Fundamental dynamics of bond-selective chemistry initiated by low-energy electrons

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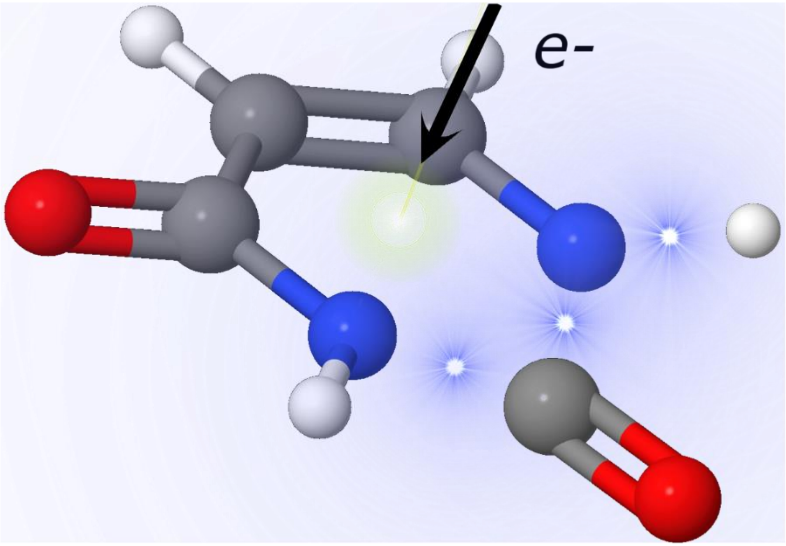
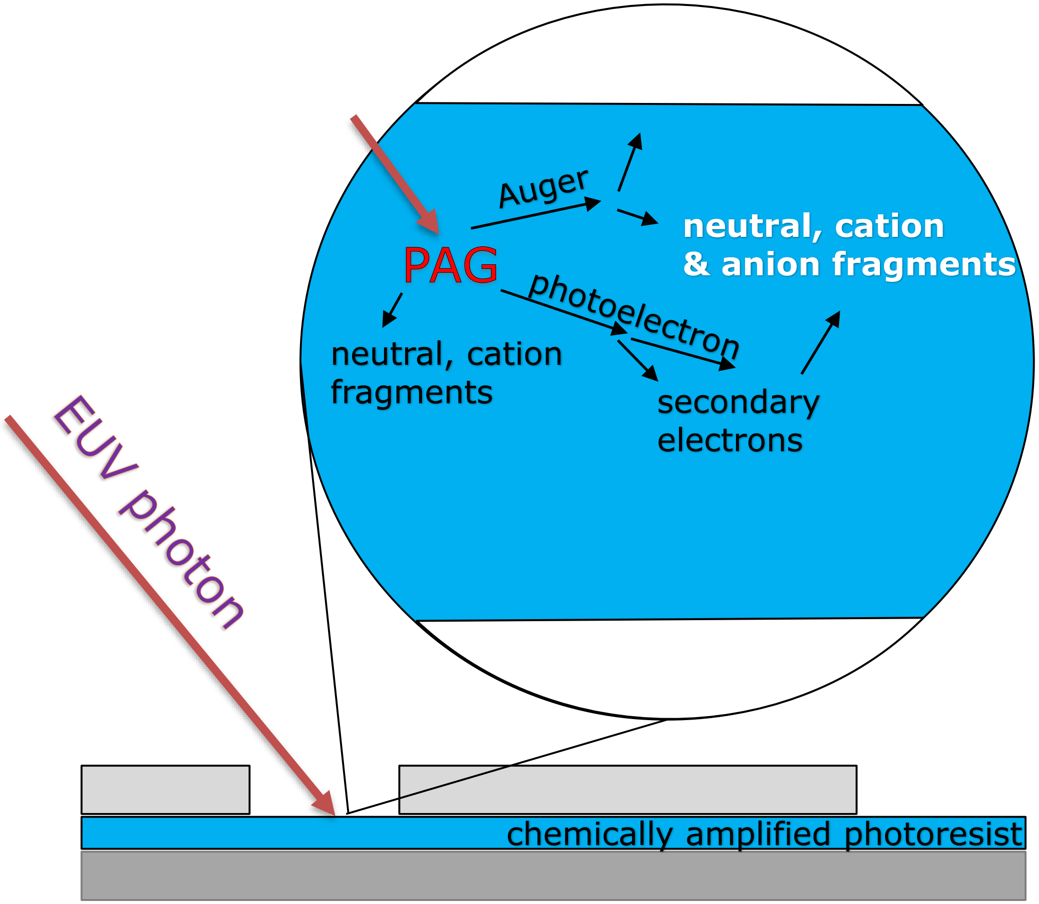
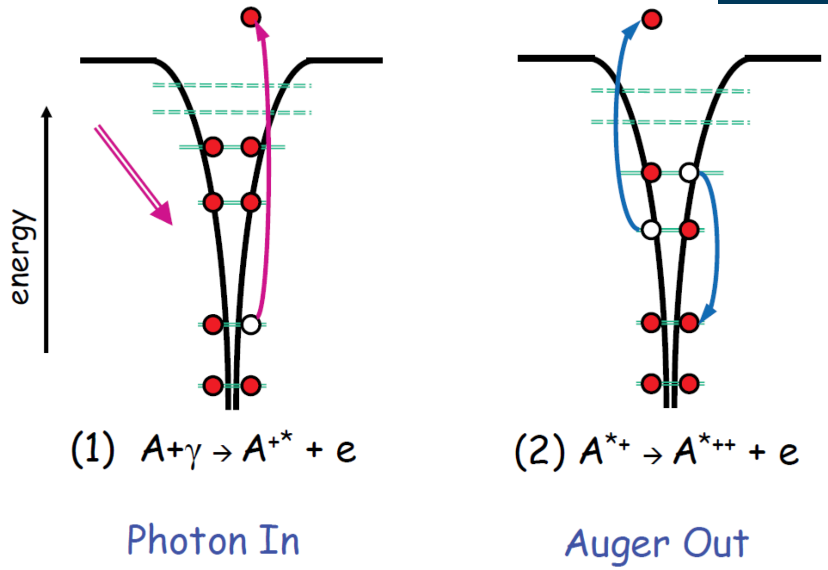


EUV photons ionize inner shell electrons

Closser *et al.* J. Chem.Phys. **146**, 164106 (2017)
doi: 10.1063/1.4981815
Kostko *et al.* J. Chem. Phys. **149**, 154305 (2018)
doi: 10.1063/1.5046521

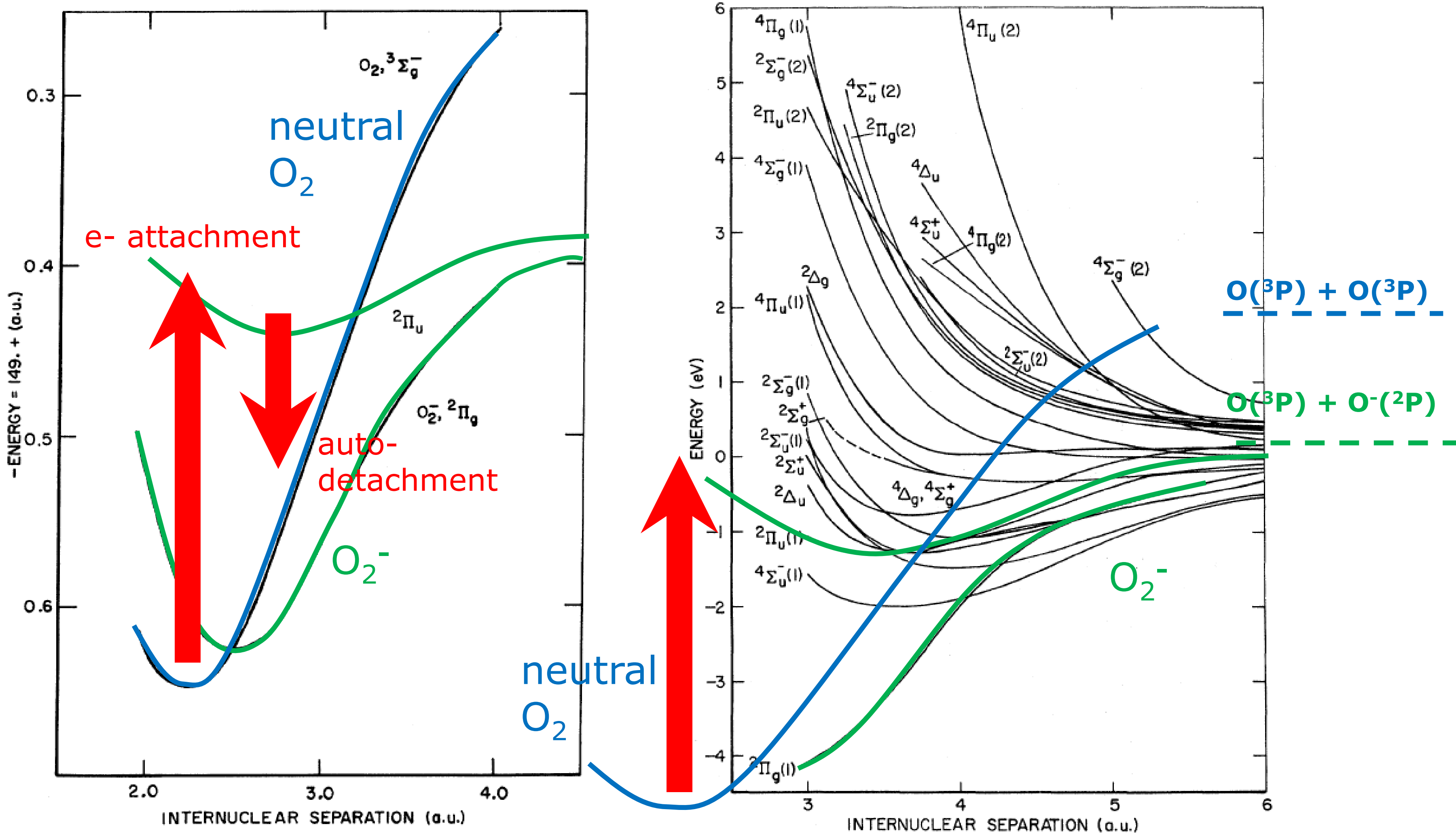




DF Ogletree, in *Next Generation Lithography*, Elsevier 2016

- Direct photoelectrons
- Auger electrons
- secondary e-driven processes
  - ionization
  - resonant excitation
  - resonant electron attachment

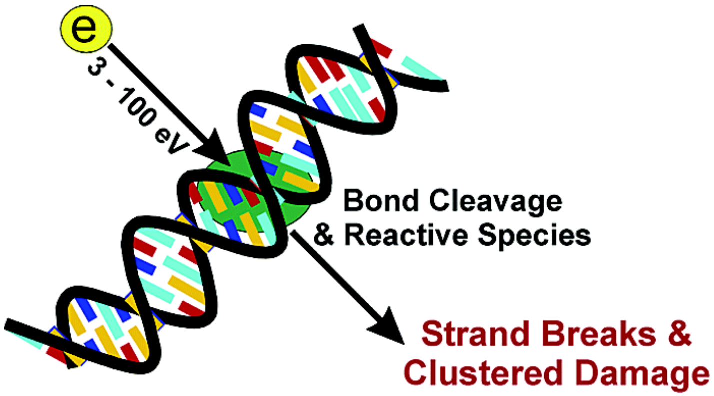
1-D example of dissociative electron attachment



from Krauss et al. (1973) Phys. Rev. A, **7** 69

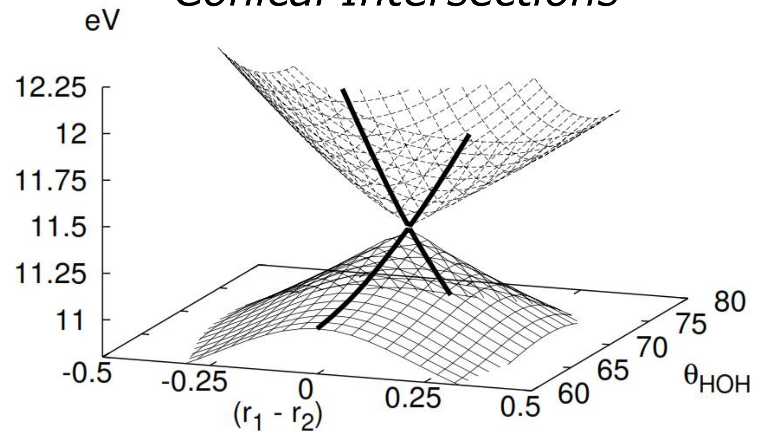
Why are low energy electrons so important?

After energy is deposited by ionizing radiation, low energy electrons damage molecules by through transient anion resonances



Huels *et al.* (2003) J. Am. Chem. Soc. **125**, 4467
Alizadeh and Sanche *(*2013) Chem. Rev. **112**, 5578

Conical Intersections



Haxton *et al.* (2007) Phys. Rev. A **57**, 012710

electronic motion ⟺ nuclear motion

Efficient conversion of electronic energy into energetic reactive ionic and radical species

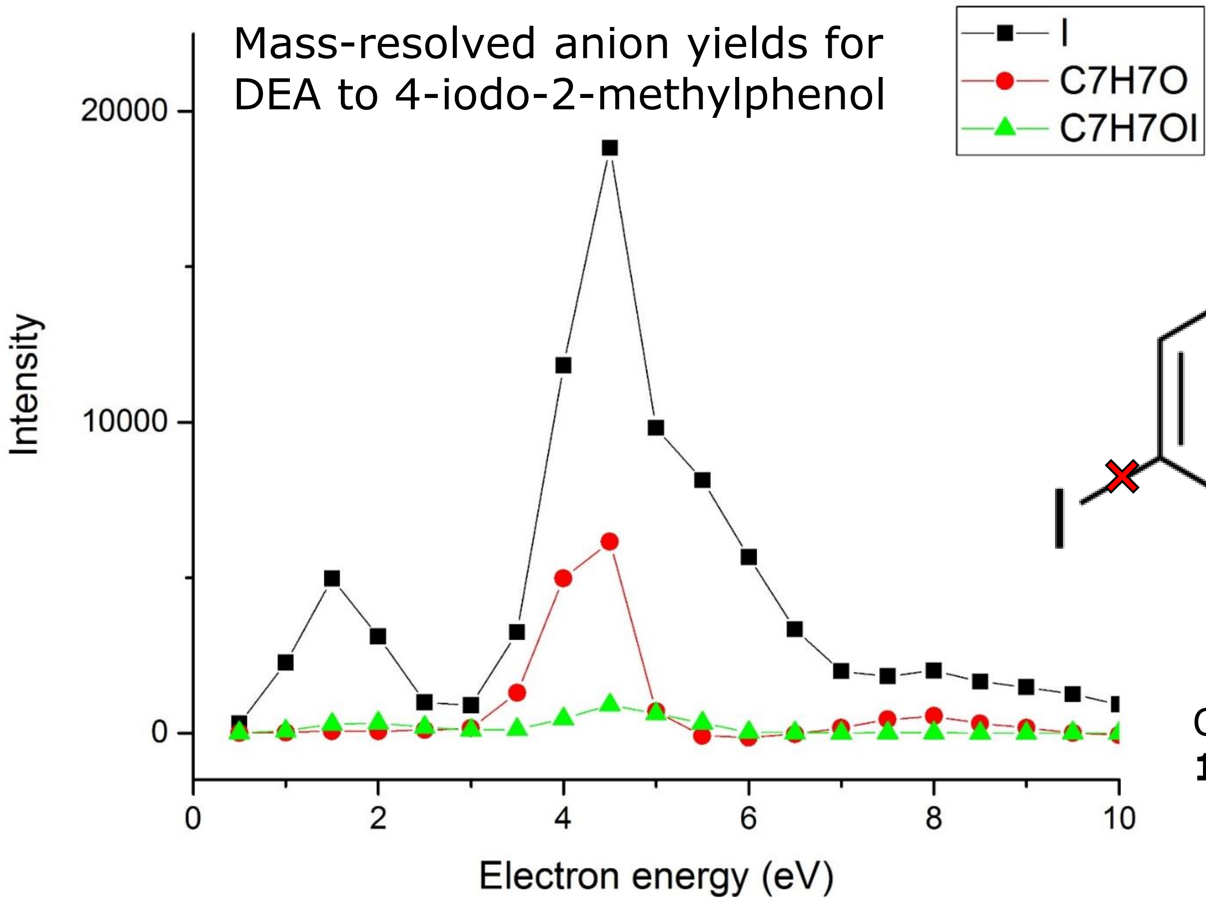
What are the molecular dynamics of these processes?

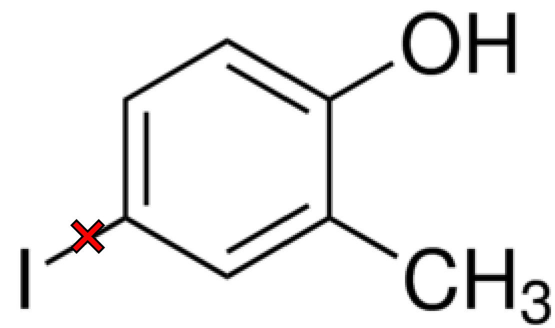
Specific electron energy leads to bond-specific dissociation

Dissociative electron attachment is a resonant electron-molecule interaction.

Incident electron energy determines the product species.

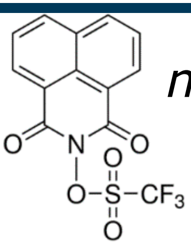
Excess energy goes into specific vibrational modes or fragment kinetic energy.





O. Kostko et al., *J. Chem. Phys.* **149**, 154305 (2018)

Site-selectivity in a model photo-acid generator



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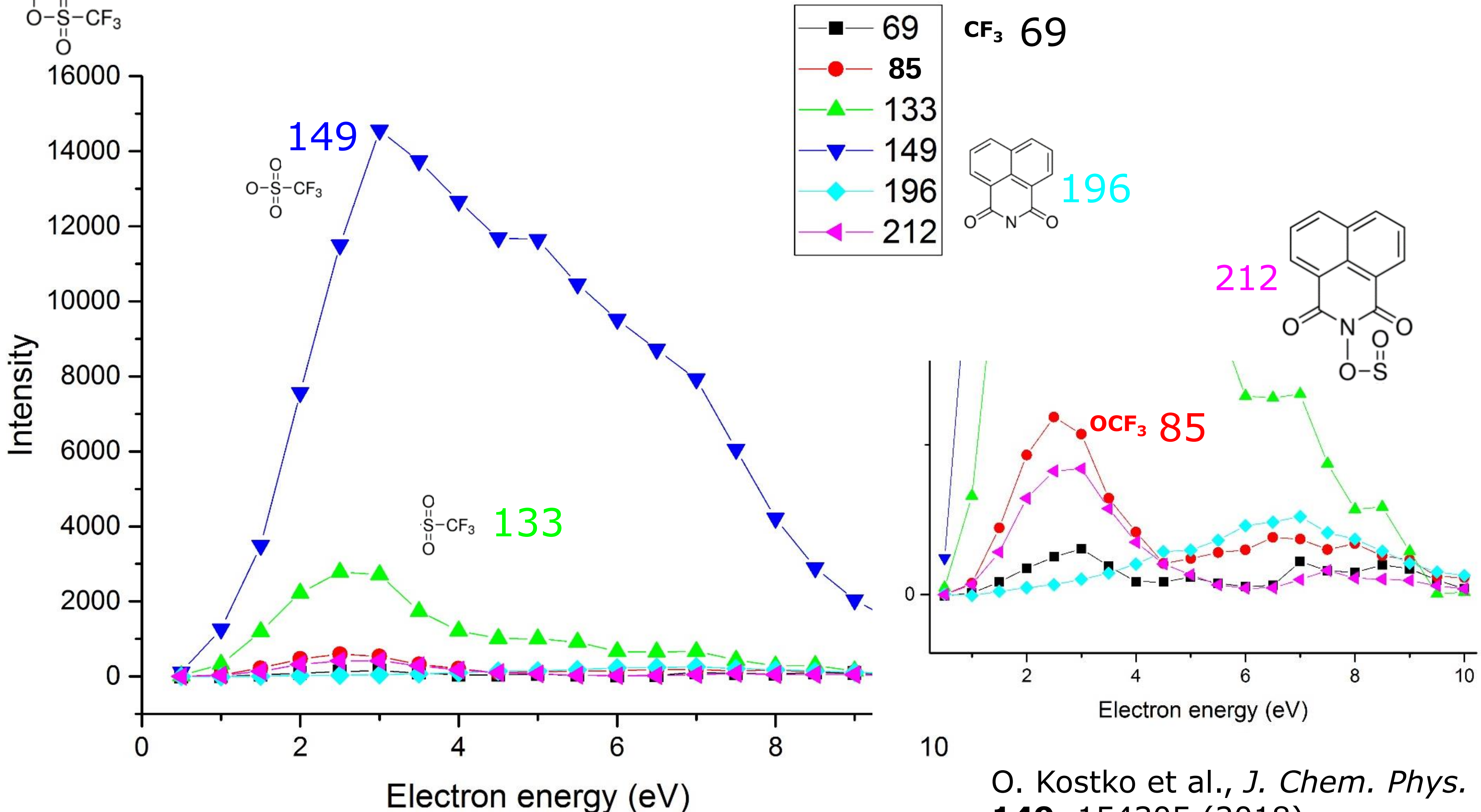
Mass-resolved anion yields for DEA to N-Hydroxynaphthalimide triflate



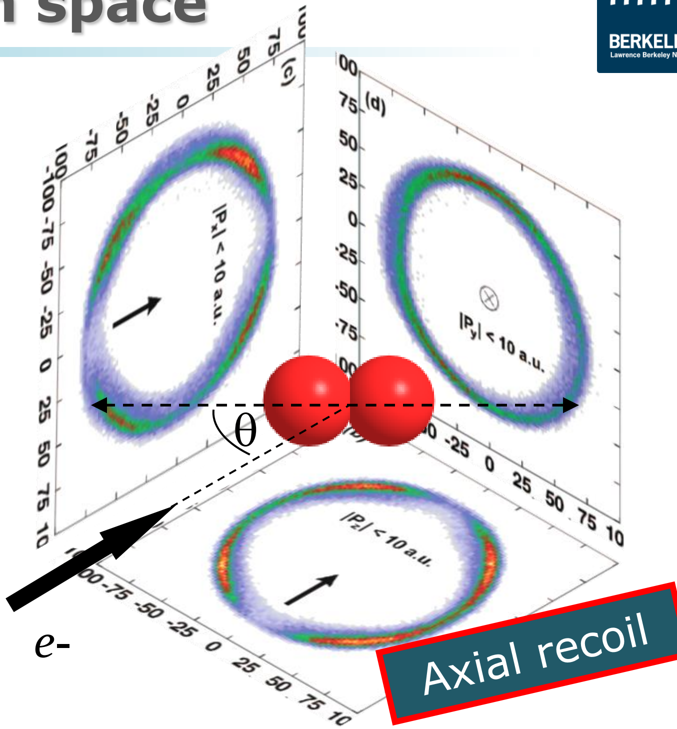
O. Kostko et al., *J. Chem. Phys.* **149**, 154305 (2018)

Interrogating reactions in momentum space

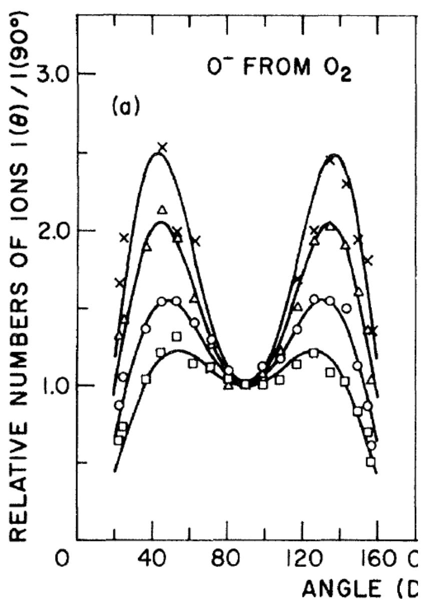
Measure each fragment ion momentum over a large volume of momentum space

All fragment ions are detected in parallel

Molecule can later be oriented in the lab frame if the axial recoil approximation holds



Van Brunt and Kieffer (1970) Phys. Rev. A **2**, 1899

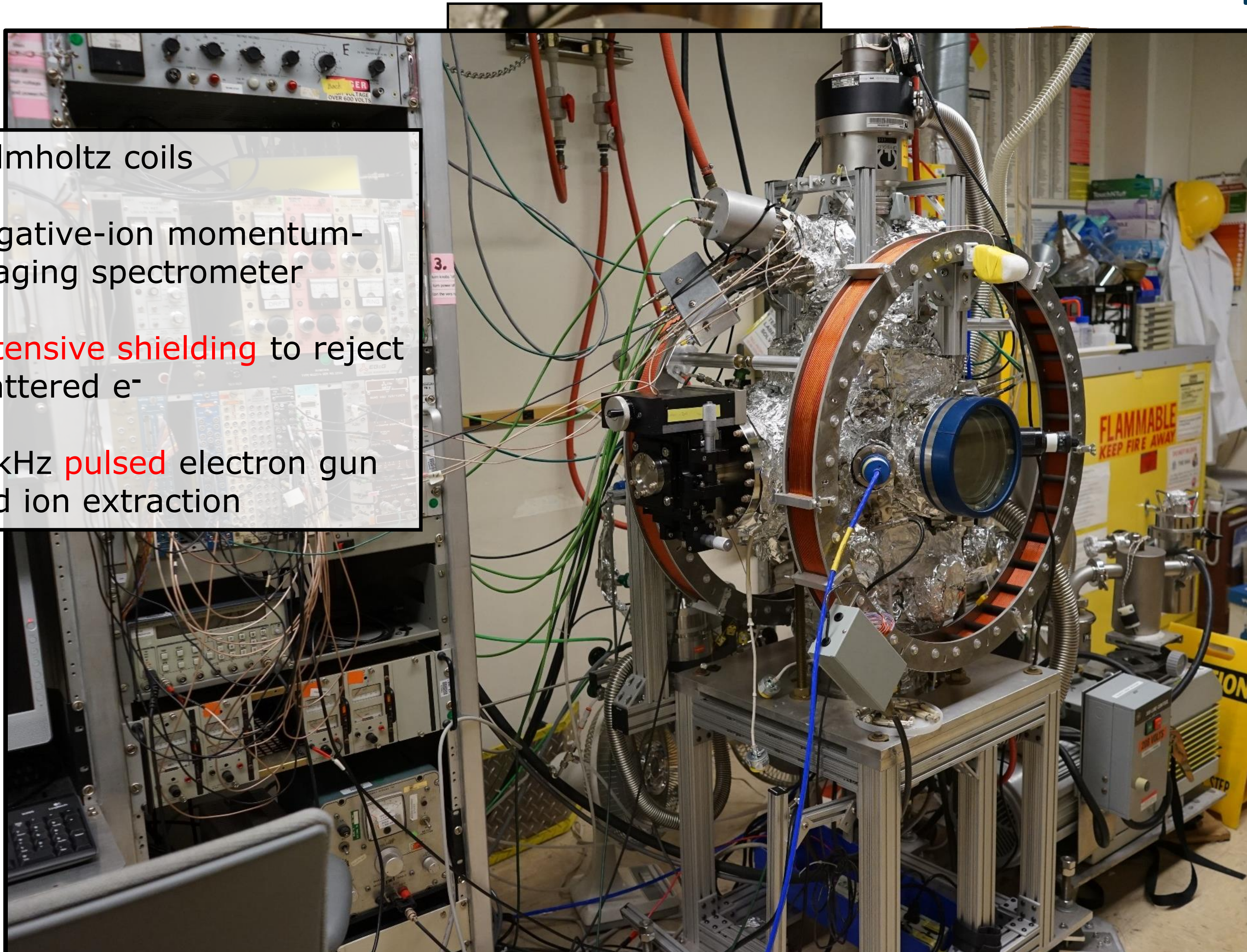


Electron scattering calculations to accurately predict electron attachment probability in the molecular frame

$\Longrightarrow$ axial recoil ion angular distribution

We can clearly see when the axial recoil approximation fails

DEA reaction microscope



Helmholtz coils

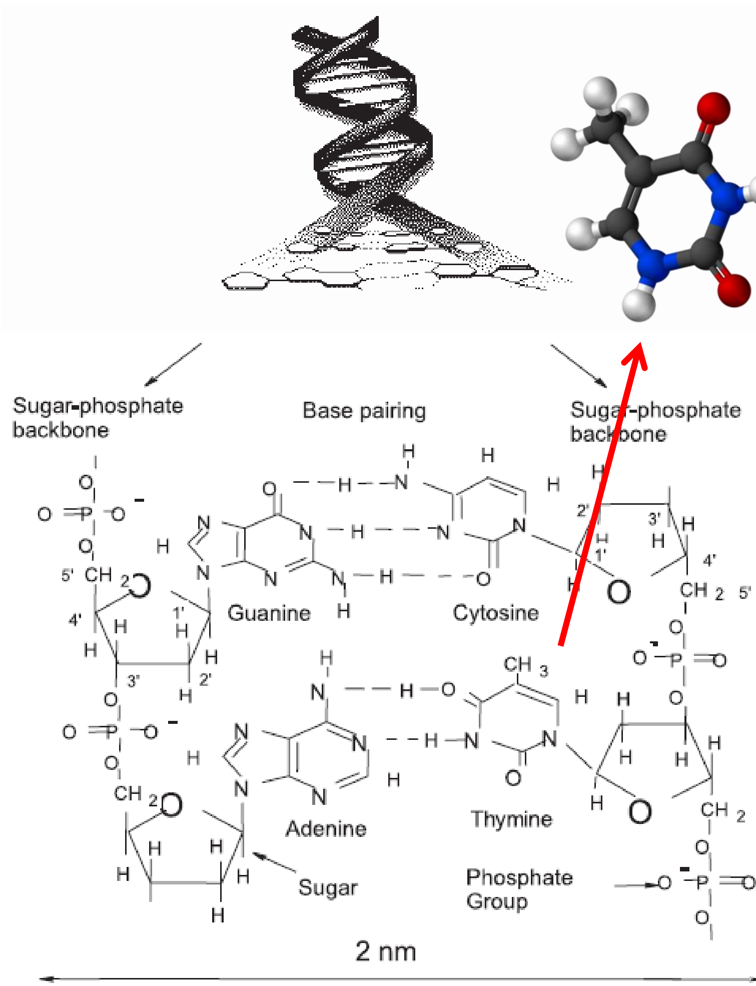
Negative-ion momentum-imaging spectrometer

Extensive shielding to reject scattered e^-

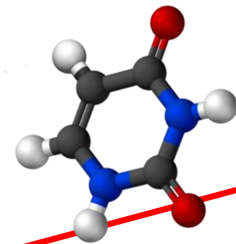
50kHz pulsed electron gun and ion extraction

Complex molecules in a molecular beam

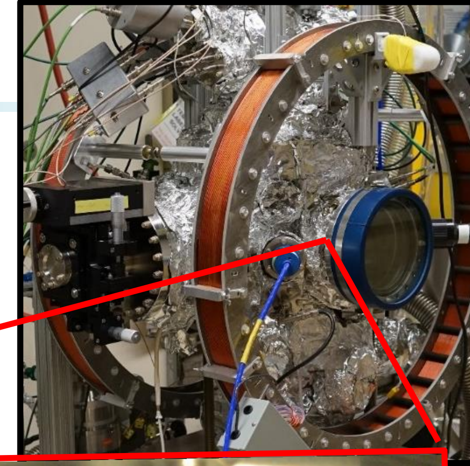
Heat in vacuum: 20°C to 300°C to create a dense gas sample

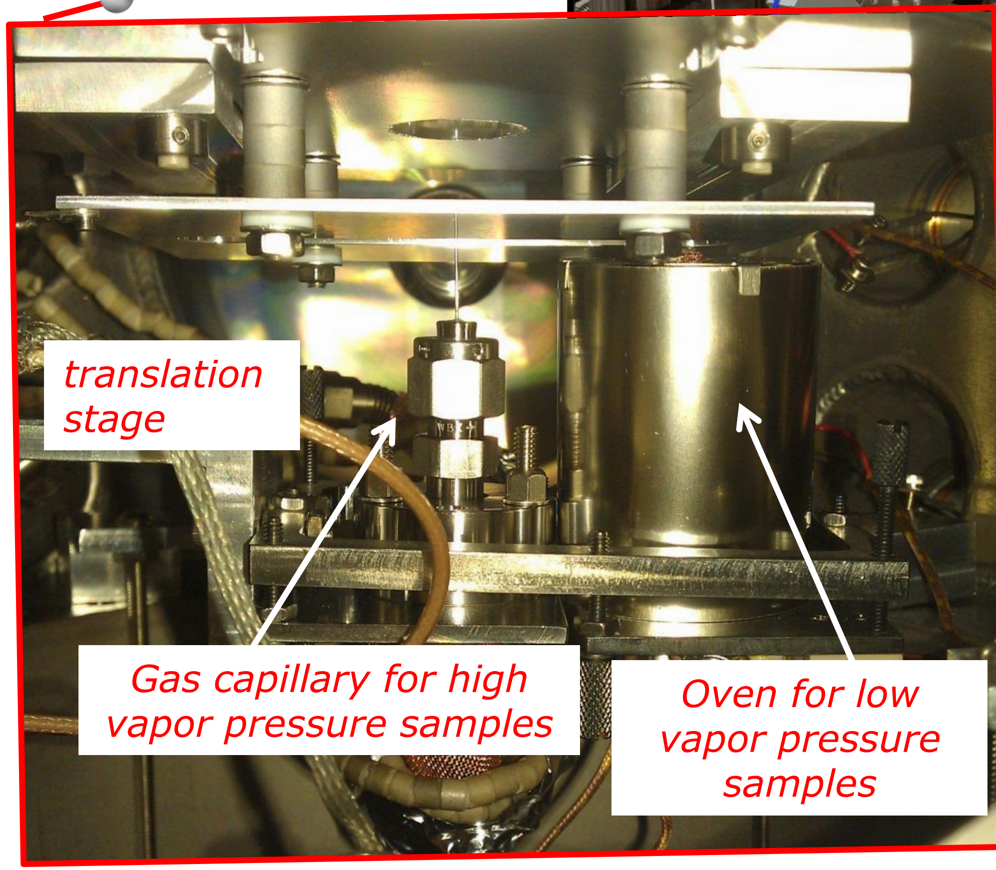


Part of DNA Structure



Uracil





Theory and computation

Calculate electron attachment amplitude: Complex Kohn scattering theory

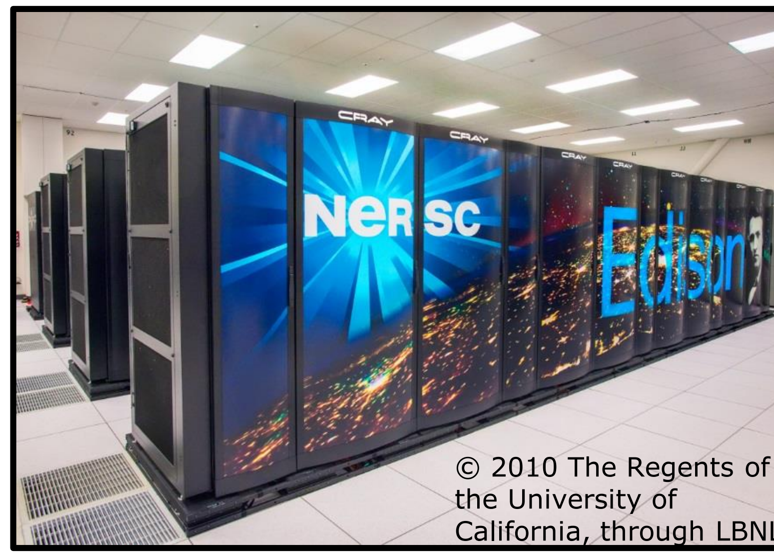
Complex potential energy surfaces of the anion states are computed using Multi-Reference Configuration Interaction

Anion dynamics can be modelled using classical trajectories on multiple PES
 - e.g. Haxton *et al* PRA 84 030701 (2011)





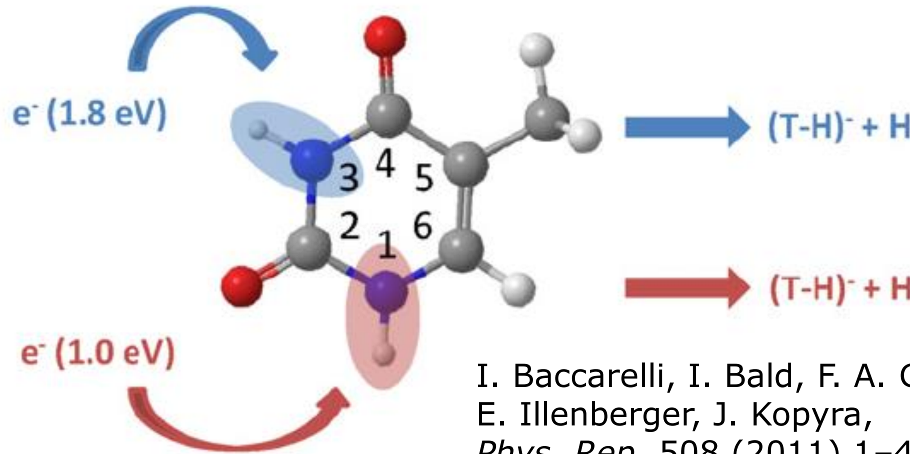
Tom Rescigno, Bill McCurdy, Dan Haxton, Ann Orel (UC Davis), Nicolas Douguet (now U. Central Florida), Cynthia Trevisan (Cal. Maritime)



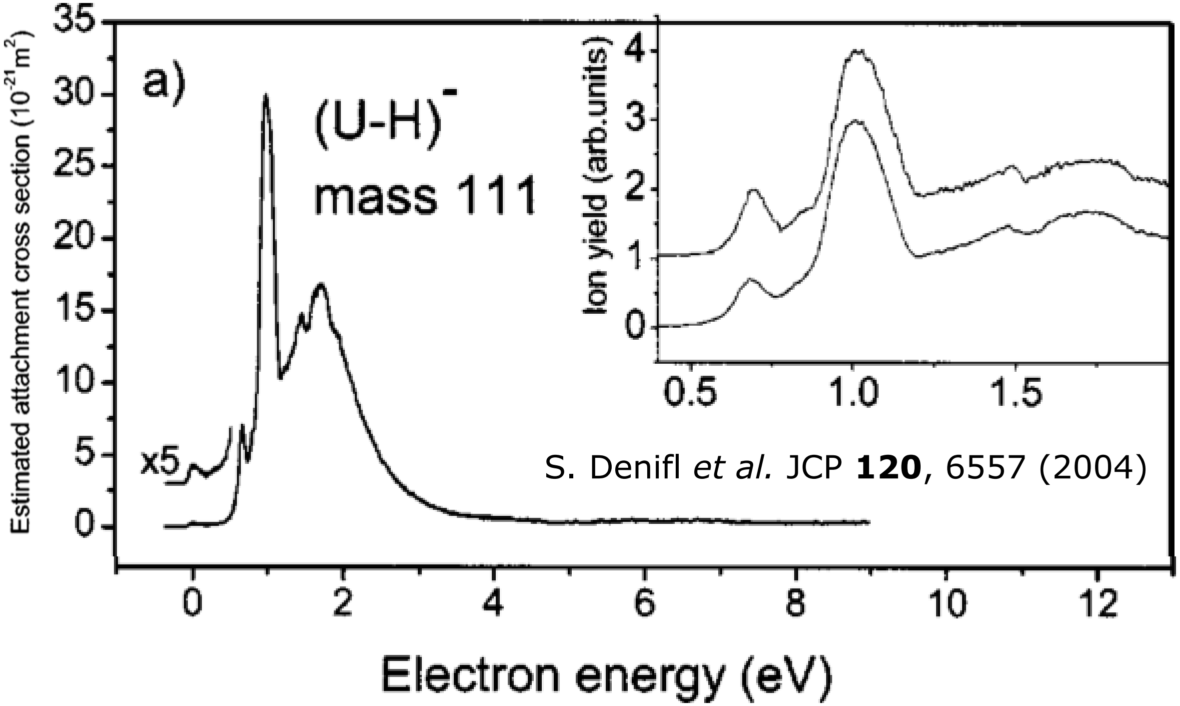
Low-energy site-selectivity in DNA nucleobases

Previous experiments and theory have focused on very low electron energy collisions with uracil and thymine.

A dominant dissociation channel is hydrogen loss at 1~2 eV



I. Baccarelli, I. Bald, F. A. Gianturko, E. Illenberger, J. Kopyra, *Phys. Rep.* 508 (2011) 1–44



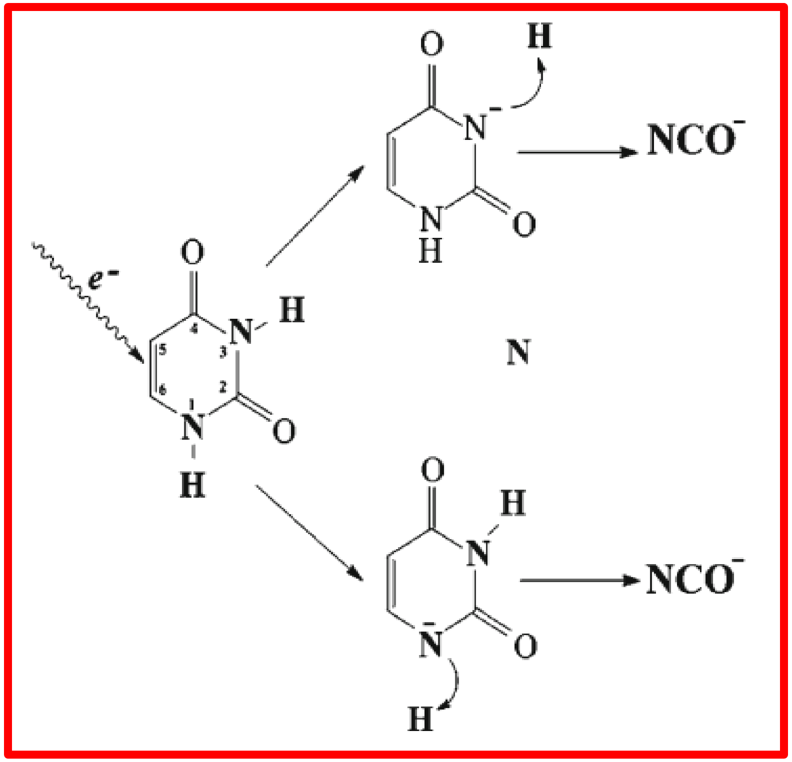
S. Denifl *et al.* JCP **120**, 6557 (2004)

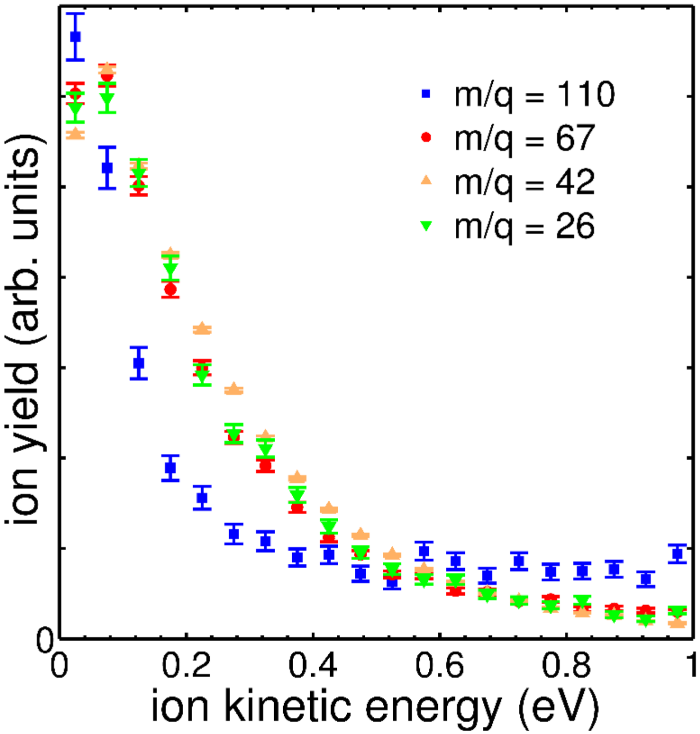
Higher electron energies > 2 eV

NCO$^-$ production was found to be a sequential process

Site selectivity is retained through the sequence

Momentum imaging experiments determined that most of the excess energy excites vibrational modes of the neutral product.

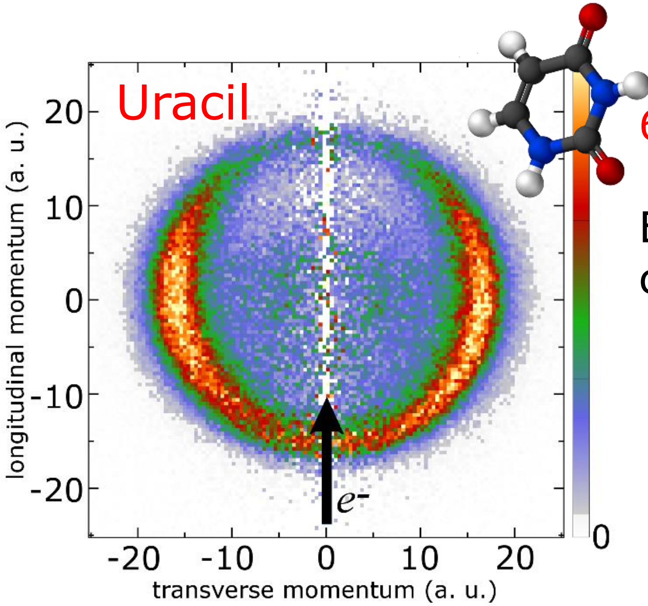




Y. Kawarai, Th. Weber, Y. Azuma, C. Winstead, V. McKoy, A. Belkacem, D. S. Slaughter, *J. Phys. Chem. Lett.* (2014) 5 3854

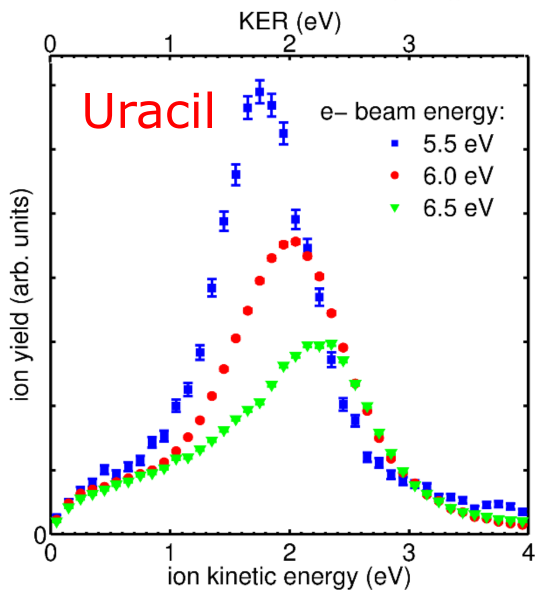
F. Ferreira da Silva *et al. J. Am. Soc. Mass Spectrom*. (2013) 24:1787
S. Denifl *et al. Chem Phys Chem* (2008), 9, 1387;

Uracil and thymine: H⁻ fragment

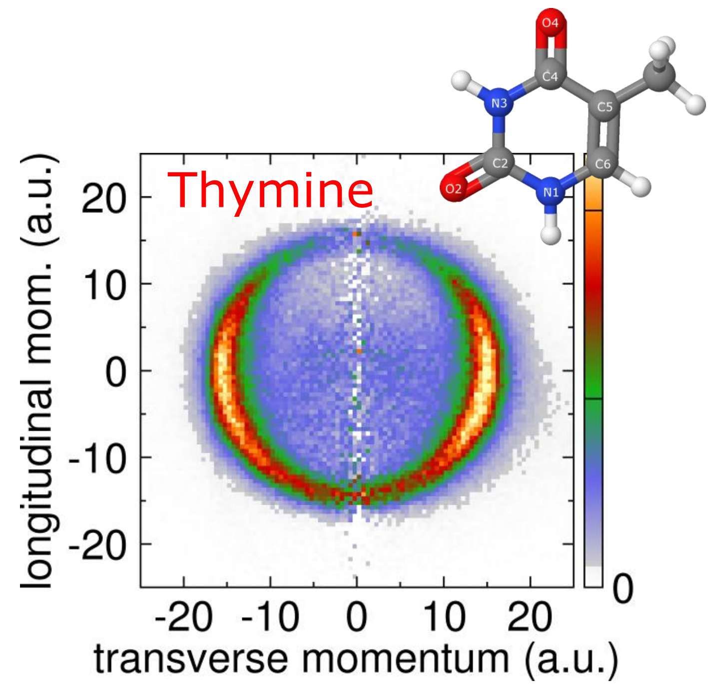


6 eV e-attachment, narrow-high kinetic energy release

Excited anion is repulsive along the 2-body dissociation coordinate

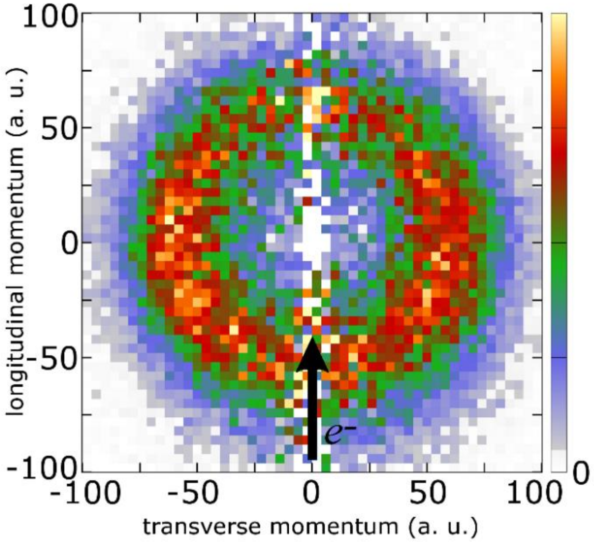


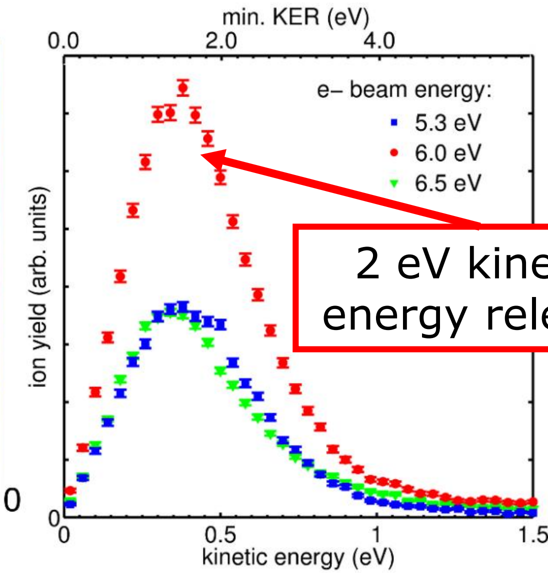
Thymine H^- momentum image is almost identical



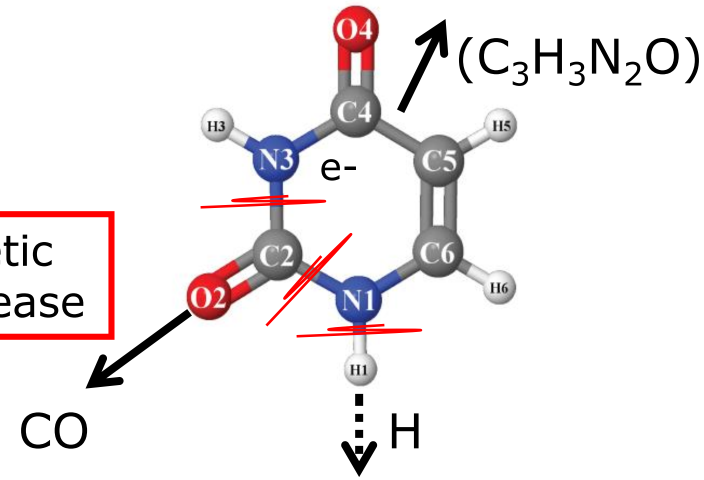
Y. Kawarai, Th. Weber, Y. Azuma, C. Winstead, V. McKoy, A. Belkacem, D. S. Slaughter, *J. Phys. Chem. Lett.* (2014) 5 3854

Uracil: $C_3H_3N_2O^-$ fragment





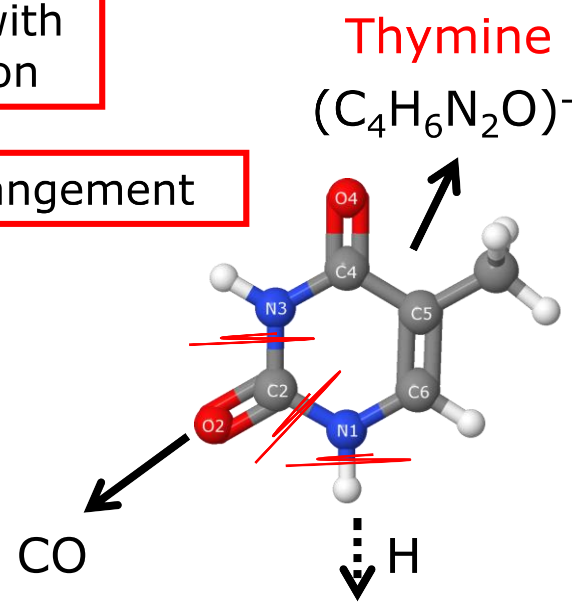
2 eV kinetic energy release

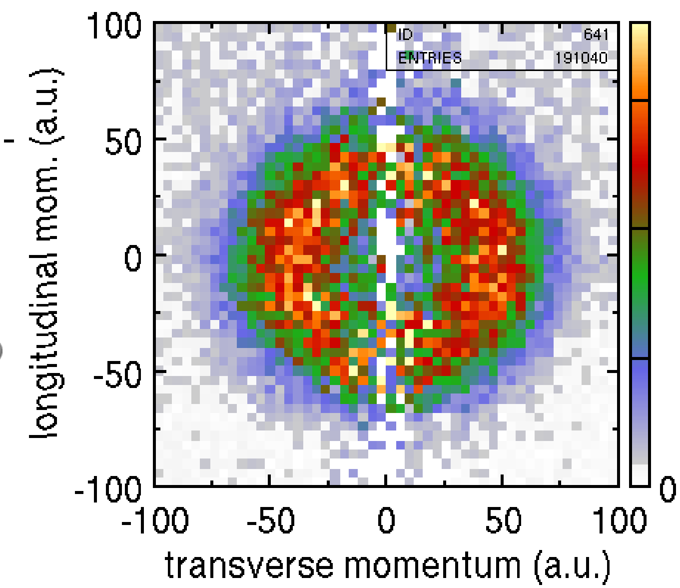


Kawarai *et al.*
J. Phys. Chem. Lett. (2014) **5** 3854

3 bonds breaking with only 5.3 eV collision

Bond formation, rearrangement

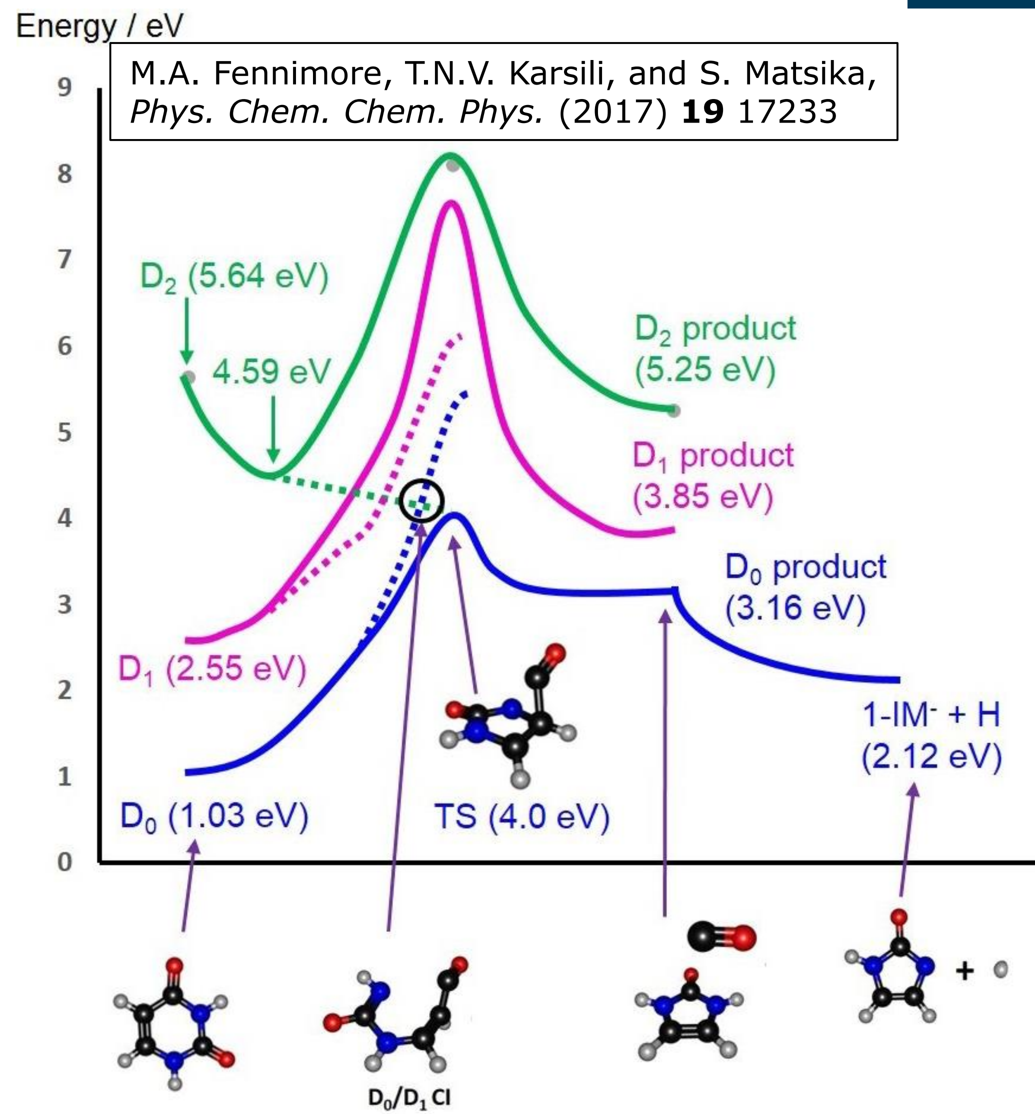




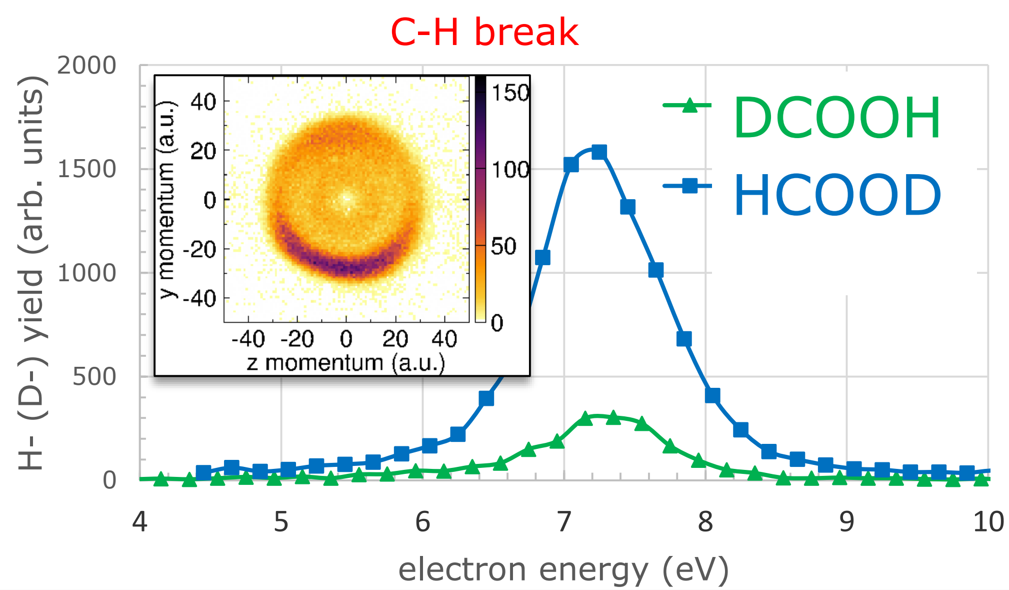
Potential energy surfaces for uracil

S. Matsika (Temple U.) found conical intersections between the resonance anion potential energy surface.

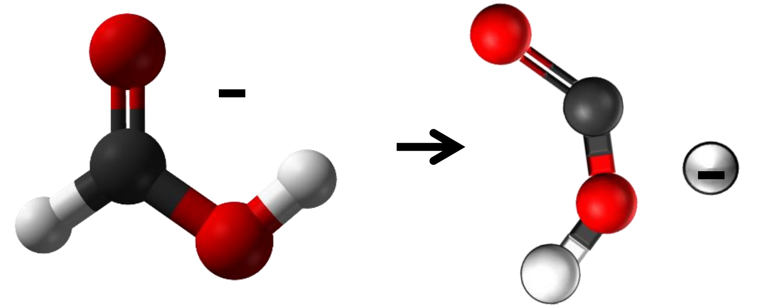
CO elimination from the ring, followed by H elimination.

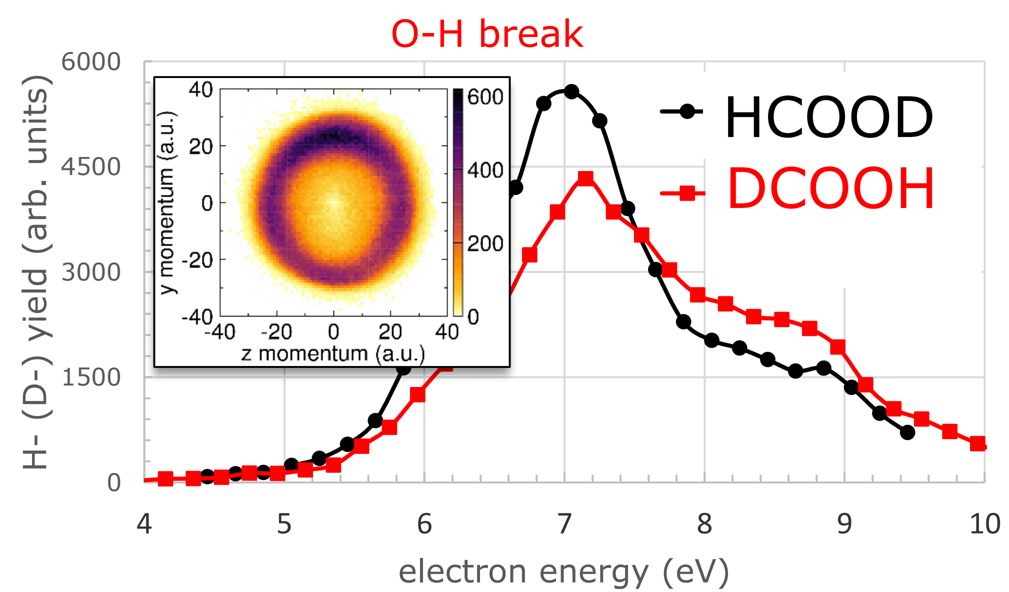


Site selectivity in formic acid: relative ion yields



$HCOOH + e^{-} \rightarrow H^{-} + HOCO$





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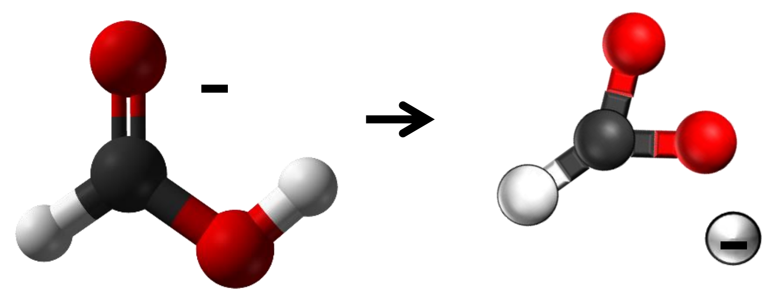
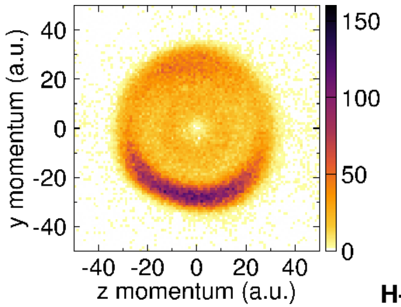
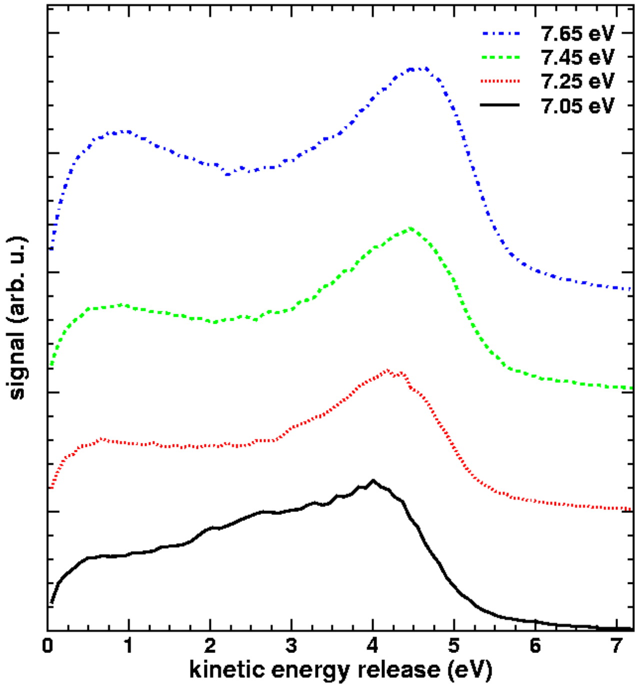


Kinetic energy released in dissociation products

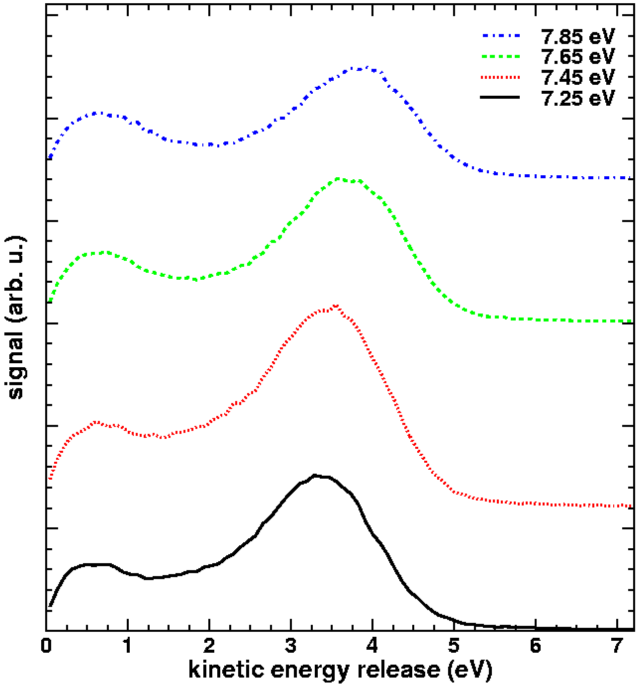


C-H break, H- (or D-) kinetic energy

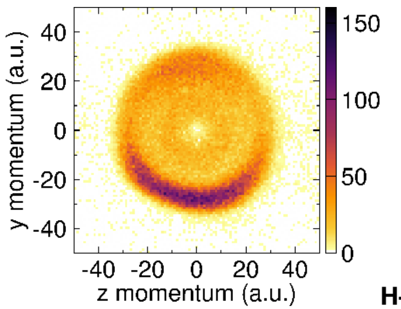
H-/HCOOD KER



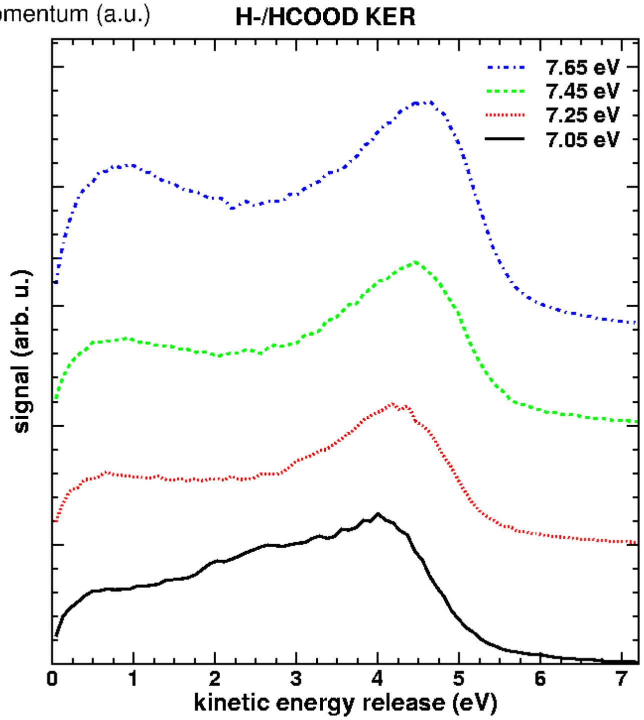
D-/DCOOH KER

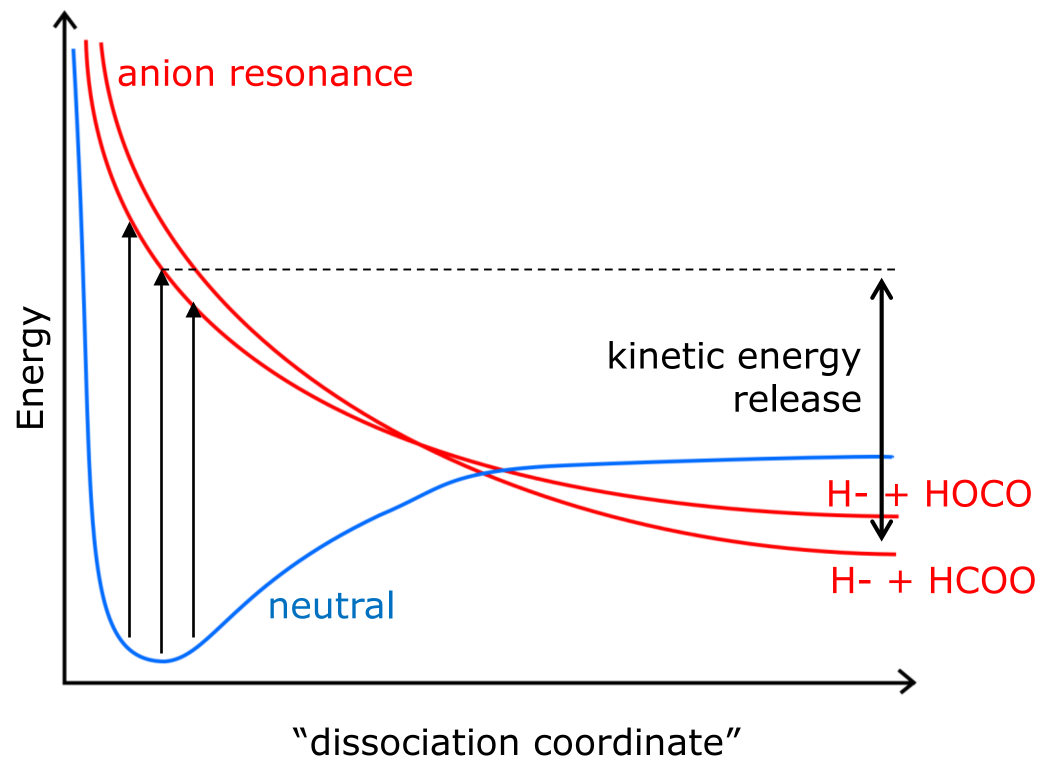


Kinetic energy released in dissociation products



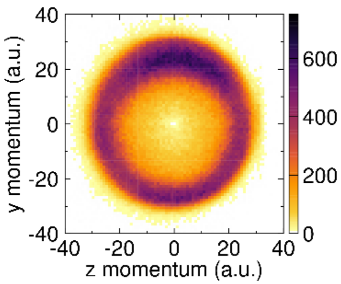
C-H break, H- (or D-) kinetic energy

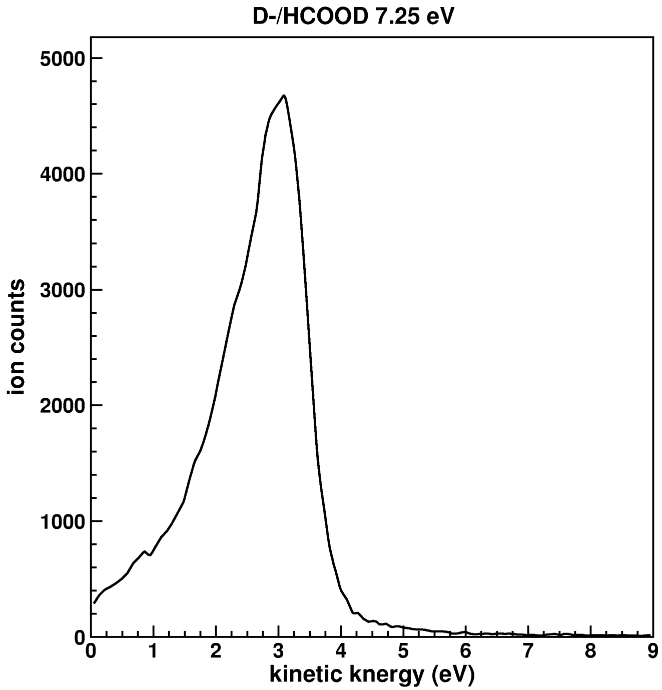


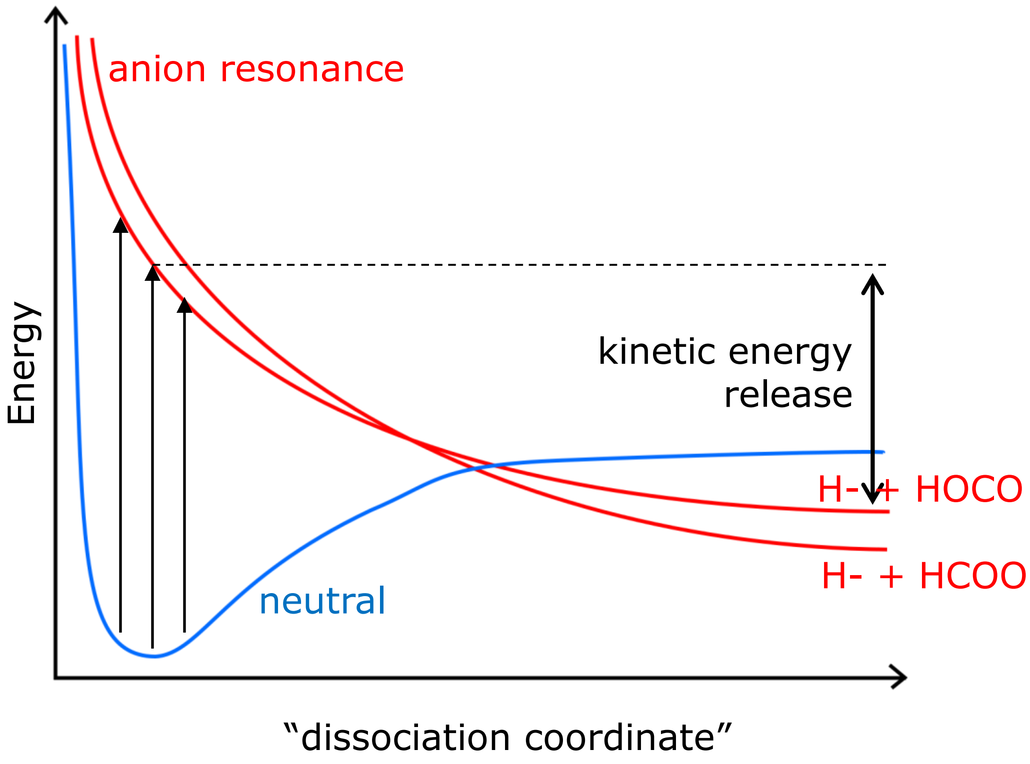


Kinetic energy released in dissociation products

O-H break, H- (or D-) kinetic energy

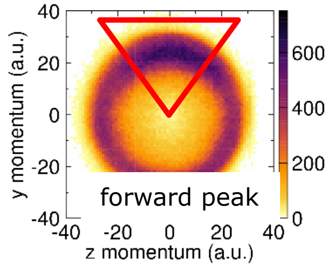


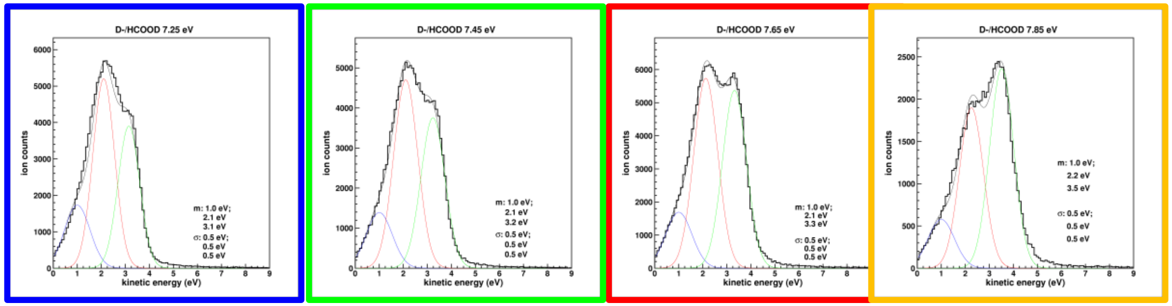


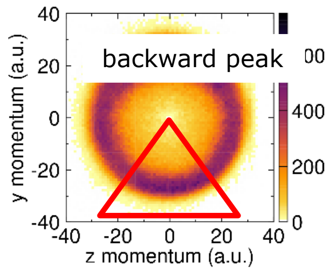


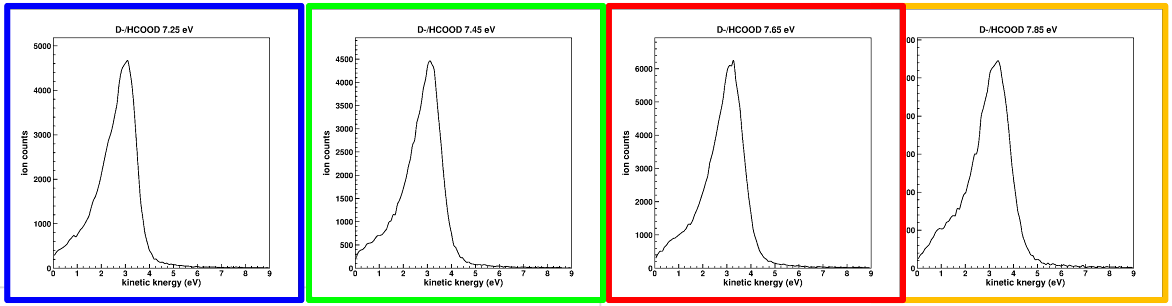
Kinetic energy released in dissociation products

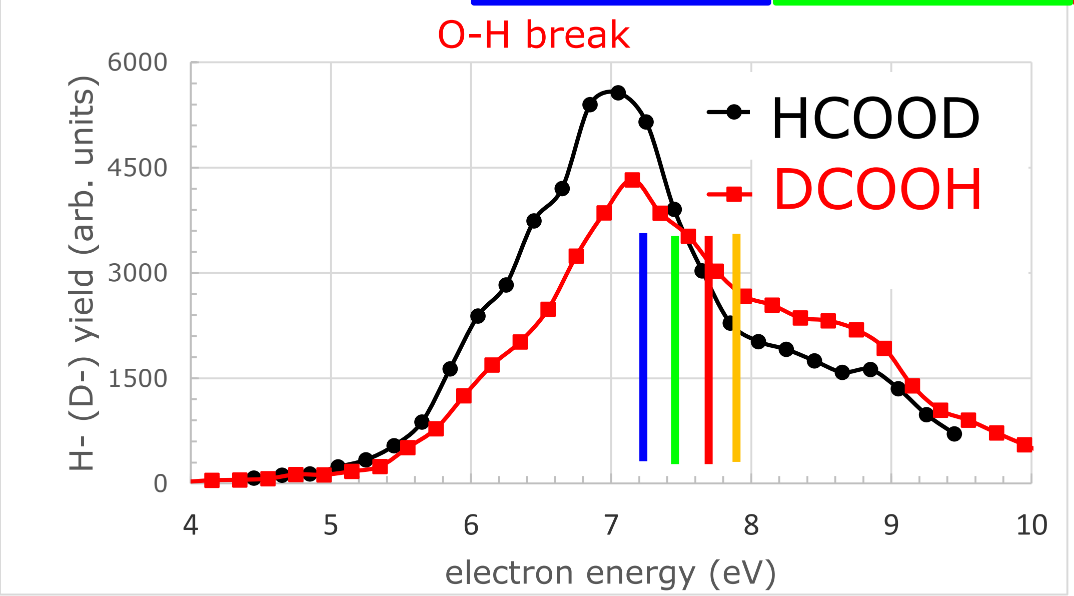
D⁻ / HCOOD (O-D break)



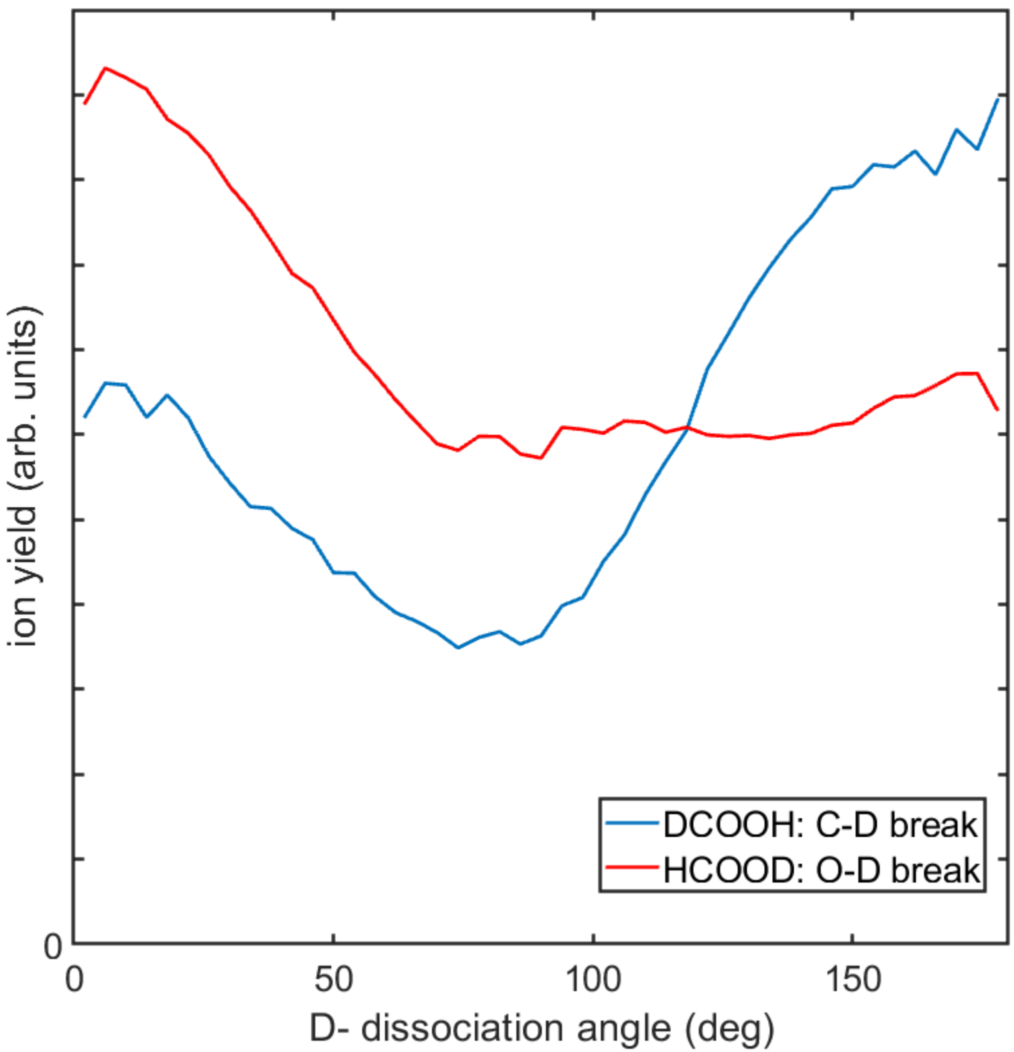




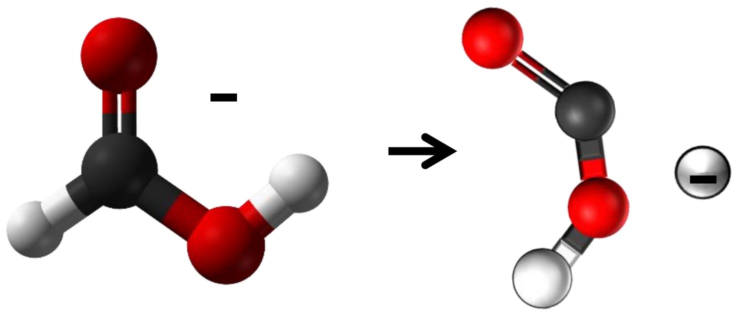




Laboratory-frame angular distributions



HCOOH + e⁻ → H⁻ + HOCO



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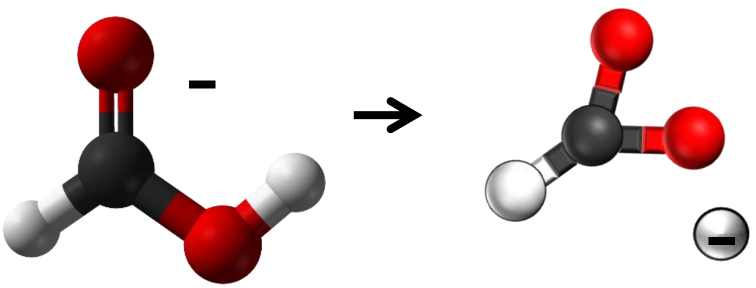
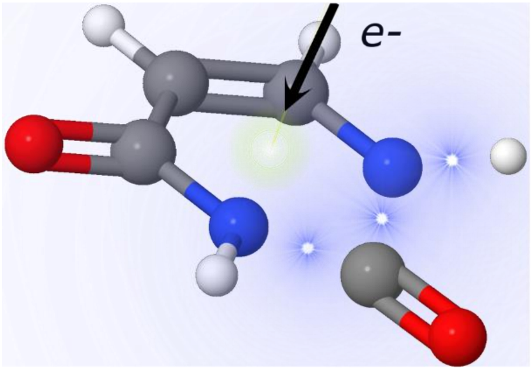


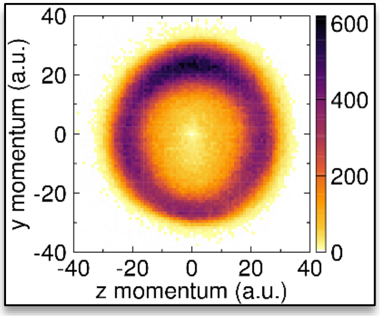
Conclusions and summary

Anion fragment momentum imaging reveals chemical dynamics initiated by low energy electrons.

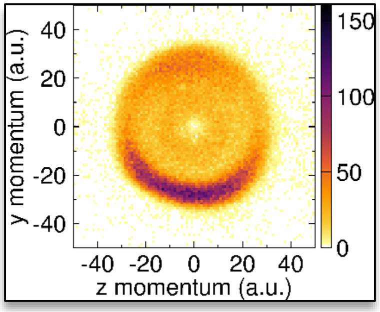


This has direct relevance to chemical reactions occurring as ionizing radiation deposits energy in matter.

The nucleobases uracil and thymine dissociate by H- or CO+H elimination with high kinetic energy release, in addition to the well-known unimolecular decay processes.



Site-specific dissociation occurs via two resonances in formic acid, and each resonance has a different momentum distribution.



Two product channels from the lower resonance implies a conical intersection between the anion potential energy surfaces. Investigation of the nonadiabatic dynamics and dissociation mechanisms is ongoing.

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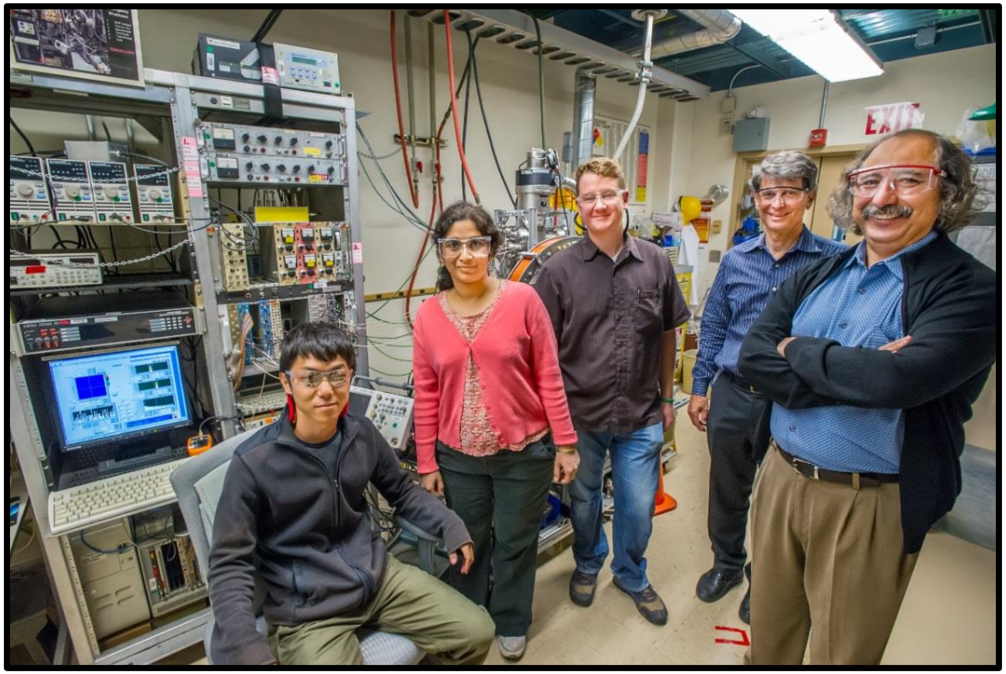

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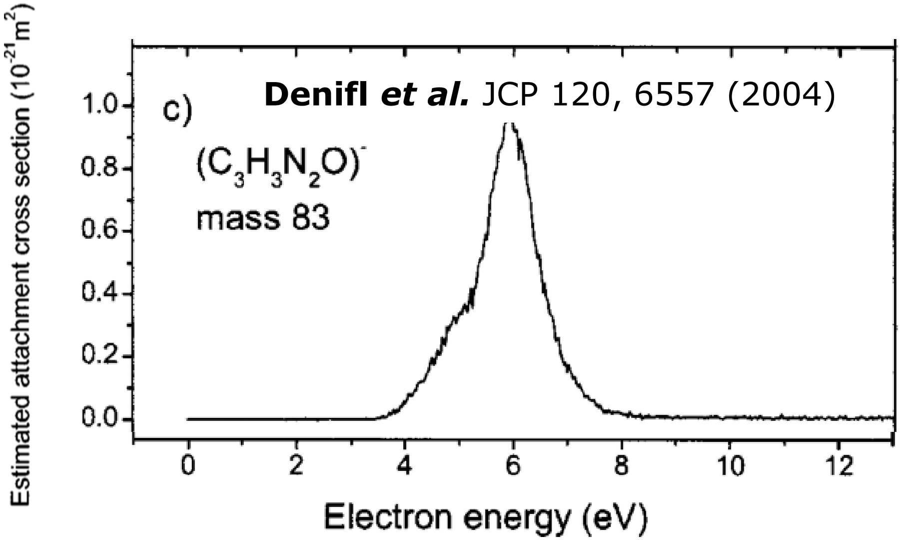
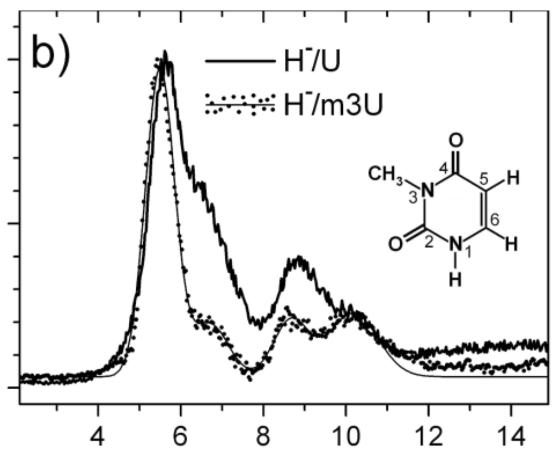
Extra slides

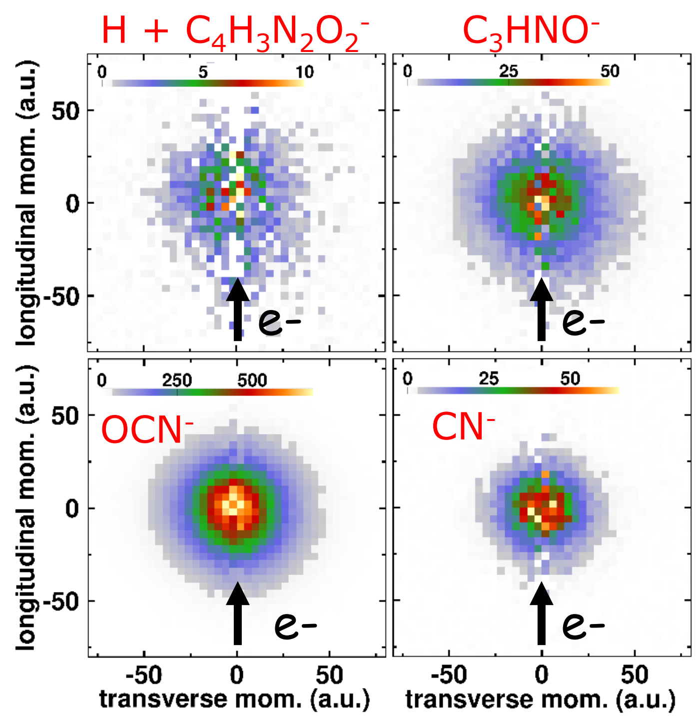
Uracil

Other breakup channels open from ~5 eV (Feshbach resonances)



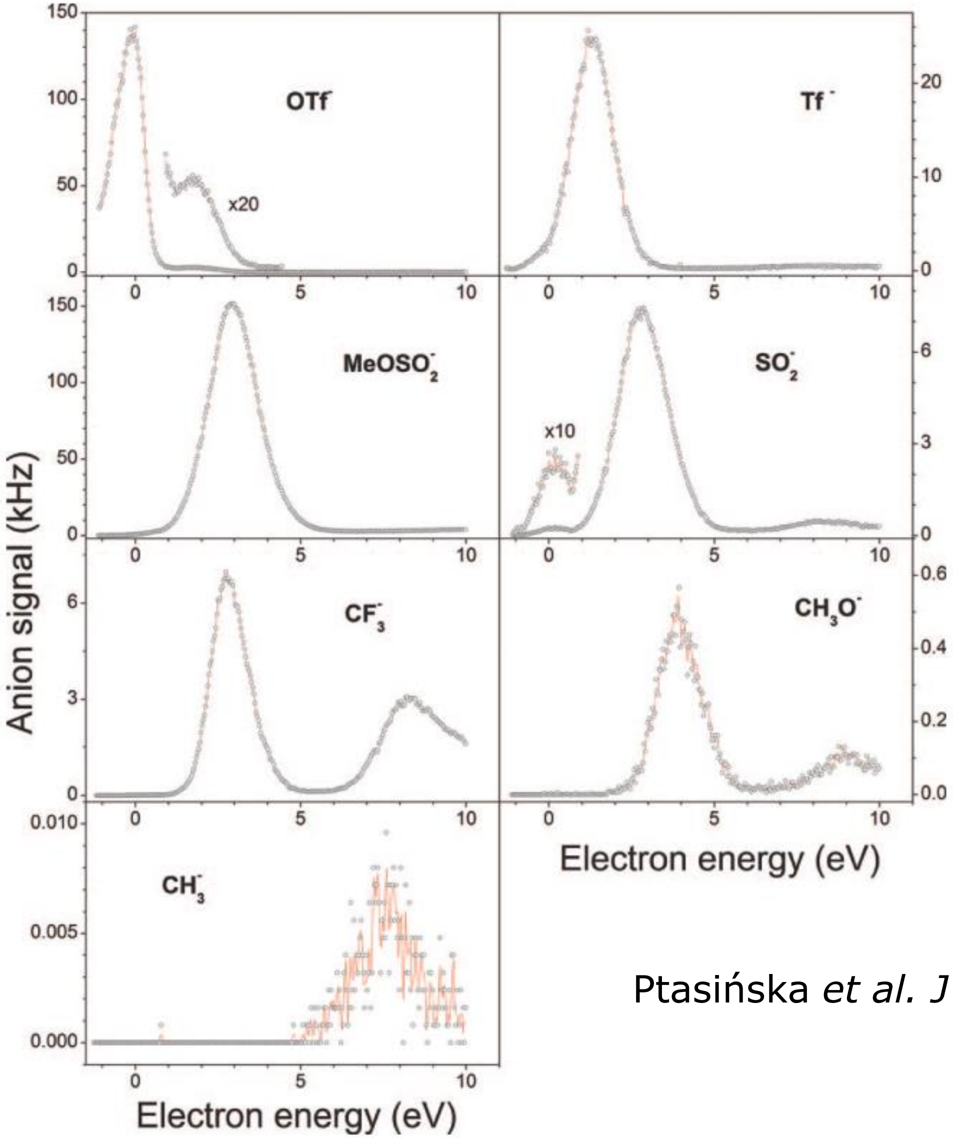


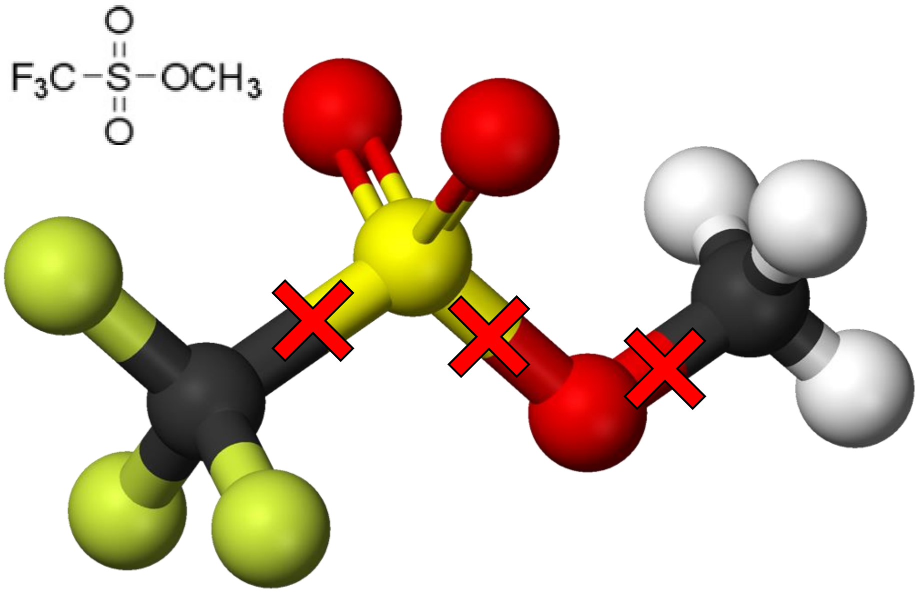
Ptasinska *et al. PRL* **95**, 093201 (2005)



Y. Kawarai, Th. Weber, Y. Azuma, C. Winstead, V. McKoy, A. Belkacem, D. S. Slaughter, *J. Phys. Chem. Lett.* (2014) 5 3854

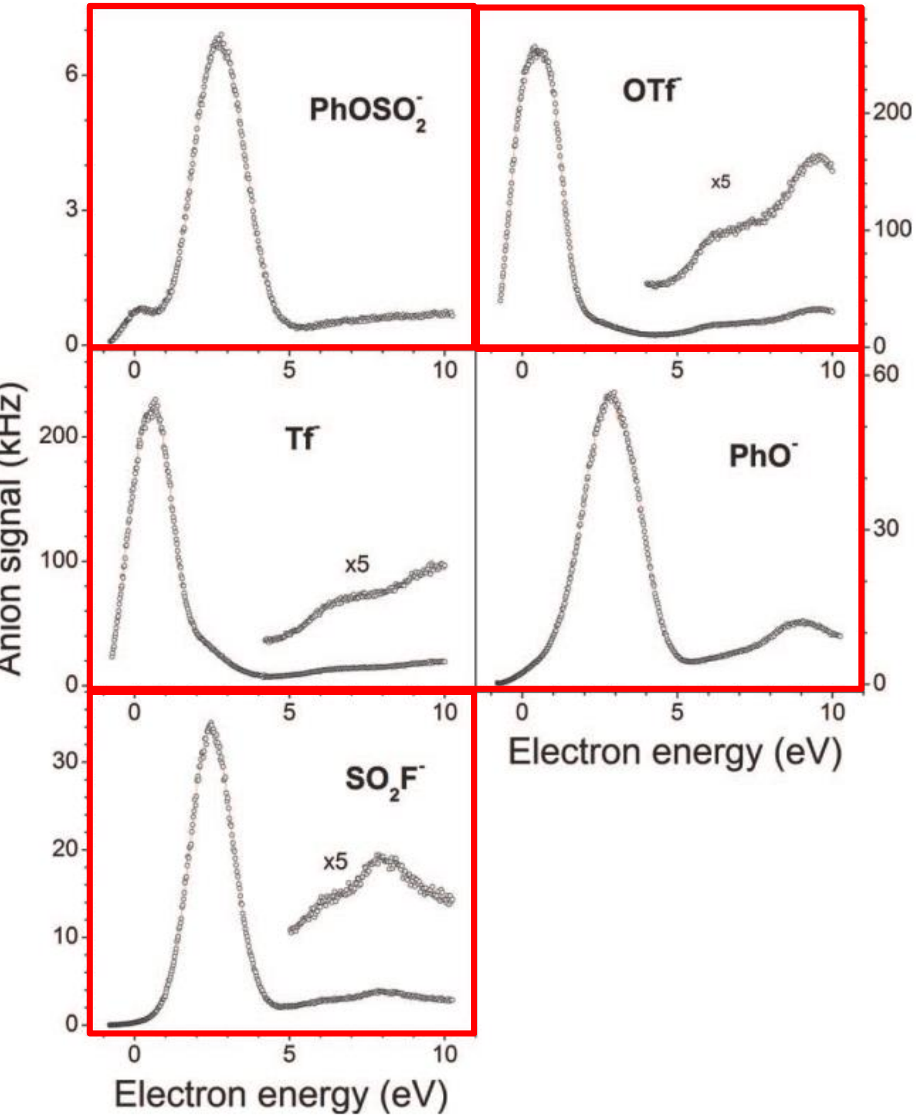
Model photo-acid generators

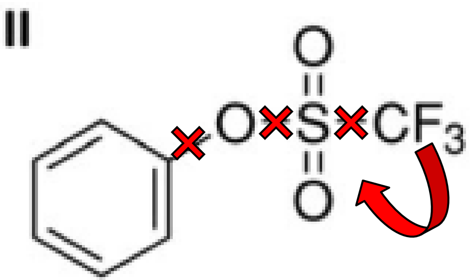




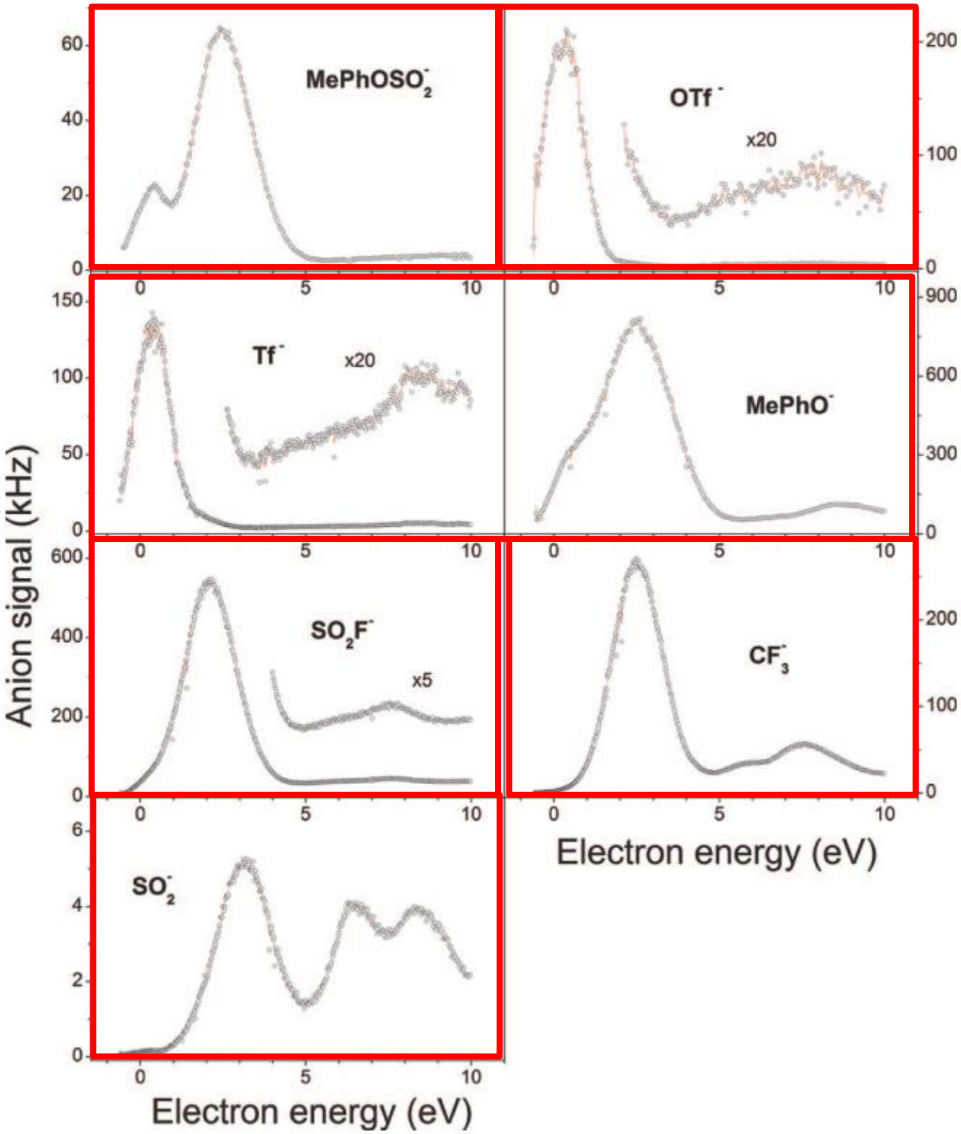
Ptasińska *et al. J Chem Phys* 135, 214309 (2011)

Phenyl triflate

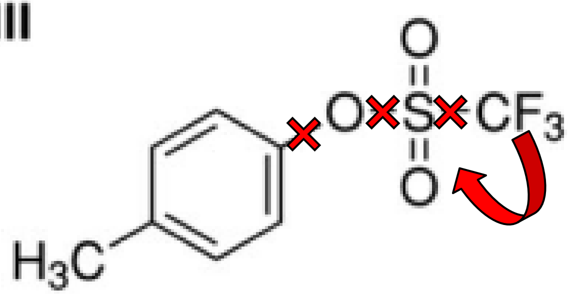




Tolyl triflate



III



Resonance shift