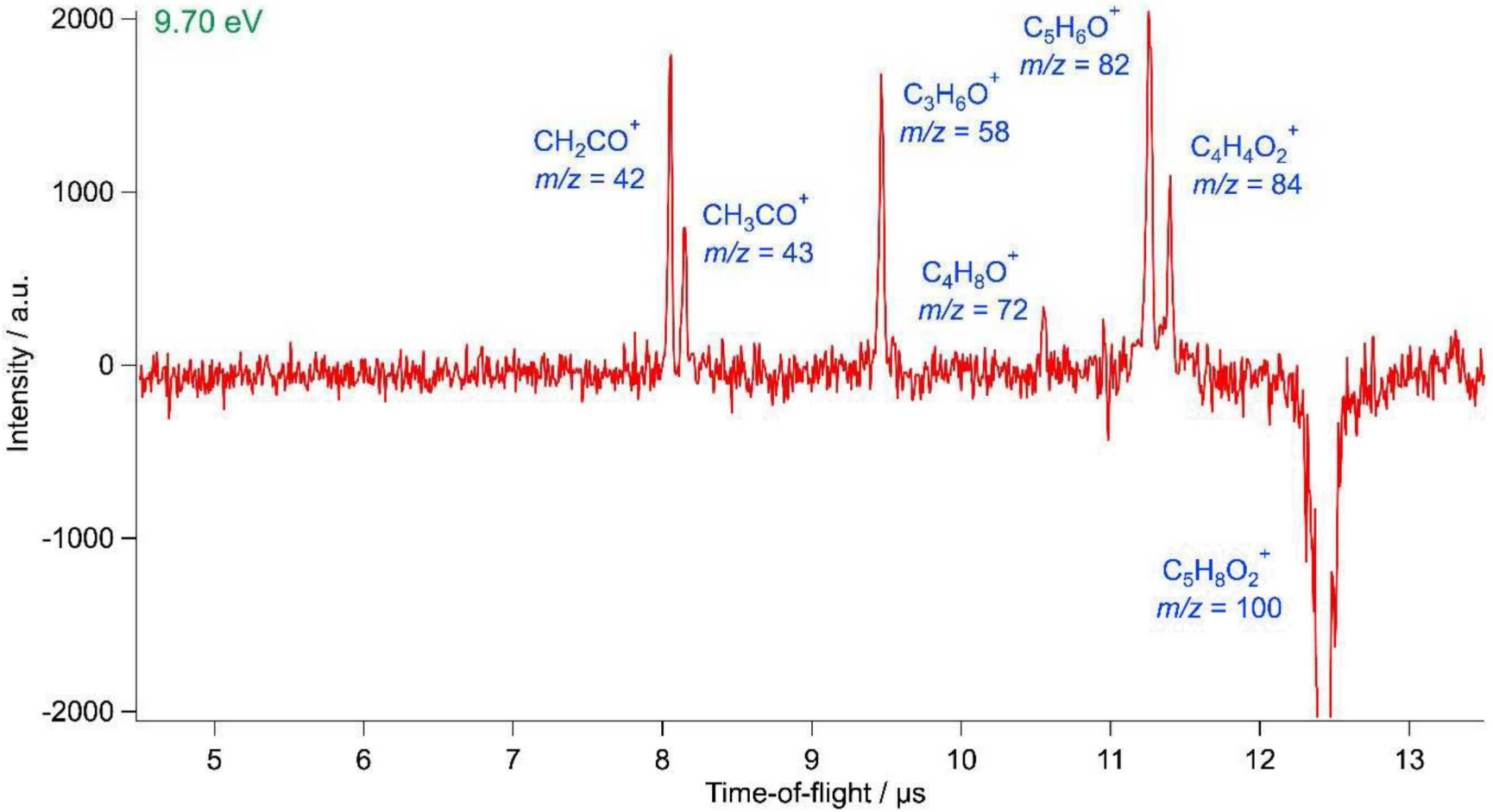
Photoelectron Spectra of Daughter Ions

Blue: Daughter ions from static acetyl acetone sample
Red: Net production of ions by photodissociation laser



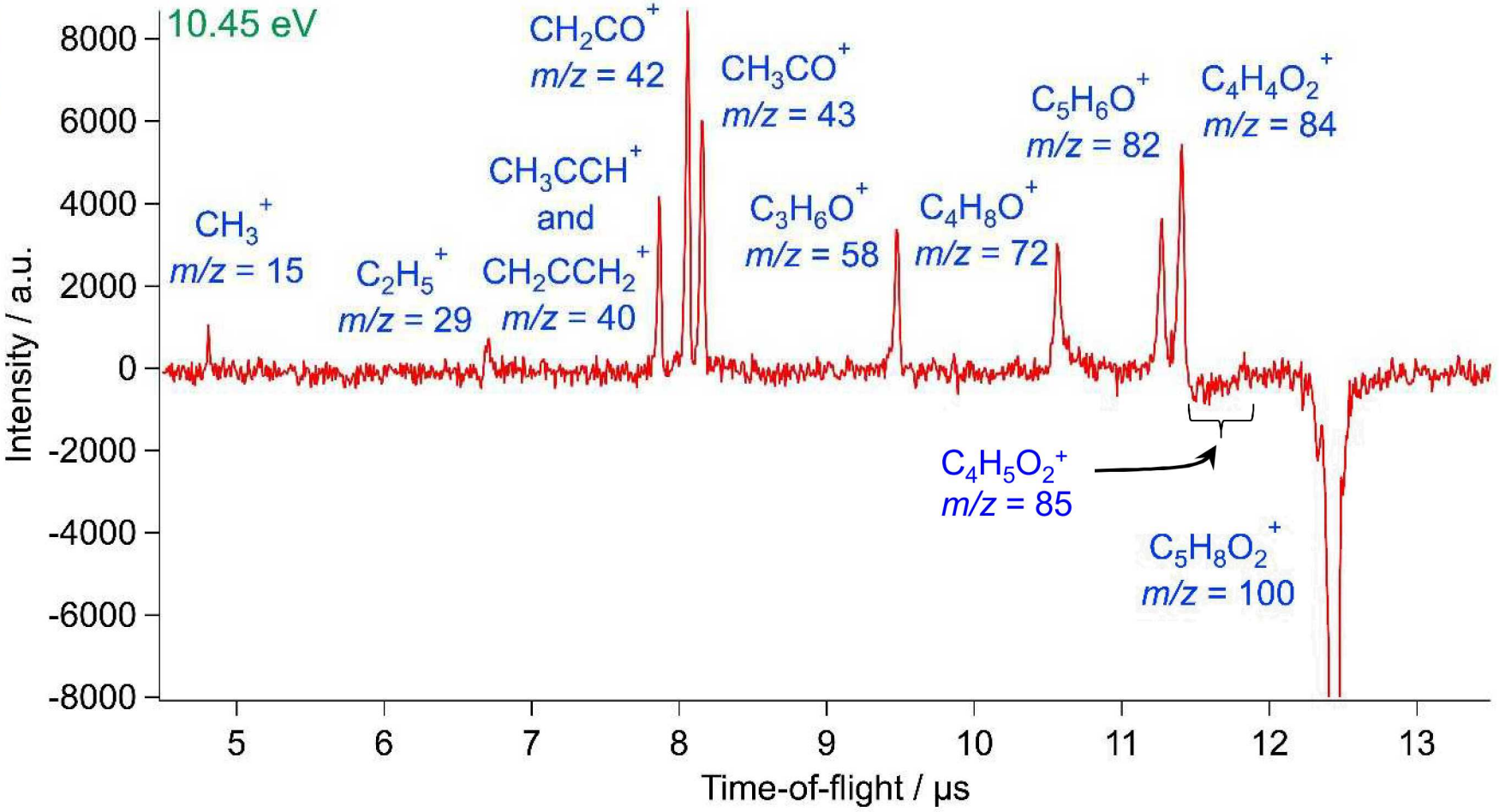


Mass Spectrum (Post Laser – Pre Laser)



900 ppm AcAc in Ar: Pressure 0.6–0.9 mbar; T = 300 K

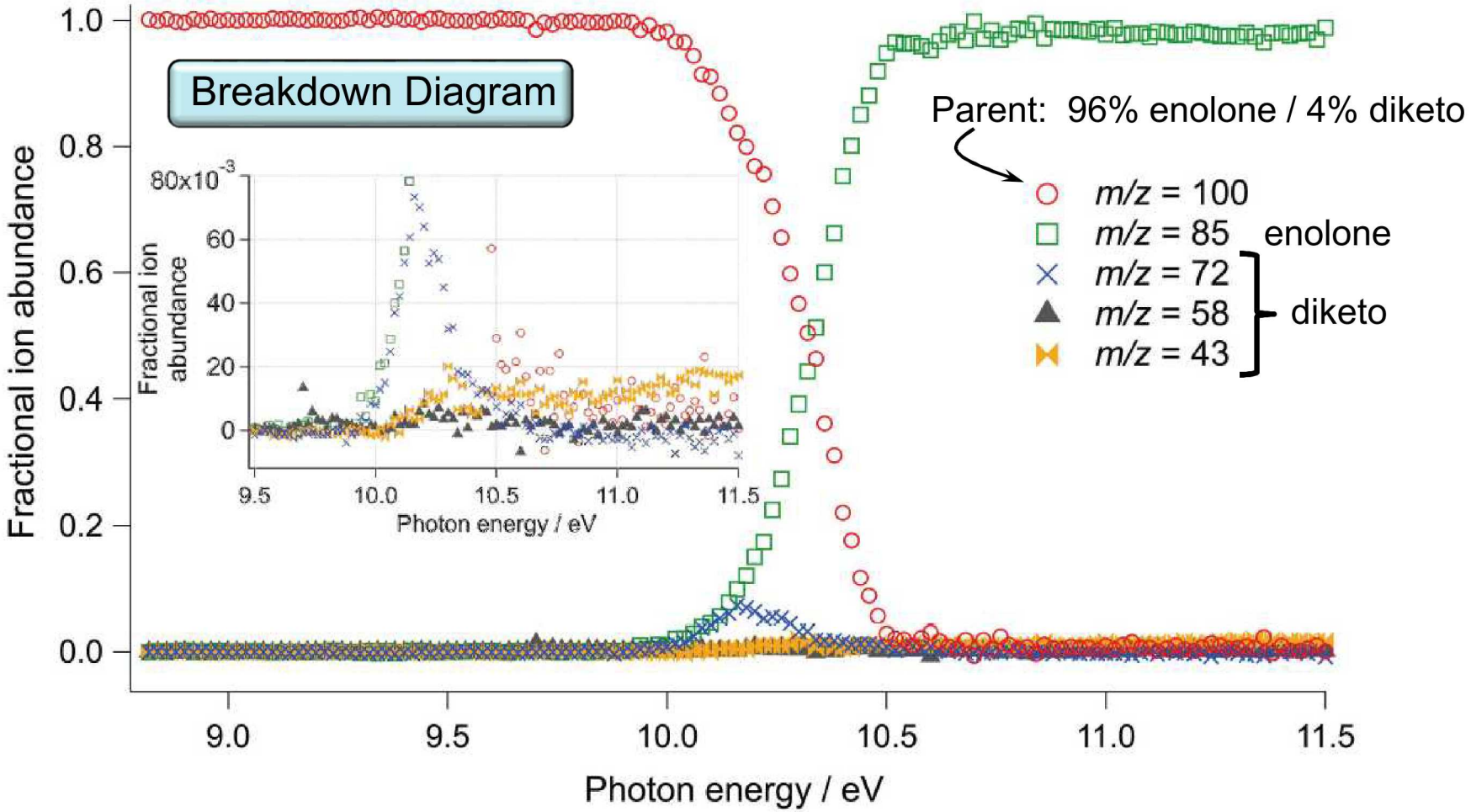
Mass Spectrum (Post Laser – Pre Laser)



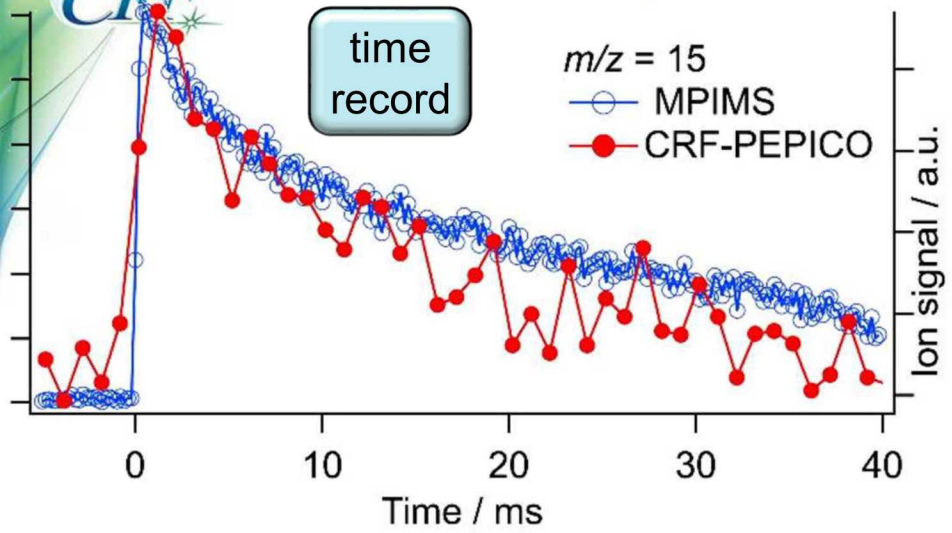
900 ppm AcAc in Ar: Pressure 0.6–0.9 mbar; T = 300 K

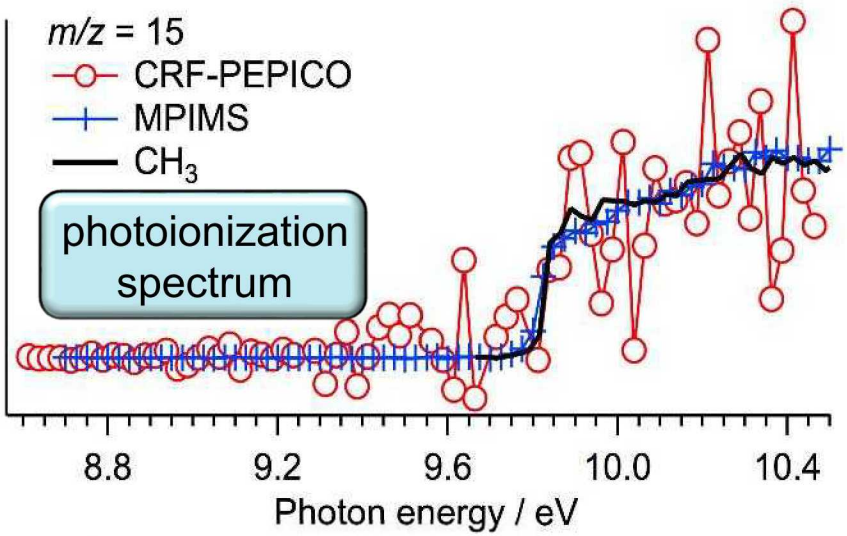
Evidence for Phototautomerization

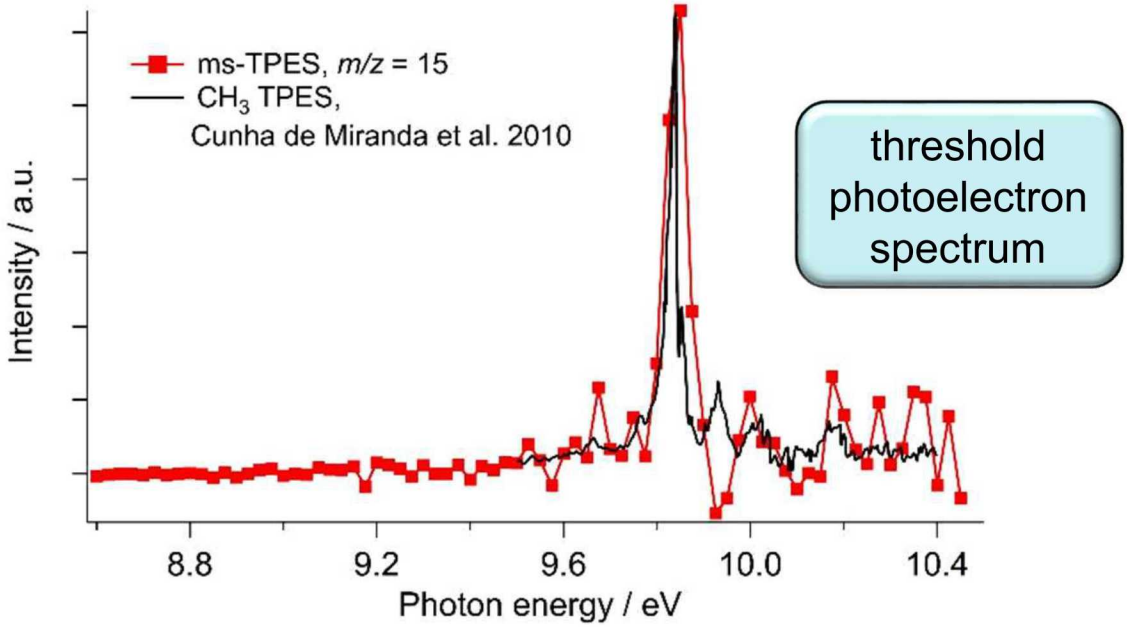
Daughter ions of enolone are distinct from diketo daughter ions



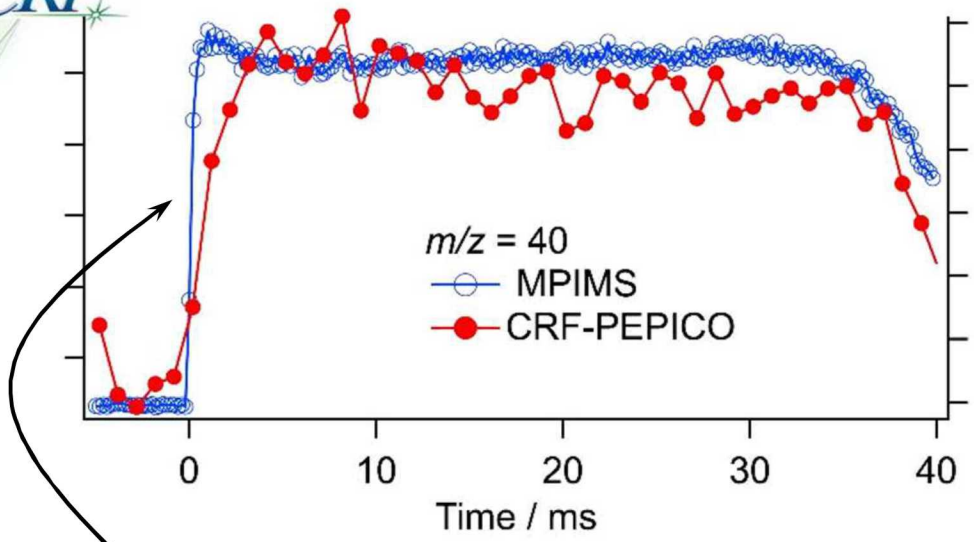
m/z = 15 ⇒ Methyl Radicals





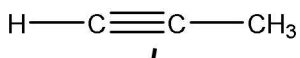


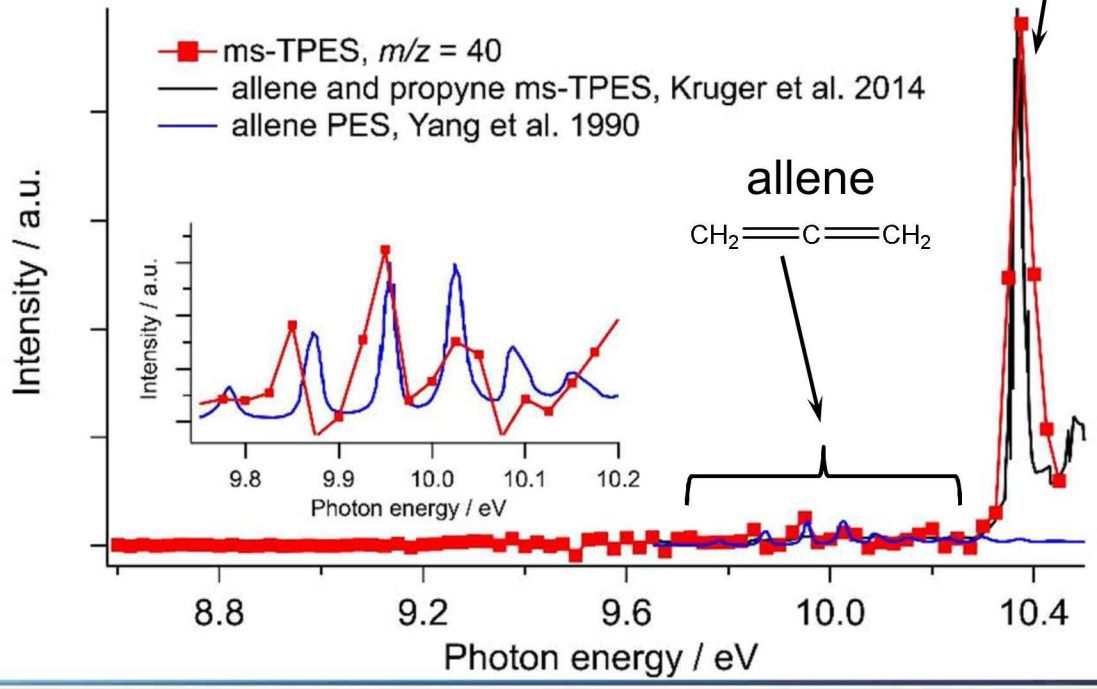
m/z = 40 ⇒ Mostly Propyne



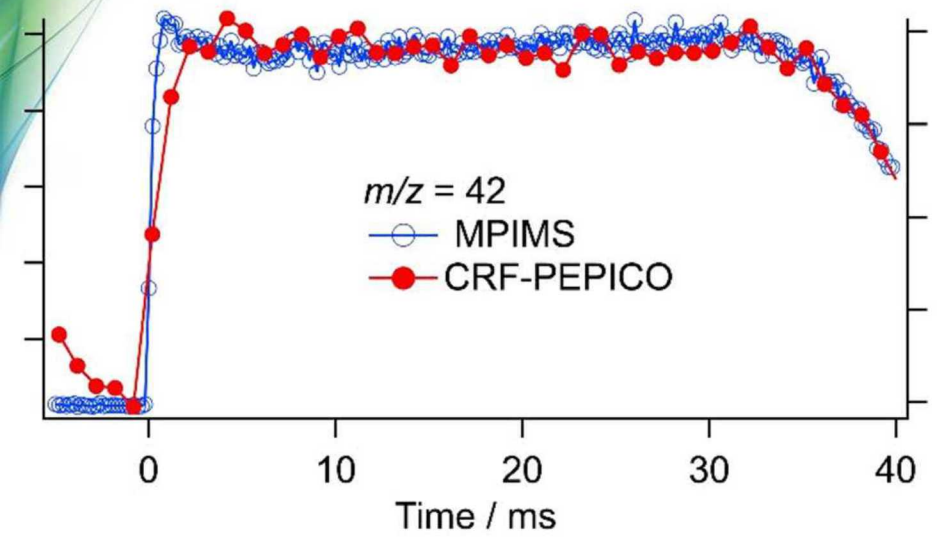
prompt production

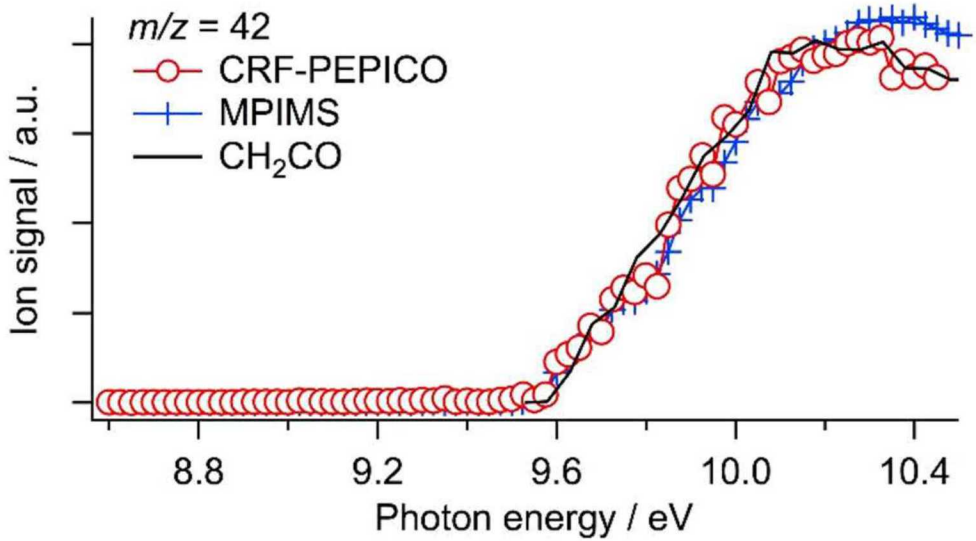
propyne

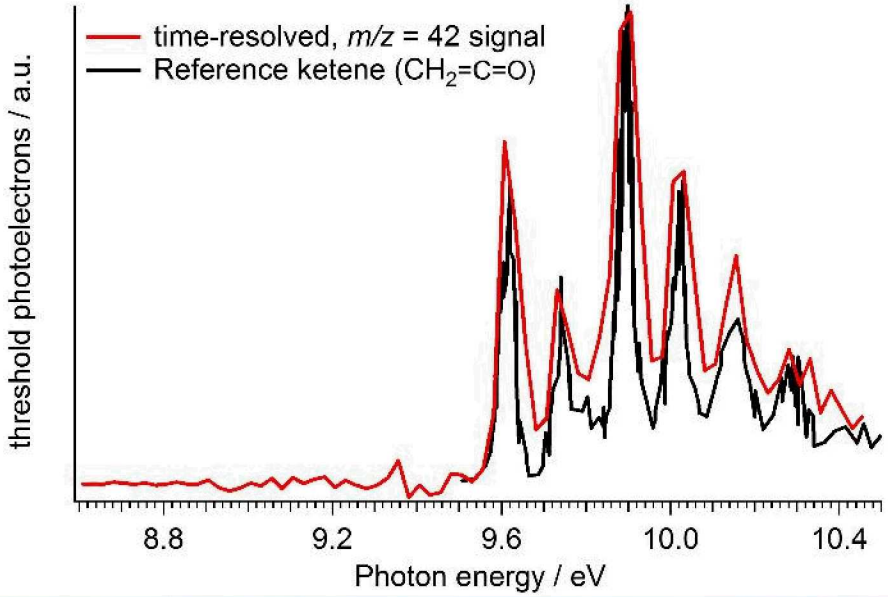




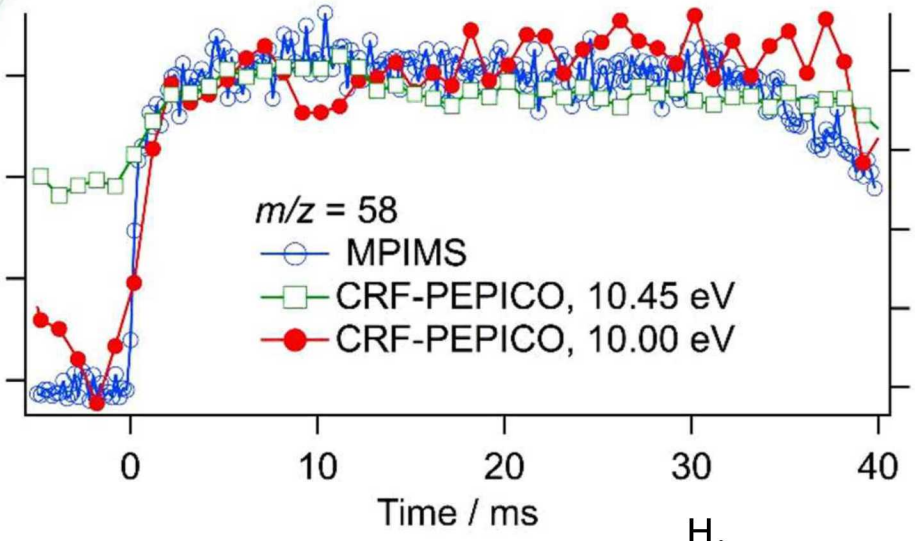
m/z = 42 ⇒ Ketene (CH_2=C=O)

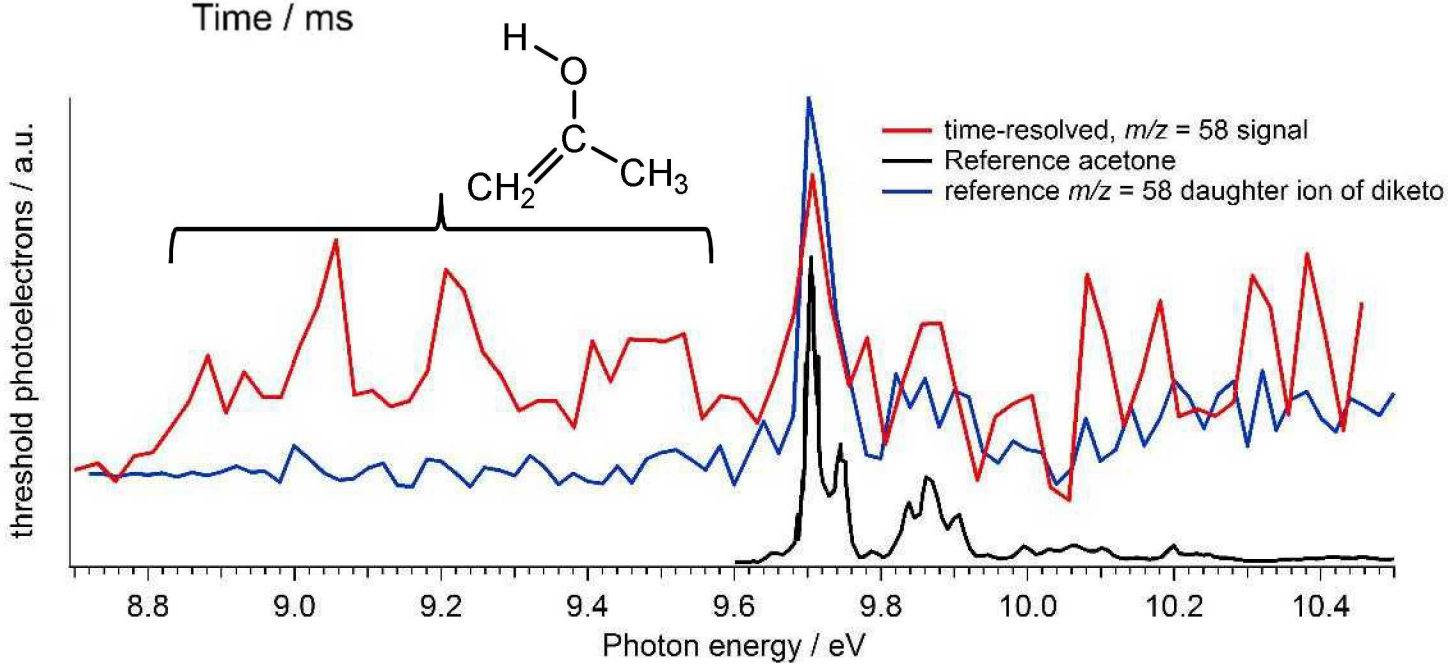




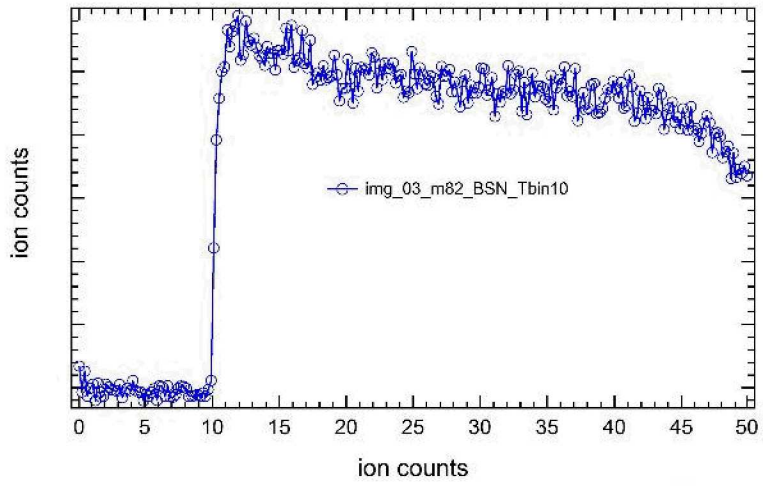


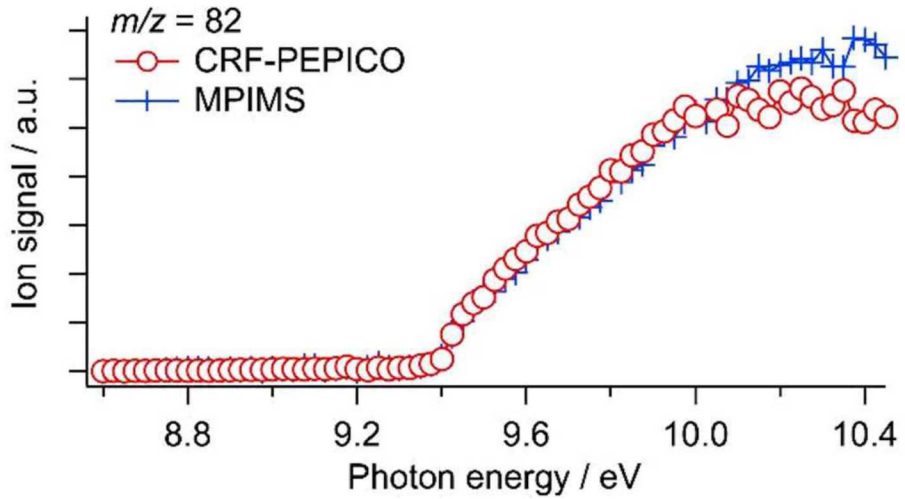
m/z = 58, mostly 1-propene-2-ol

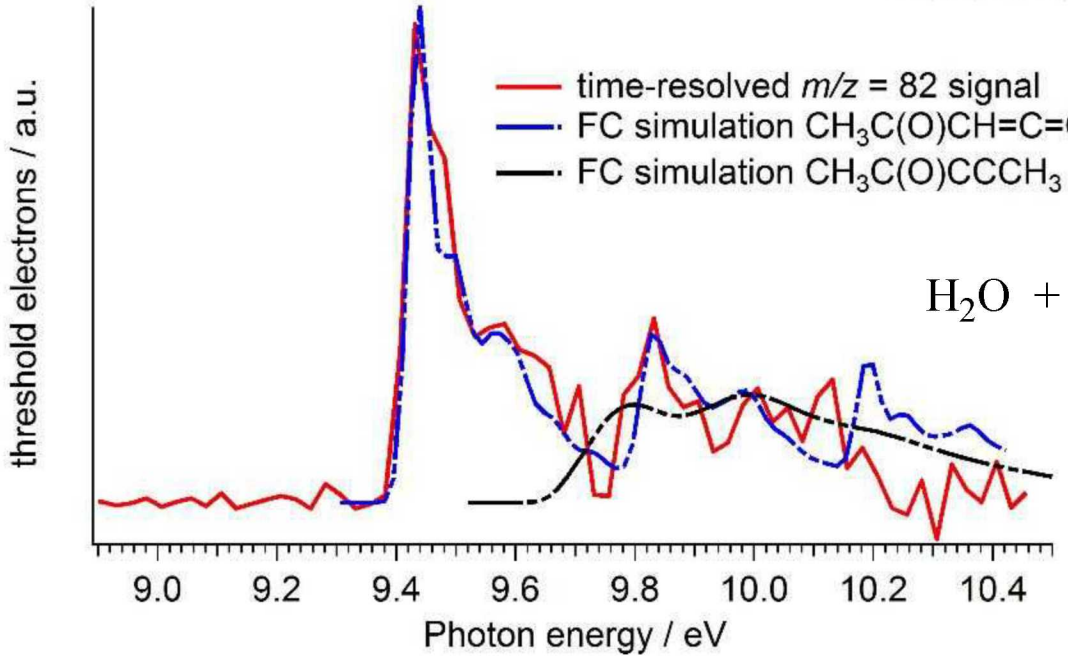




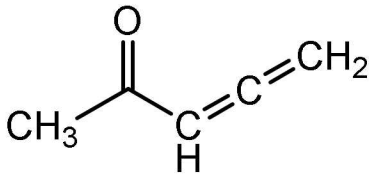
m/z = 82, only acetyl allene





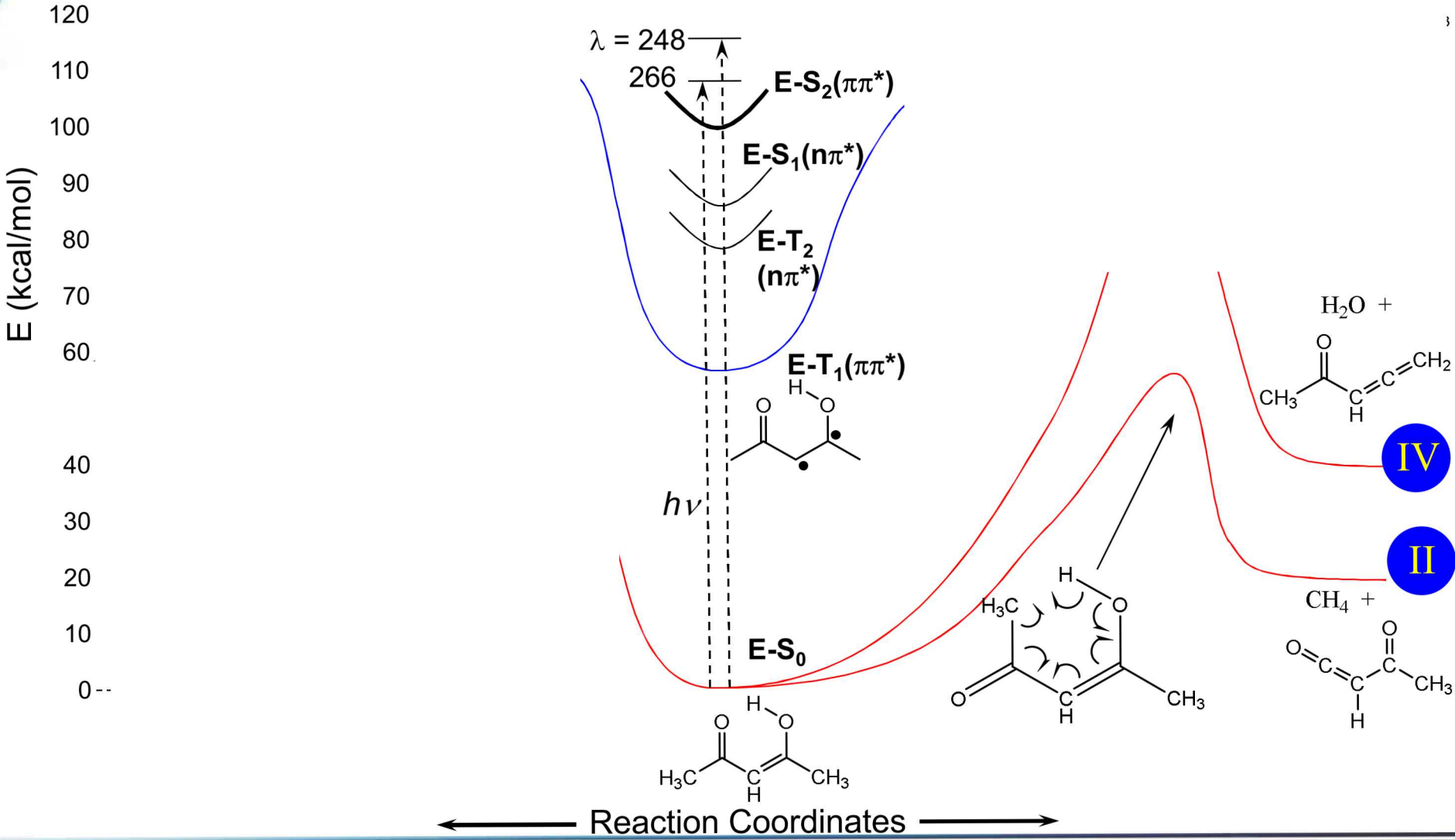


H_2O +



Photodissociation Pathways

Most energies from Chen *et al.* *J. Phys. Chem. A, Vol. 110, No. 13, 2006*



Photodissociation Pathways

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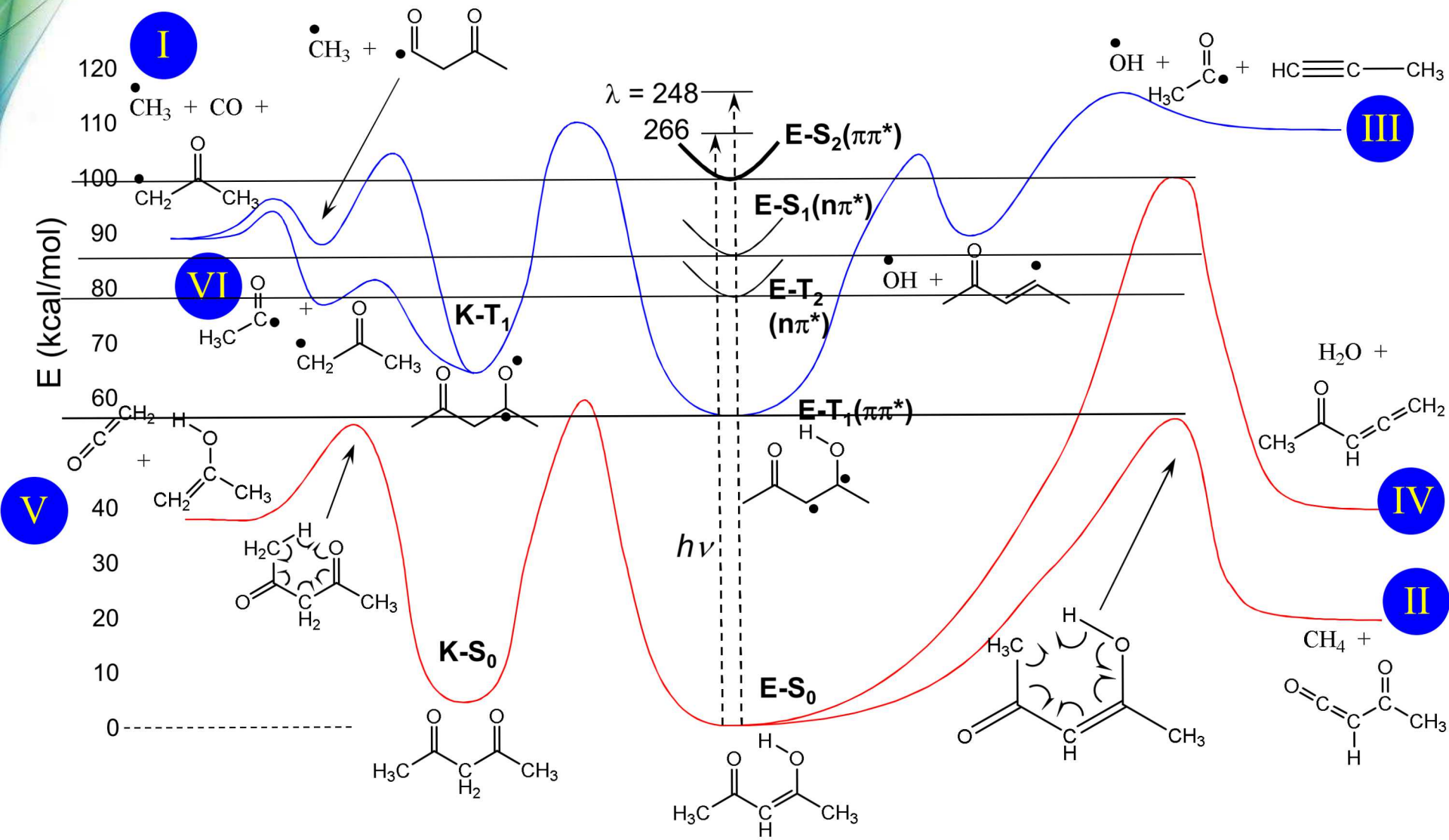

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