Fundamental aspects of low energy electron driven chemistry

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Cynthia Trevisan, Ann Orel, Tom Rescigno & Bill McCurdy (theory and computation)

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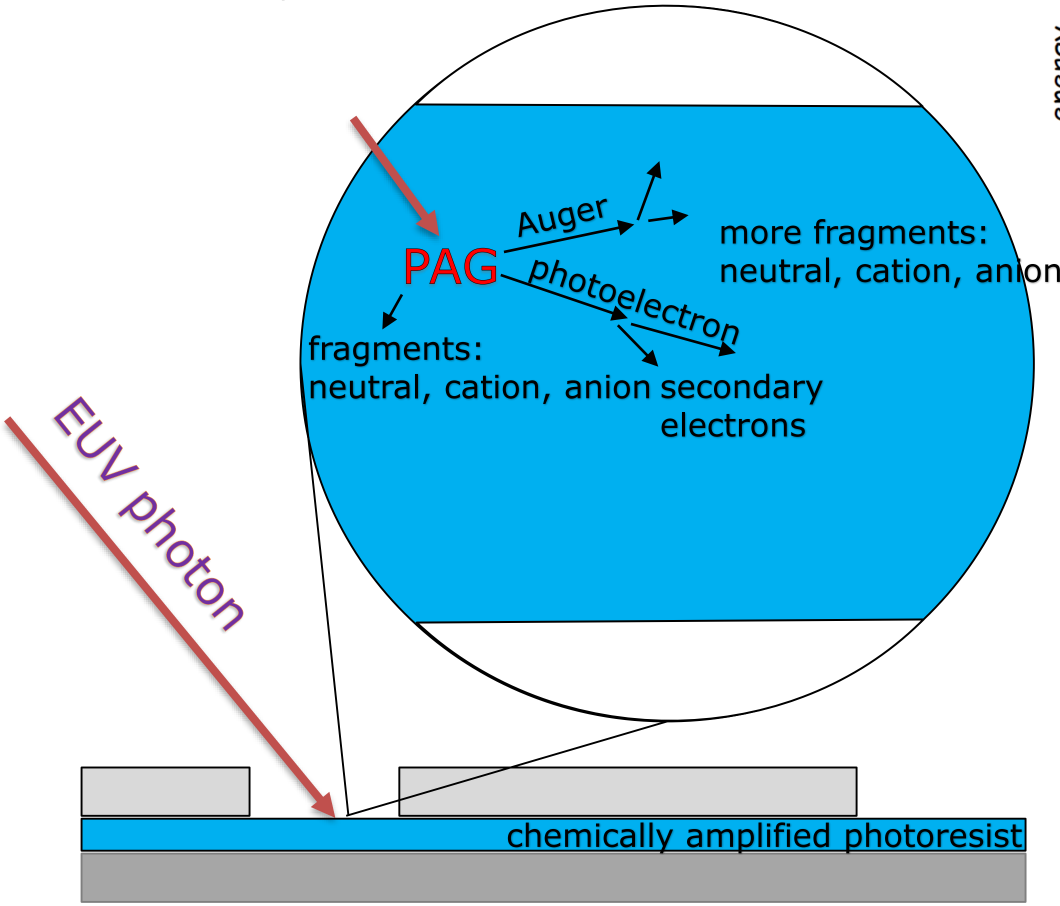
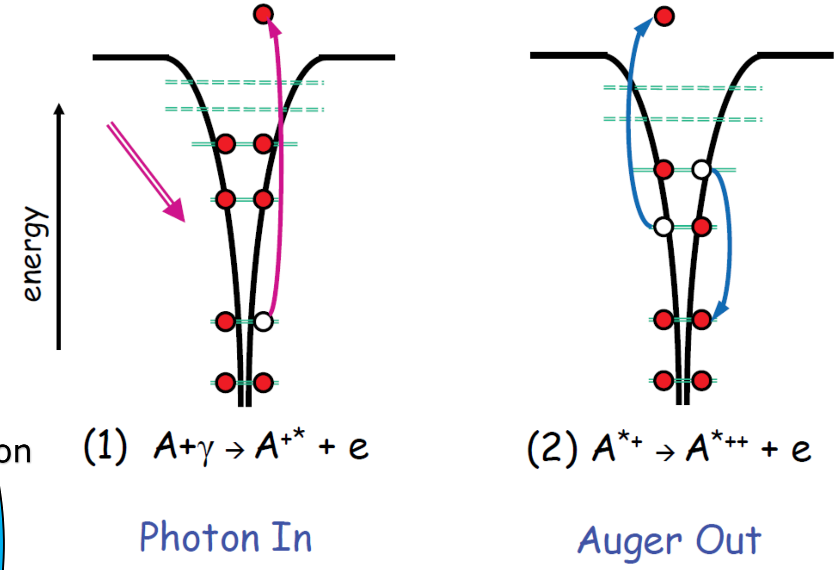
Fundamental physical and chemical processes in EUV photoionization

EUV photons ionize inner shell electrons

Closser et al. J. Chem.Phys. **146**, 164106 (2017)
doi: 10.1063/1.4981815





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

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

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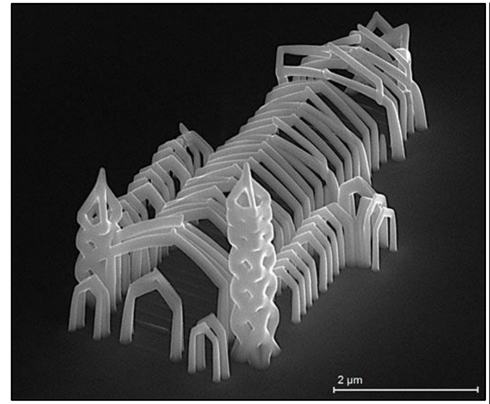
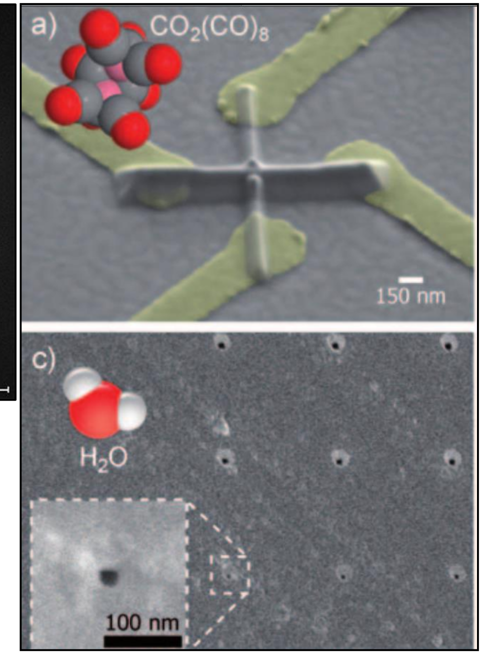
Low energy electrons and ammonia

Low energy electrons drive chemical reactions through low energy resonances

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



PtC 3D nanostructure
(Robert Winkler, FELMI-ZFE)

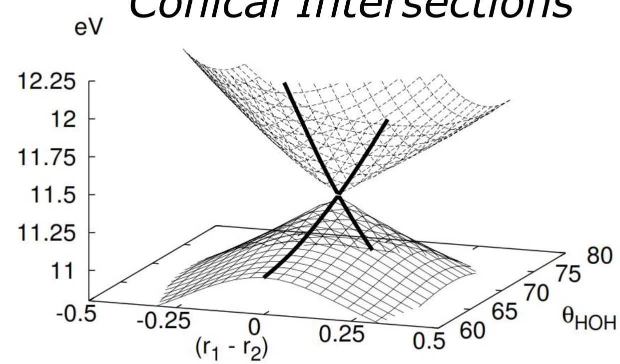


Utke and Gölzhäuser, Angew. Chem. 2010

Bond- and site-selective chemistry depending strongly on resonant electron energy

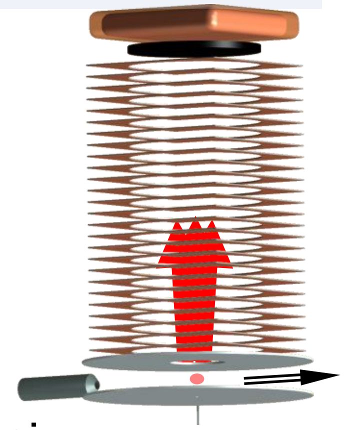
Electronic and nuclear motion highly coupled by nonadiabatic transitions (conical intersections, charge transfer)

Conical Intersections



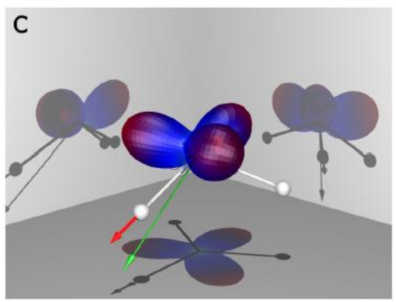
Haxton *et al.* (2007) Phys. Rev. A **57**, 012710

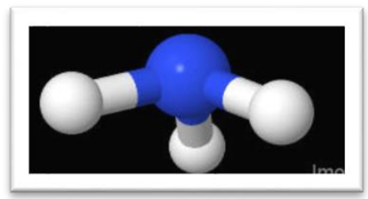
Outline



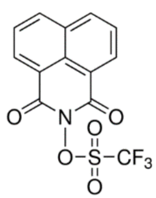
Brief experimental overview: Viewing dissociative electron attachment anion dynamics by ion momentum imaging

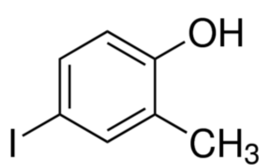
Some examples of anion dynamics in a model system: ammonia

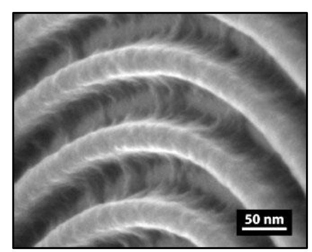




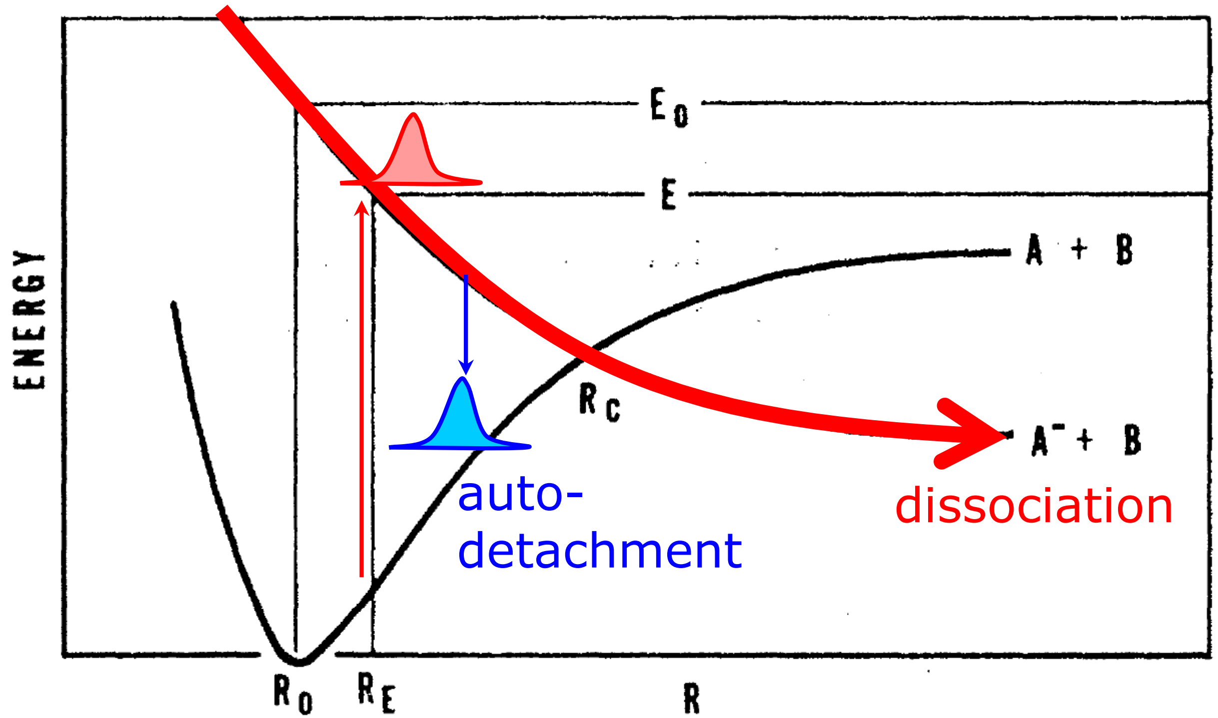
Latest and future experiments on systems relevant to nanofabrication

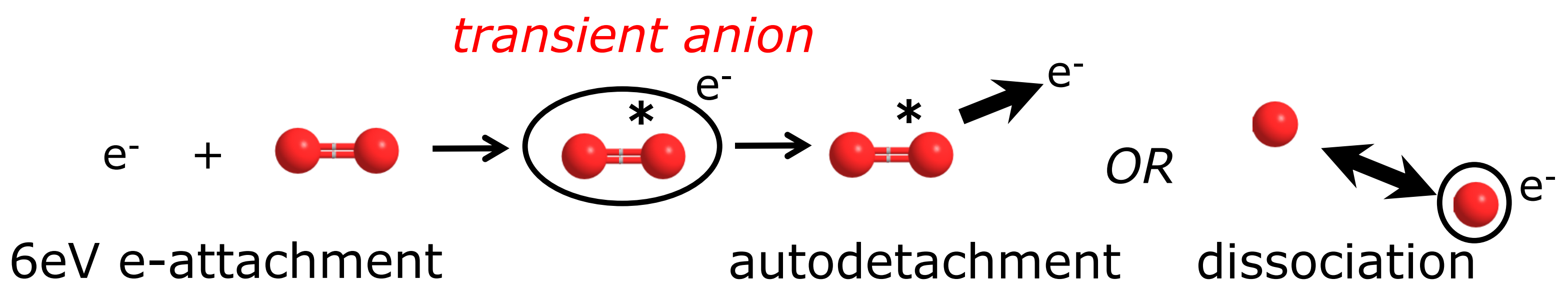






Resonant processes for low energy electrons



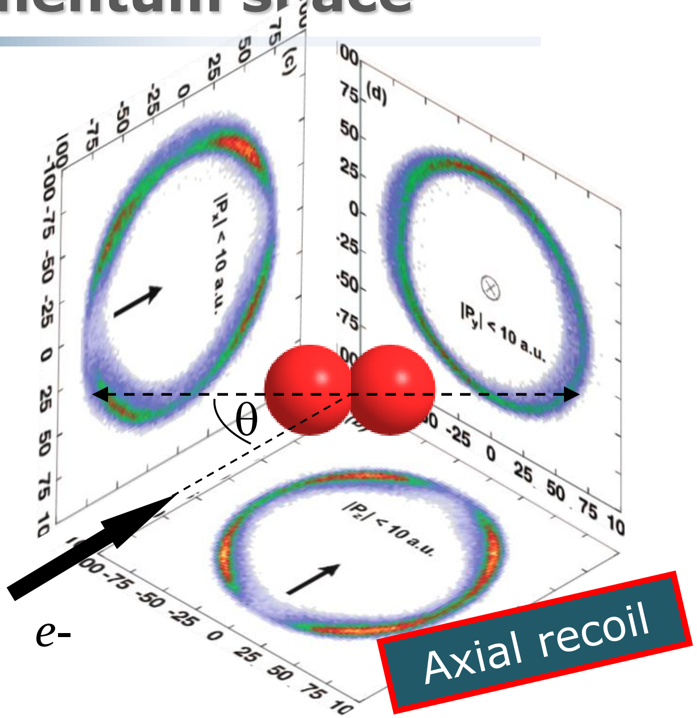


Interrogating reactions in momentum space

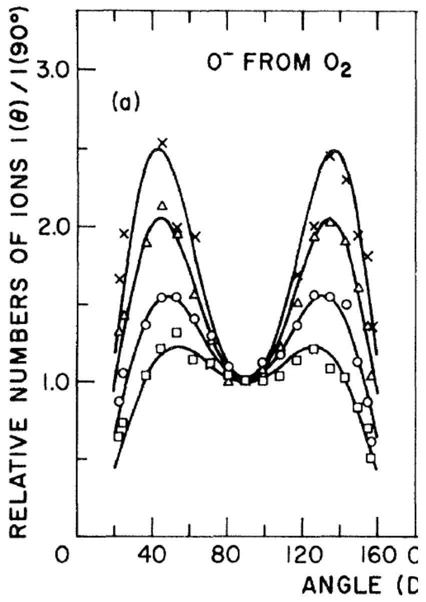
Measure each fragment ion momentum over a large volume of momentum space

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

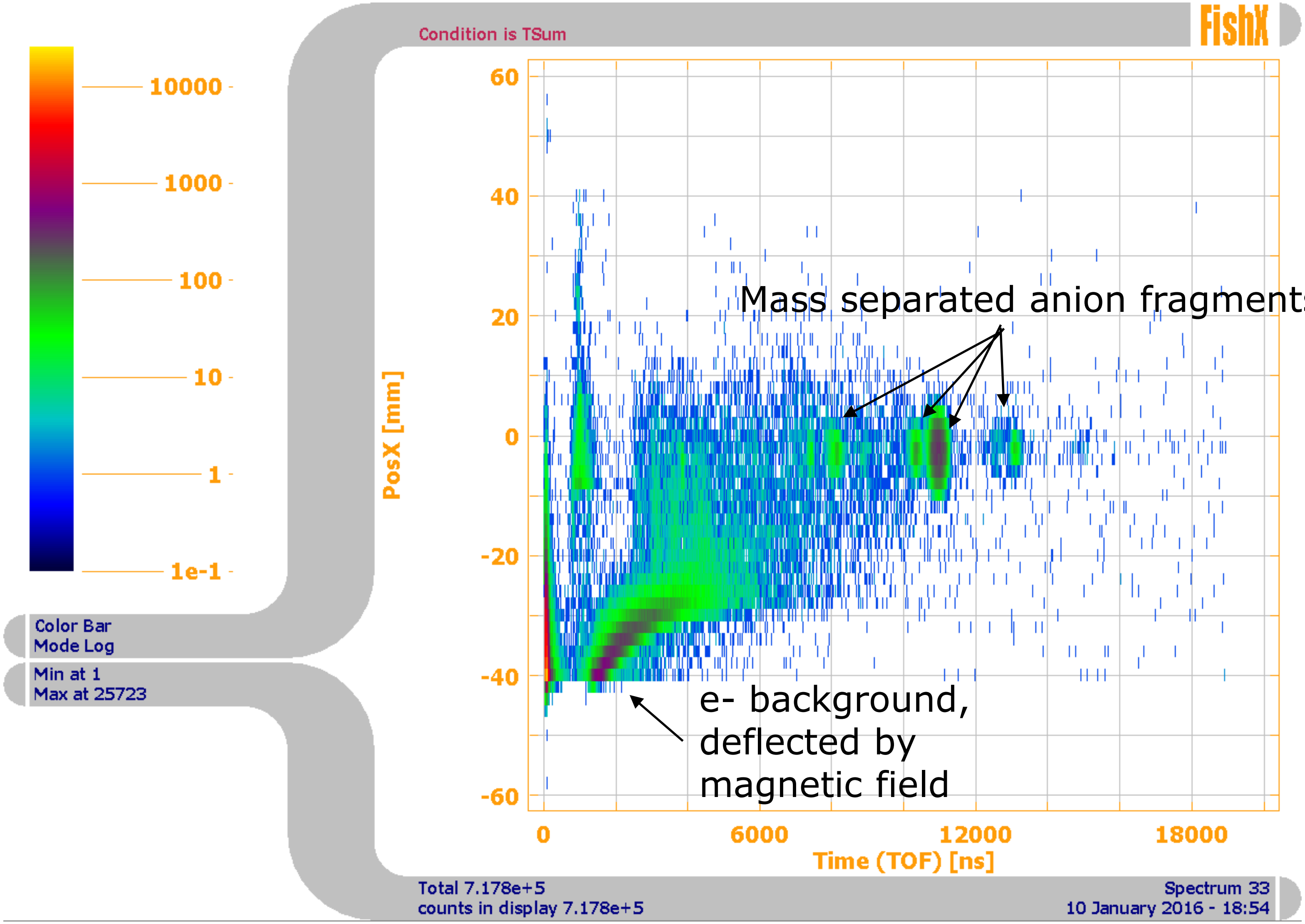


Electron scattering calculations to accurately predict electron attachment probability in the molecular frame

Predict the axial recoil ion angular distribution

One can immediately see when the axial recoil approximation fails

Mass and momentum dispersion in time of flight



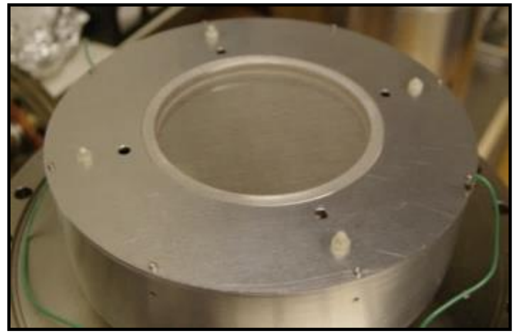
DEA reaction microscope

Helmholtz coils

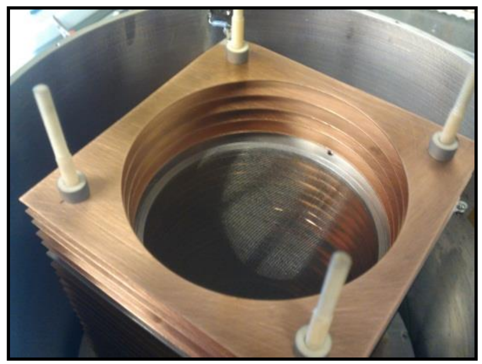
Negative-ion momentum-imaging spectrometer

Extensive shielding to reject scattered e⁻

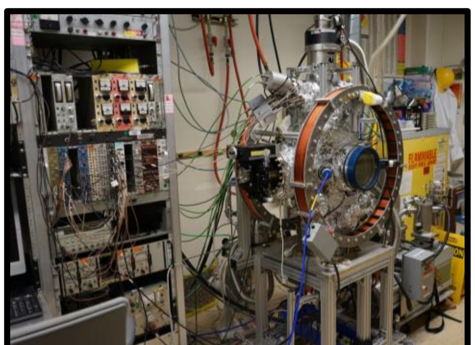
50kHz pulsed electron gun and ion extraction

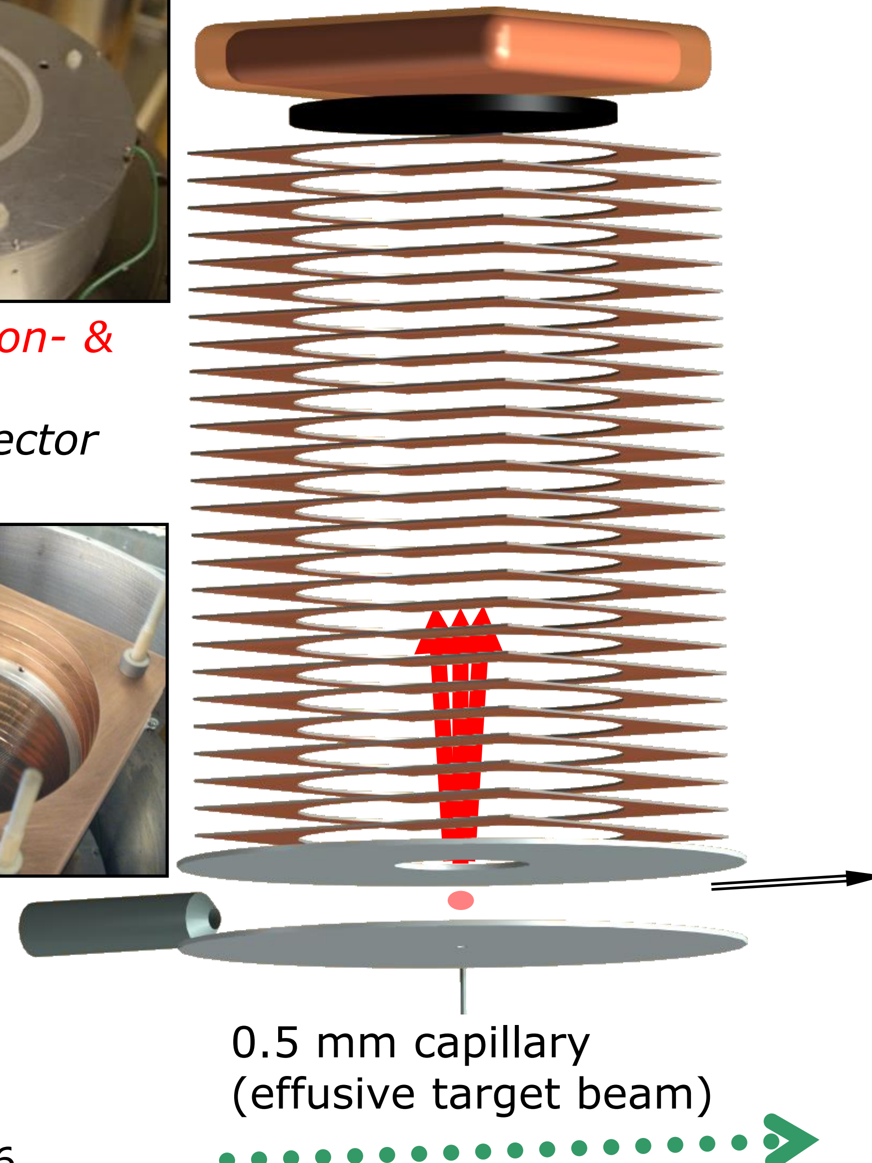


shielded position- & time-sensitive 80mm ion detector



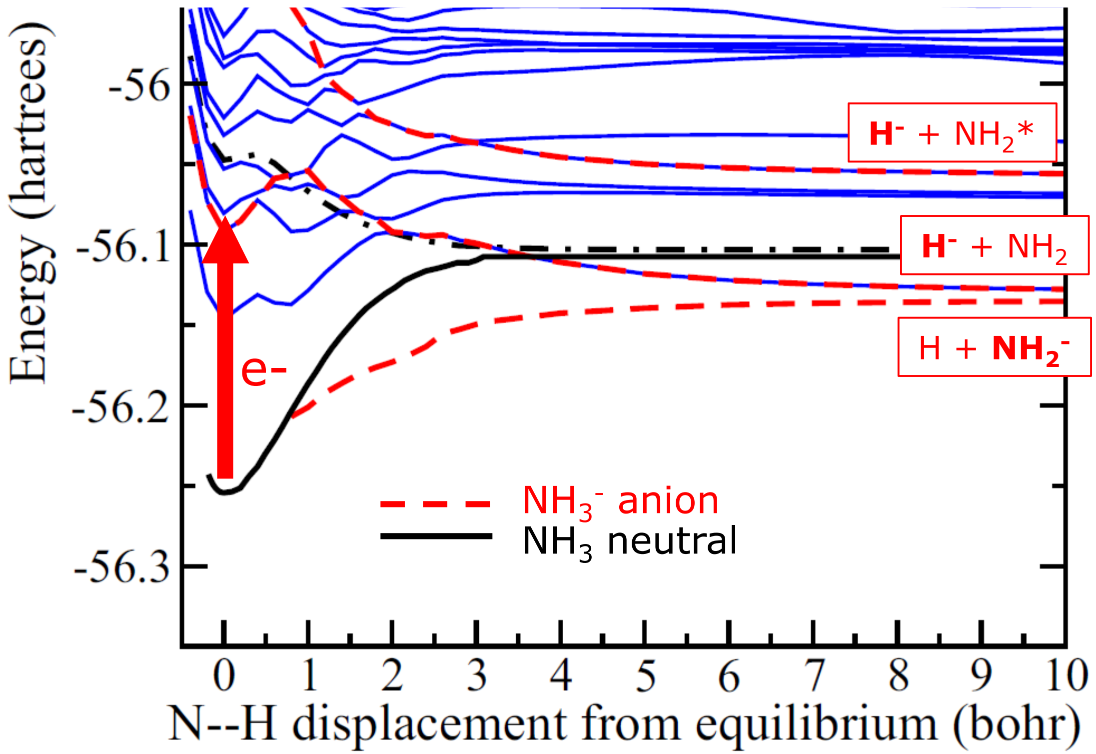
position-focusing ion spectrometer electrode array

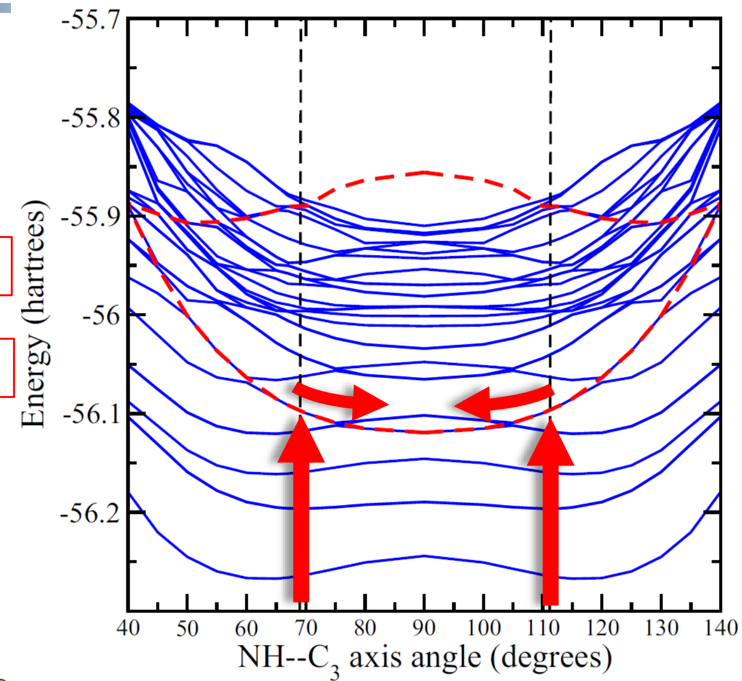


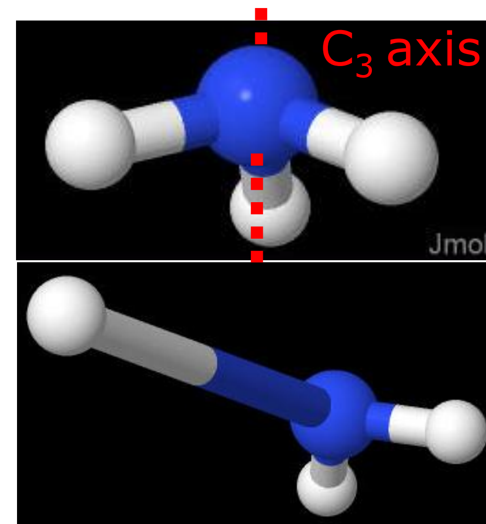


Adaniya *et al.* (2012)
Rev. Sci. Inst. **83**, 023106

5 eV NH_3^- Feshbach resonance







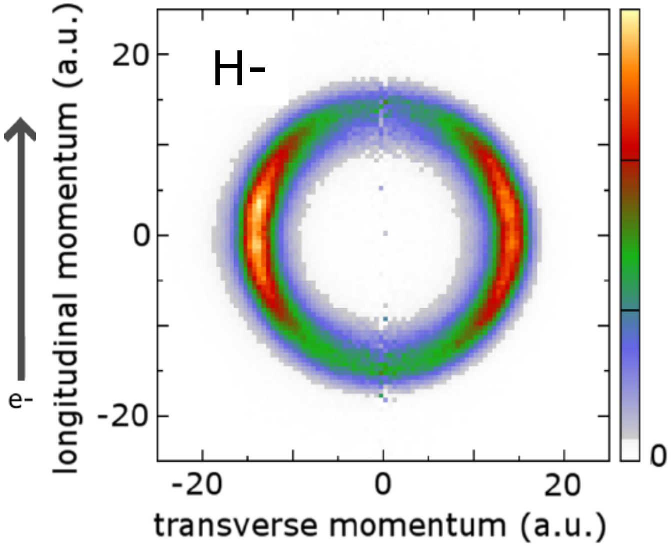
NH_3 ($^1A_1$: ($1a^2_1$ $2a^2_1 1e^4 3a^2_1$) + e- (5 eV)

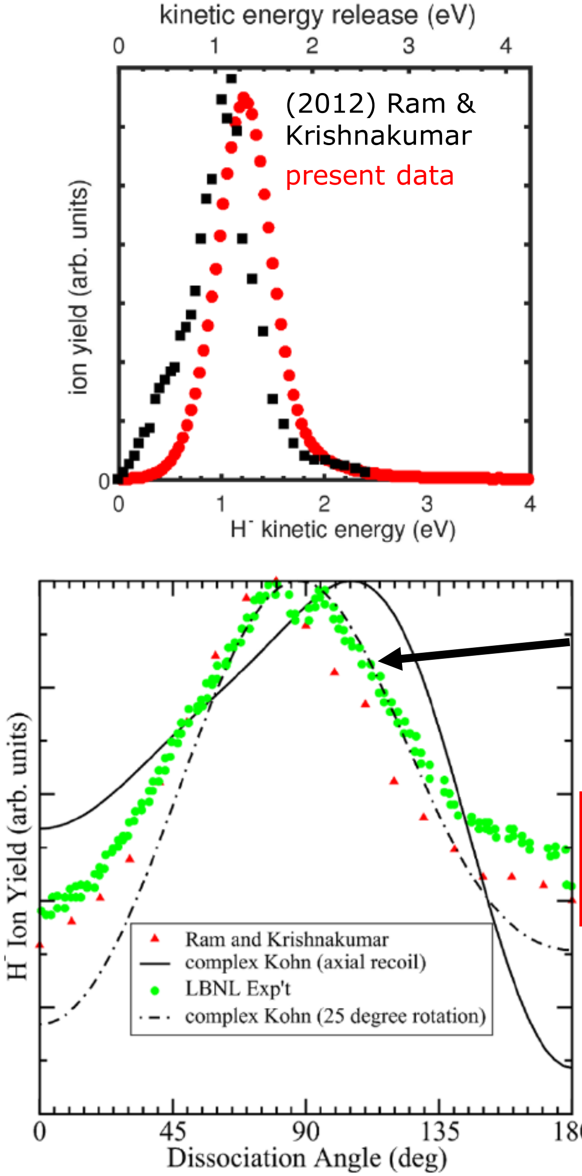
→ NH_3^- ($^2A_1$: $1a^2_1$ $2a^2_1 1e^4 3a_1 4a^2_1$) → H^- + $NH_2(^2B_1)$

Potential barrier prevents dissociation, umbrella opening reduces the barrier

for details see Rescigno *et al.*, *Phys Rev A*, **93** 052704 (2016)

5 eV anion fragment momentum imaging experiments





5 eV electron attachment

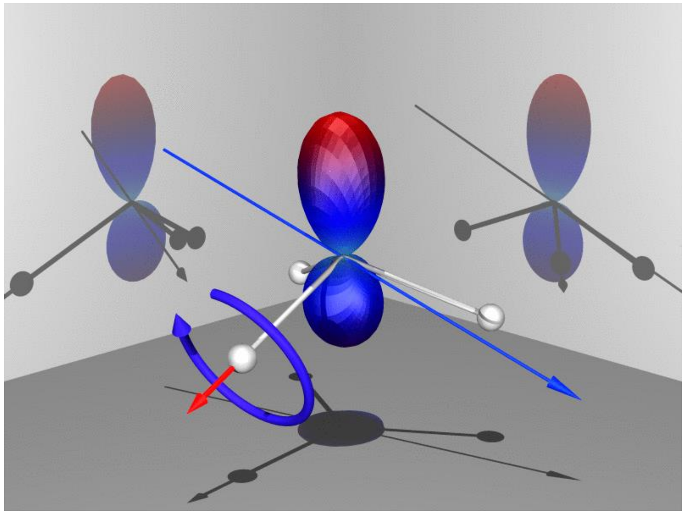
1~1.5 eV kinetic energy release

Adaniya *et al.* (2012) Rev. Sci. Inst. **83**, 023106

Axial recoil angular distribution

rotation of the N-H recoil axis by 25°

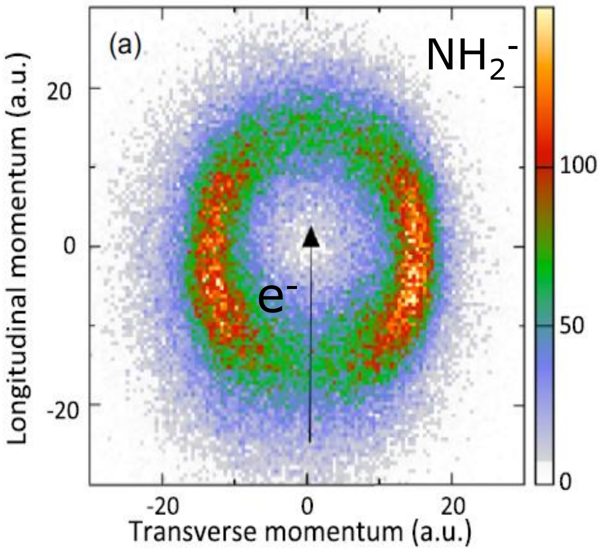
NH_3^- is flattening during dissociation

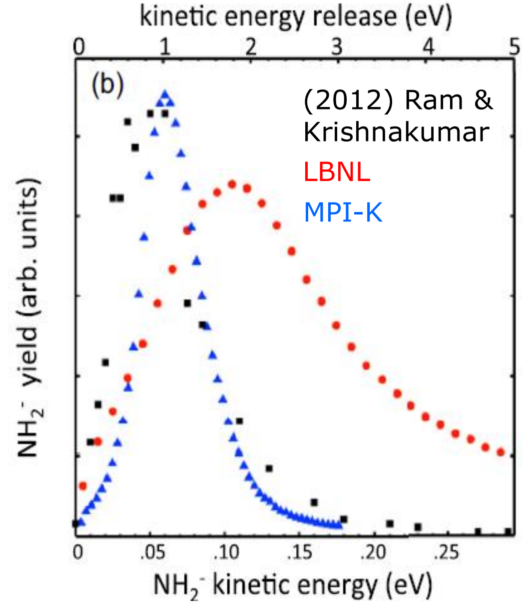


attachment probability (Complex Kohn calculation)

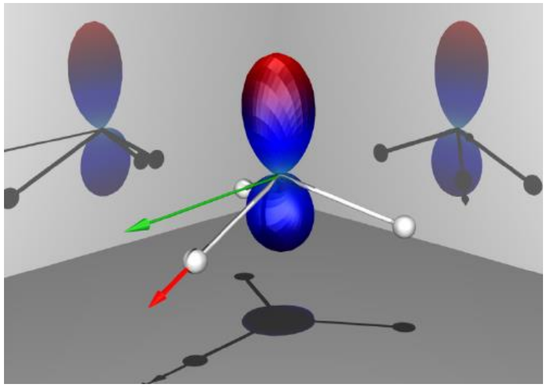
Slaughter *et al.* (2016) J. Phys. B **49** 222001

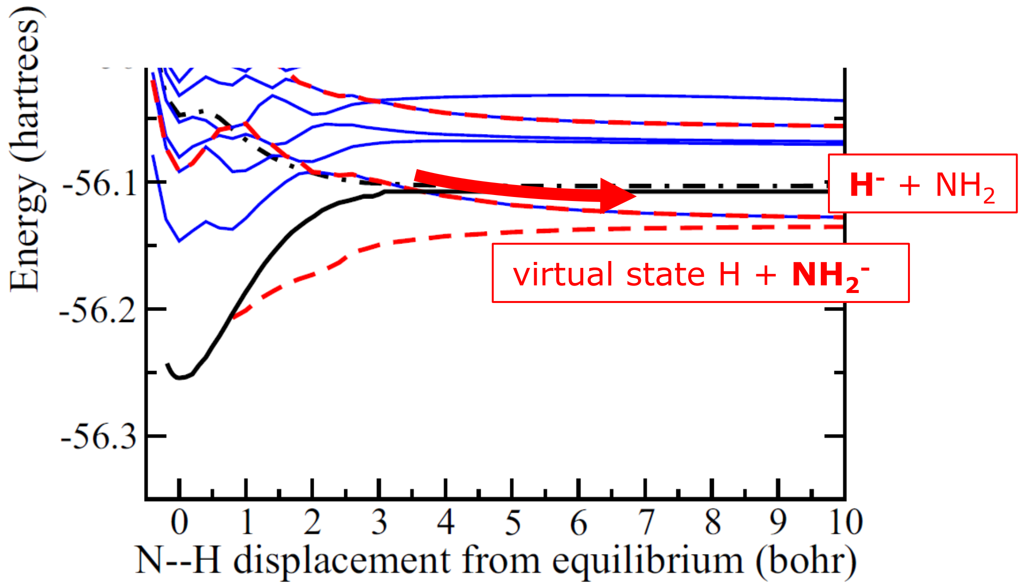
NH_2- momentum, DEA at 5 eV

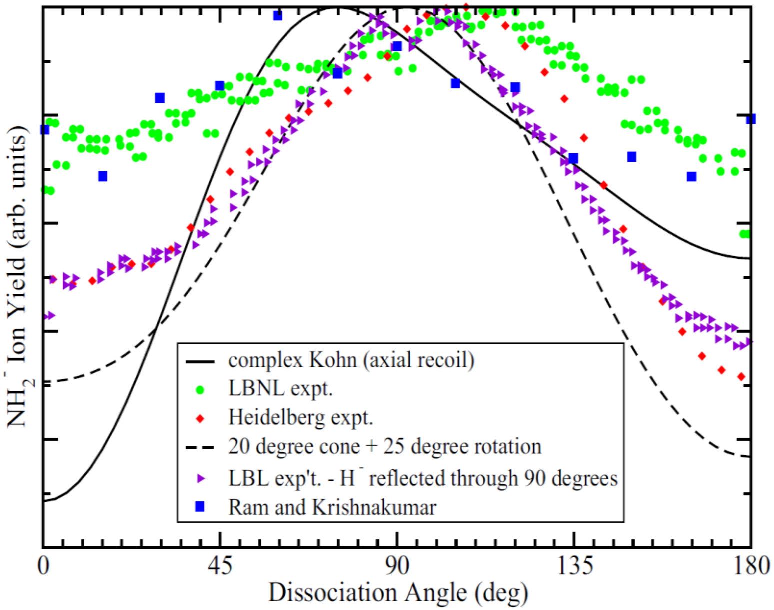




5 eV resonance molecular frame attachment probability





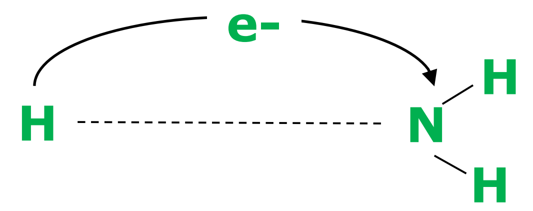


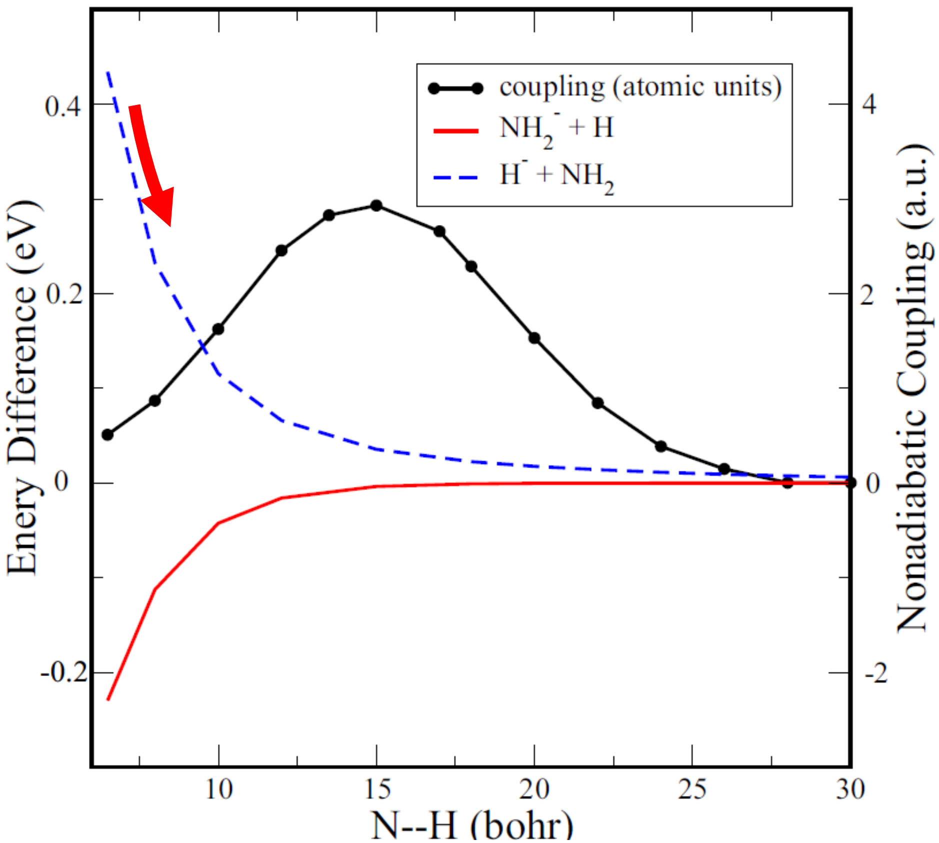
H^- to NH_2^- electron transfer

Asymptotic potential energy curves

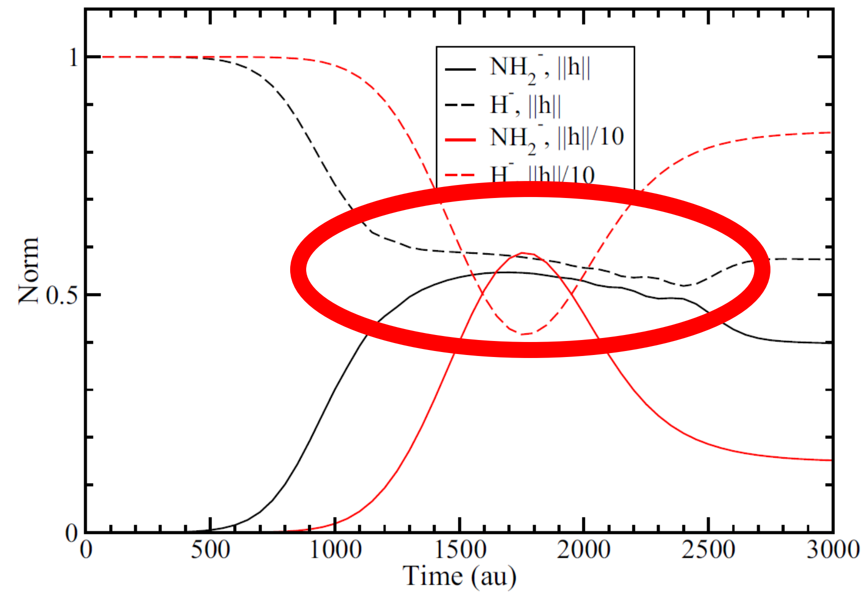
Non-adiabatic coupling

HNH fixed at equilibrium geometry



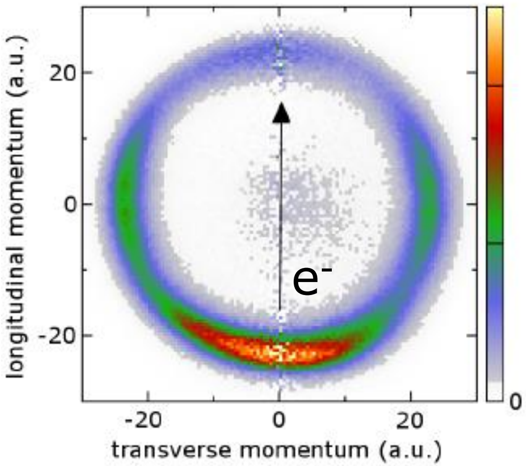


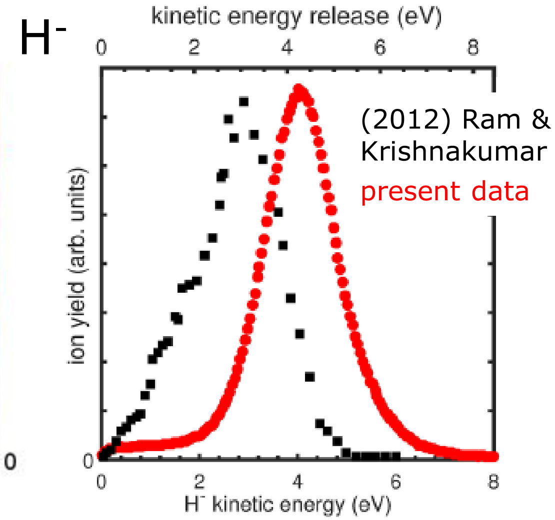
40% e- wavepacket transfer from H to NH_2

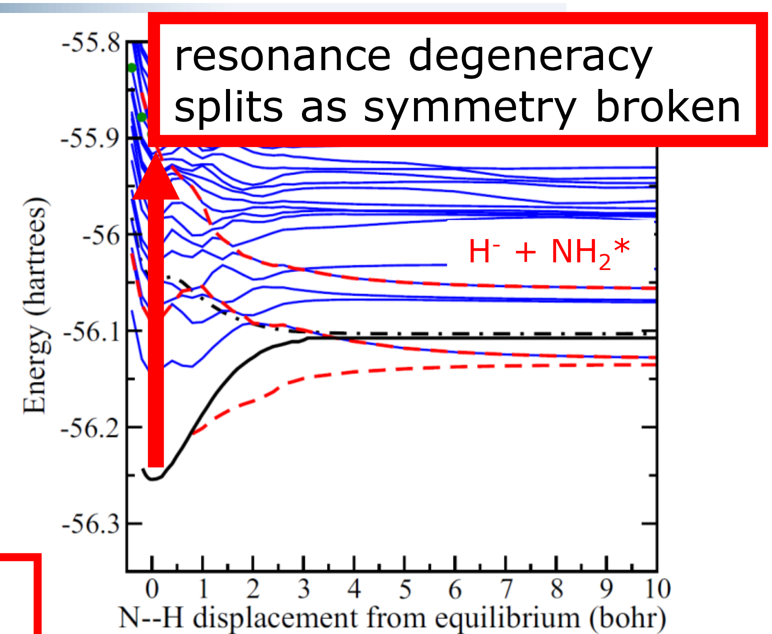


1-D time-dependent two-state population transfer

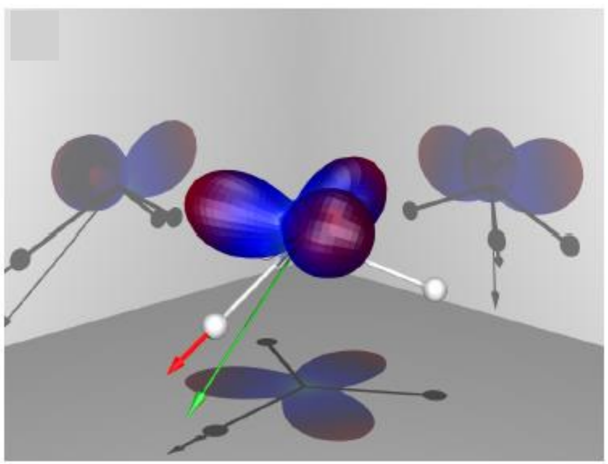
10 eV NH_3^- Feshbach resonance



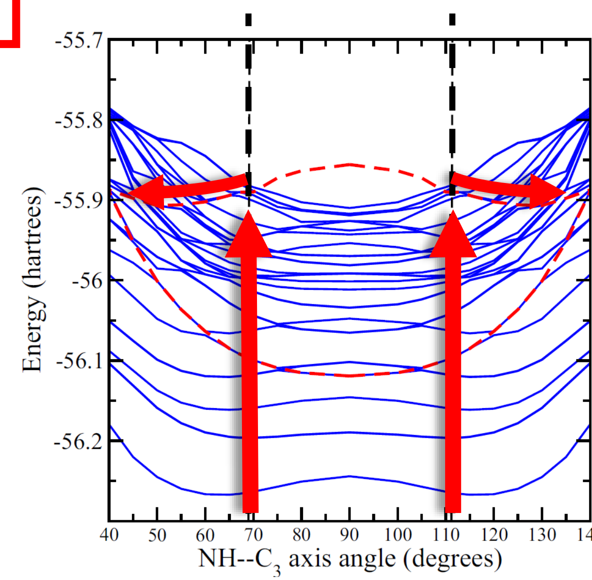




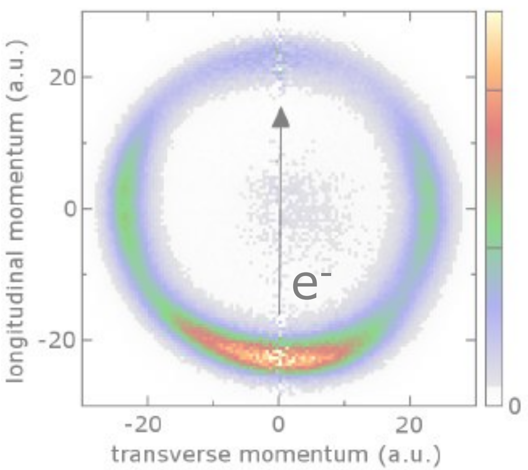
From KER, the neutral fragment is excited NH_2 ($^2A_1$)

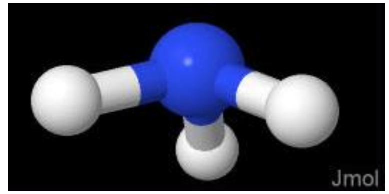


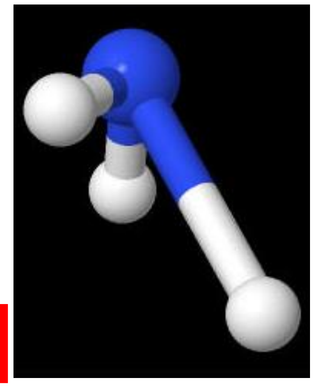
10 eV resonance molecular frame attachment probability

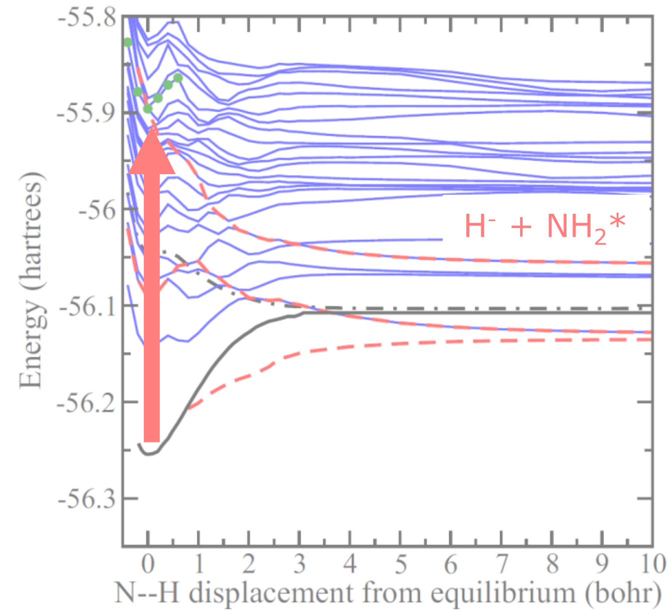


10 eV NH_3^- Feshbach resonance

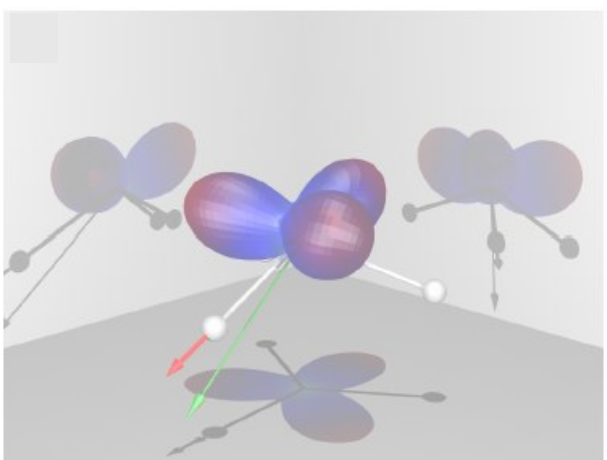


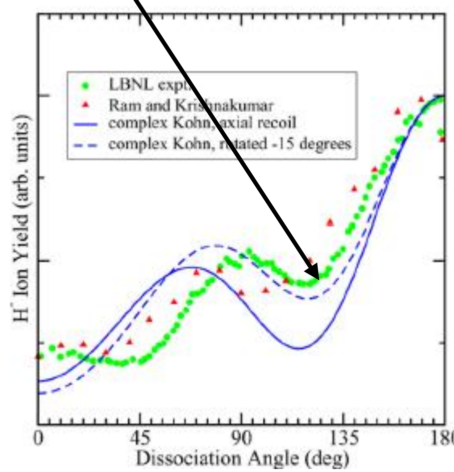


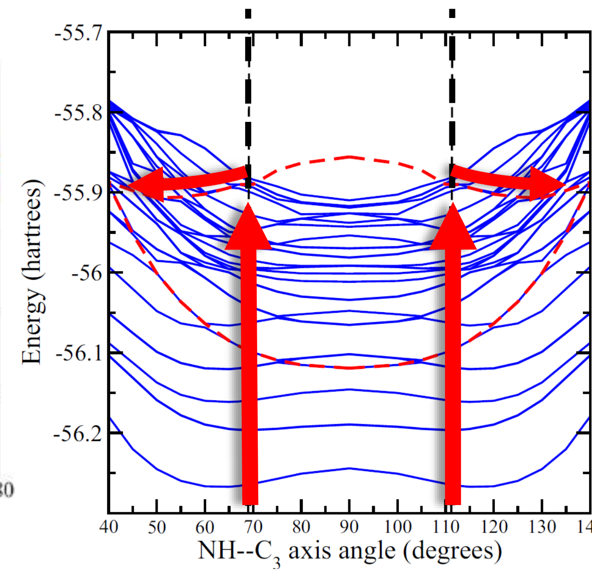




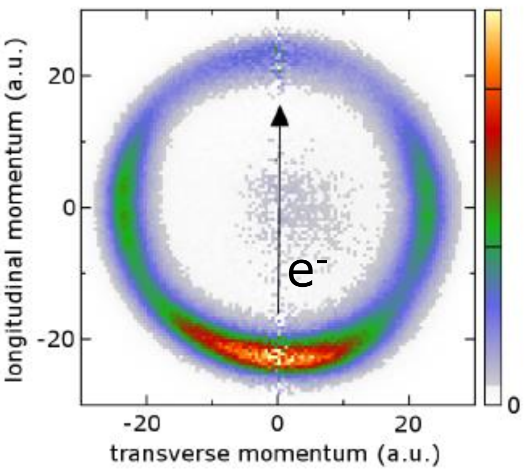
Umbrella-closing ~15°



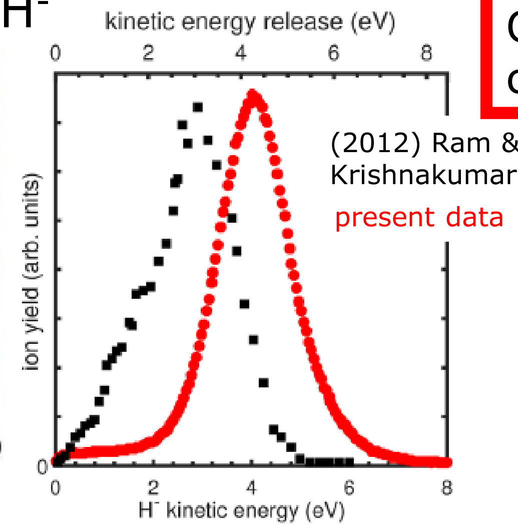




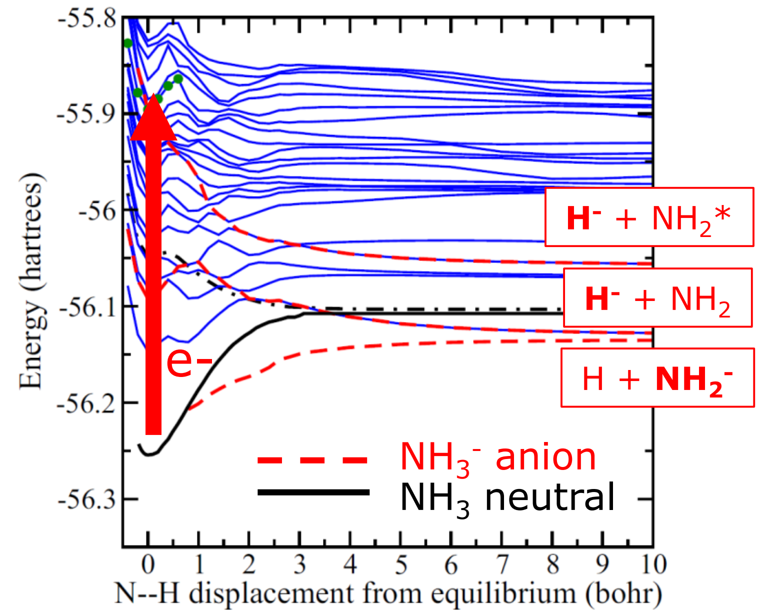
NH_2- momentum, DEA at 10 eV

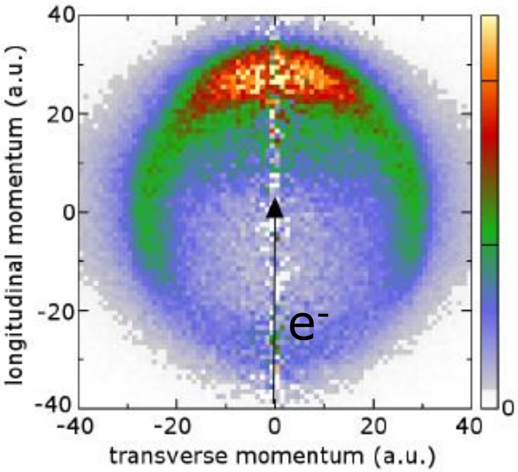


H^-

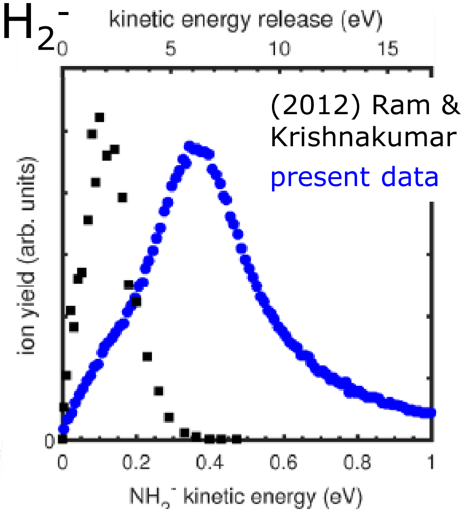


Open question: what indirect process could produce NH_2^- at 10 eV??





NH_2^-

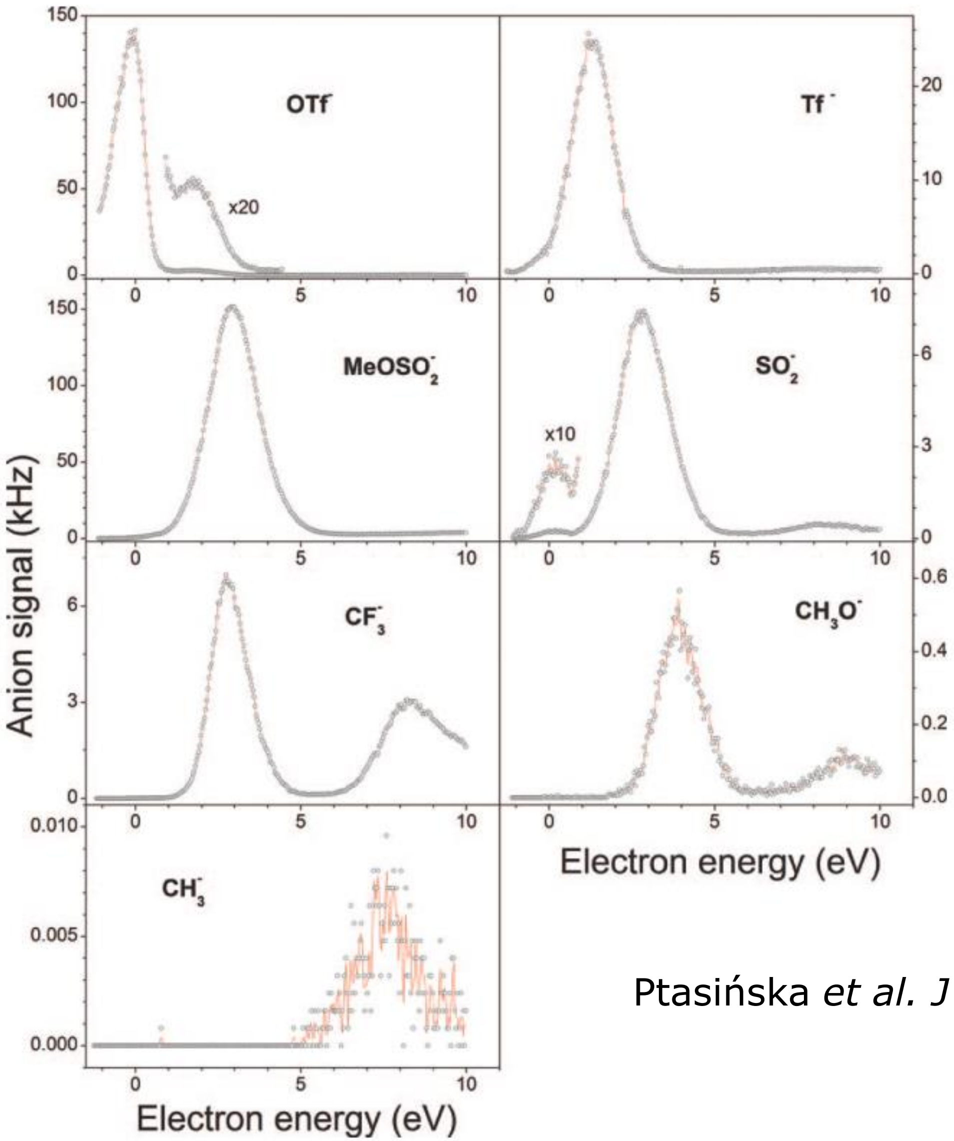


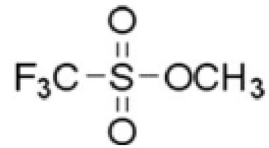
Does a well-known broad shape resonance at 7 eV play a role??

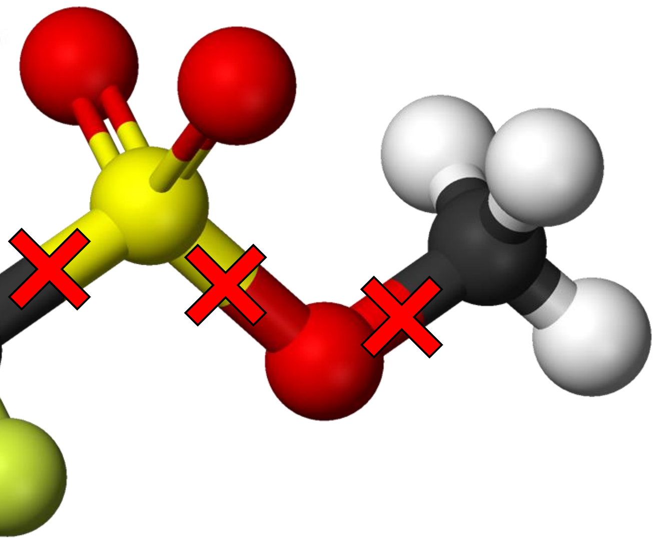
Gulley *et al.*, *J. Phys. B*, **25** 2433 (1992)

Rescigno *et al.*, *Phys Rev A*, **93** 052704 (2016)

Short history of DEA studied in model photo-acid generators

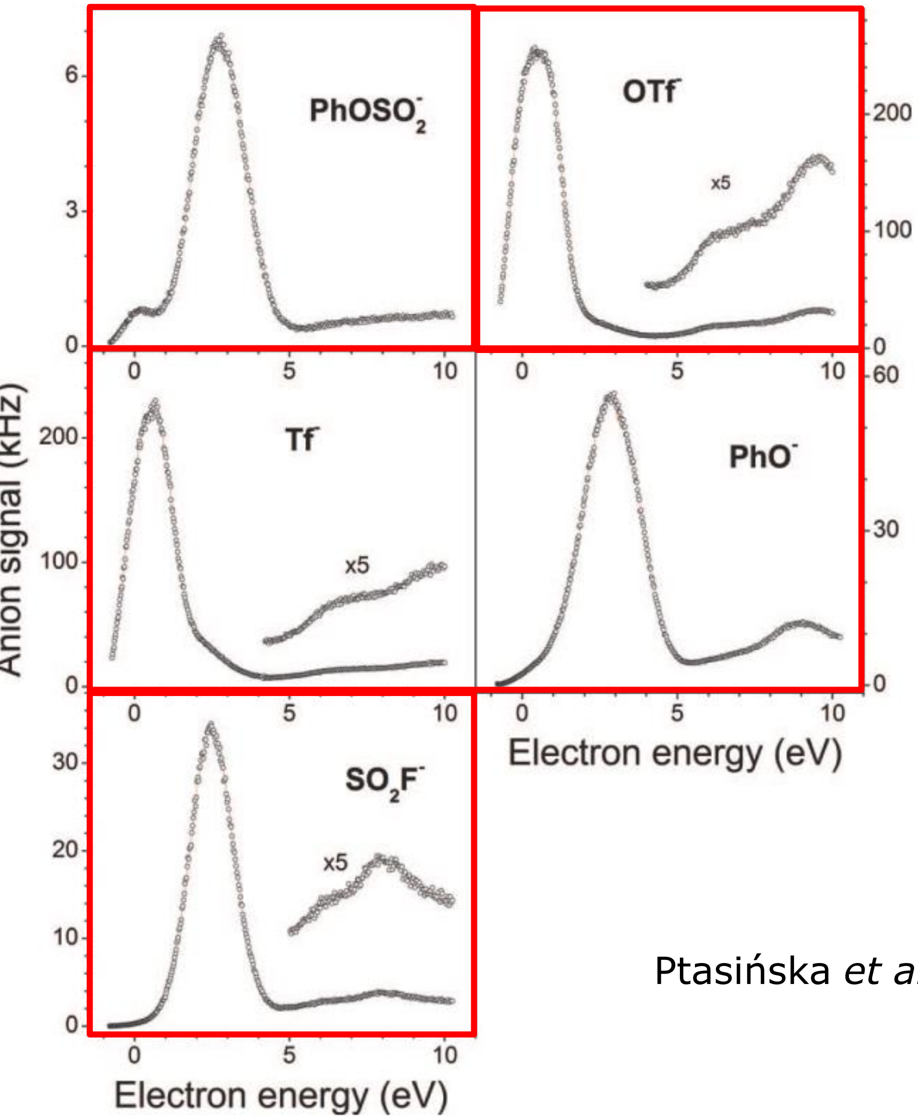


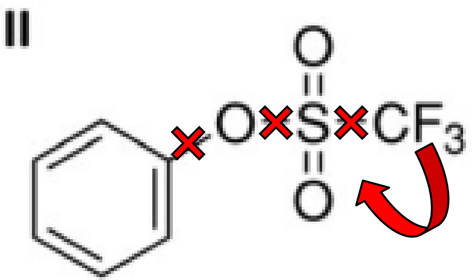




Ptasińska *et al. J Chem Phys* 135, 214309 (2011)

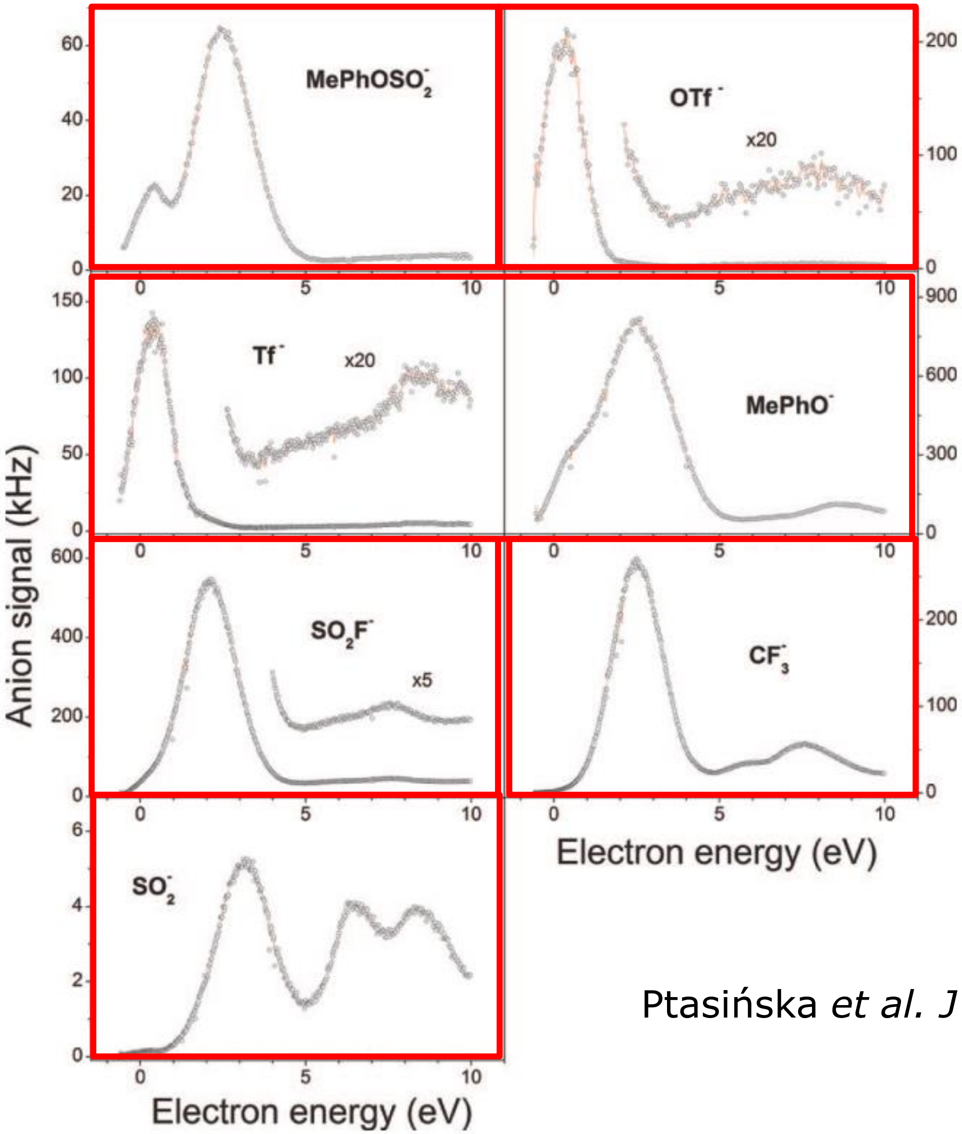
Phenyl triflate

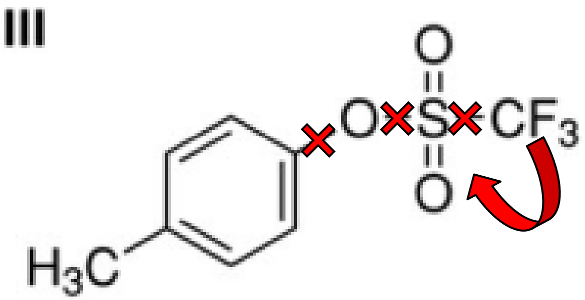




Ptasińska *et al. J Chem Phys* 135, 214309 (2011)

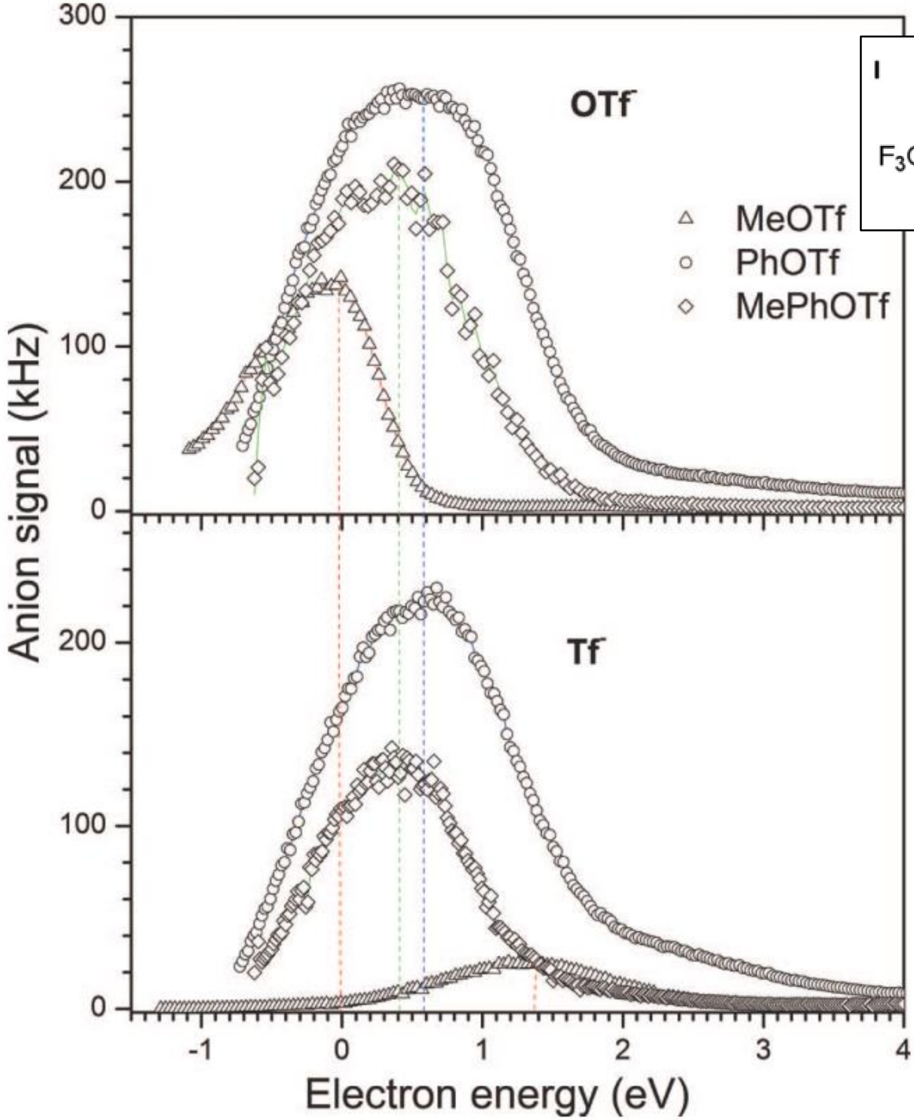
Tolyl triflate

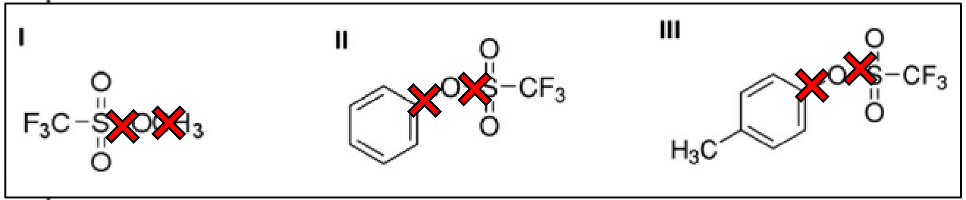




Ptasińska *et al. J Chem Phys* 135, 214309 (2011)

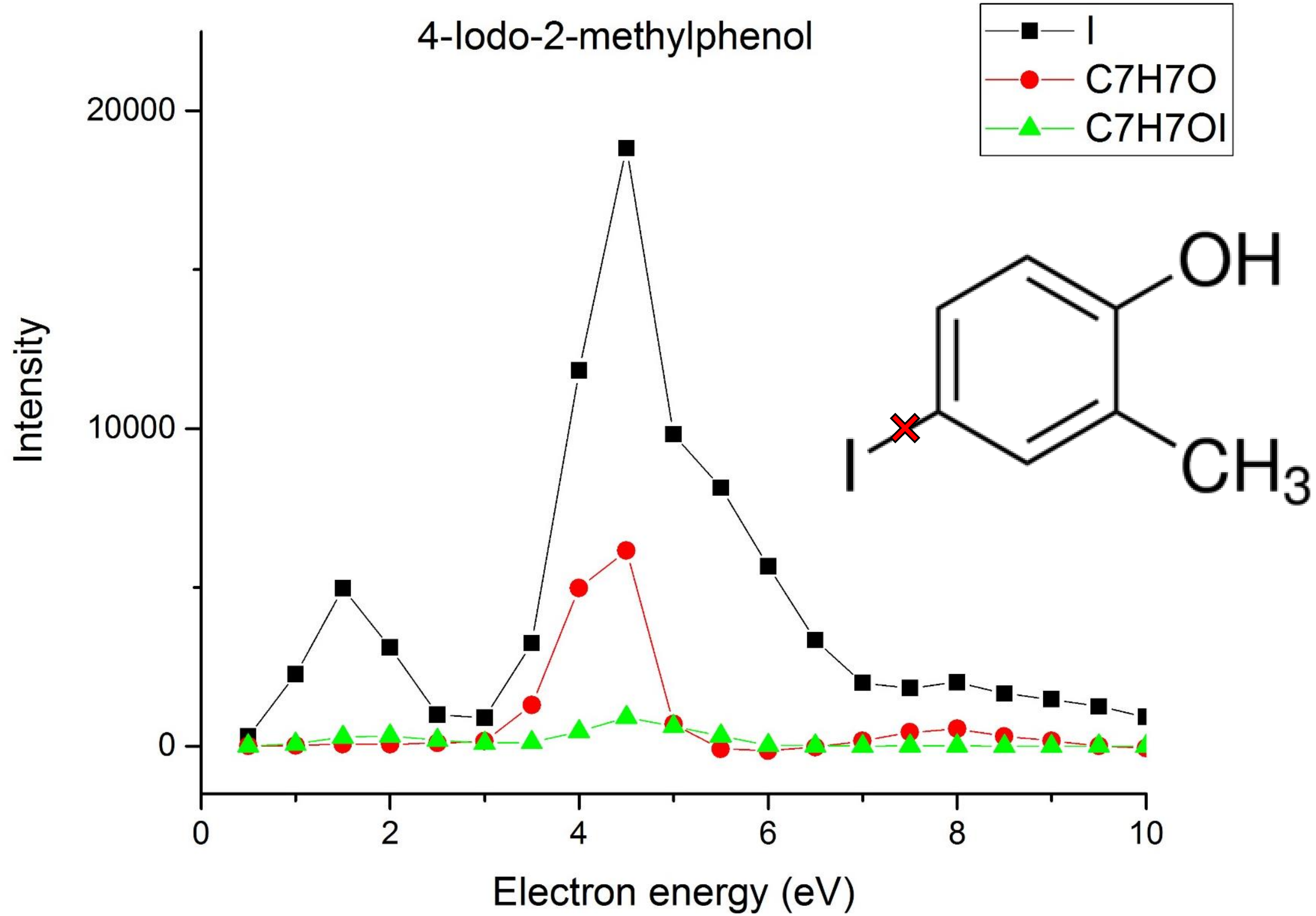
Resonance shift





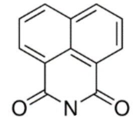
Ptasińska *et al.*
J Chem Phys 135, 214309 (2011)

LBNL measurements of e-energy dependent ion yields



N-hydroxynapthalimide triflate

m/q=345



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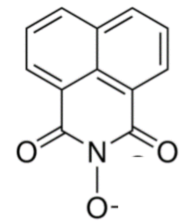
OCF_3 85



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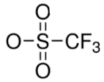

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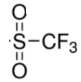

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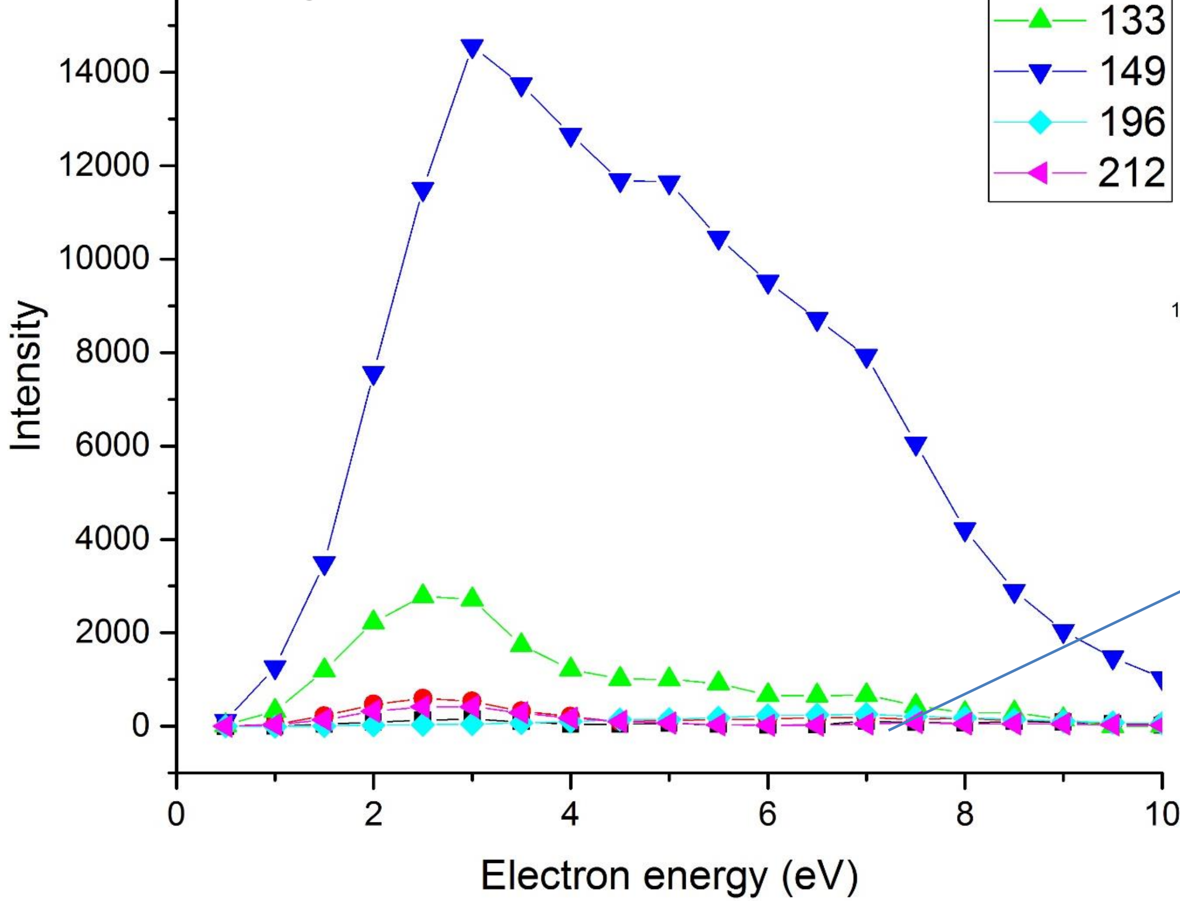
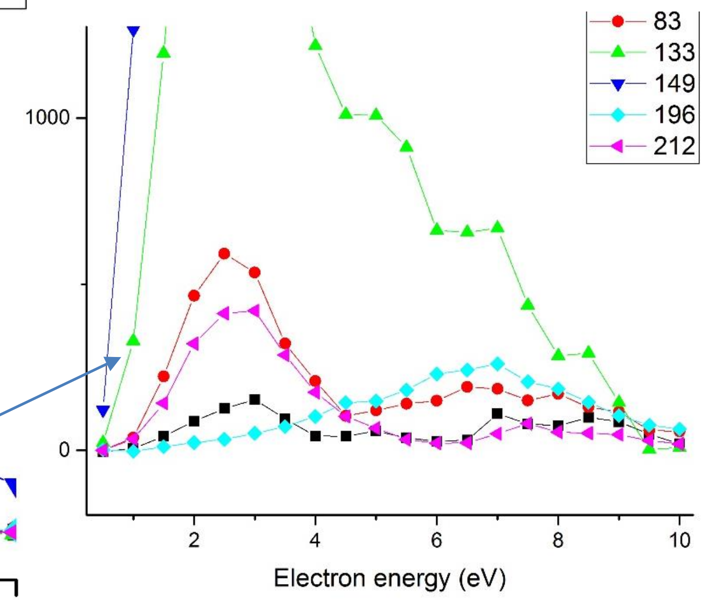
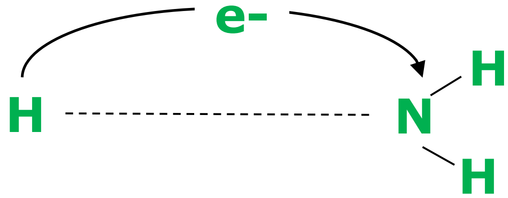
CF_3 69

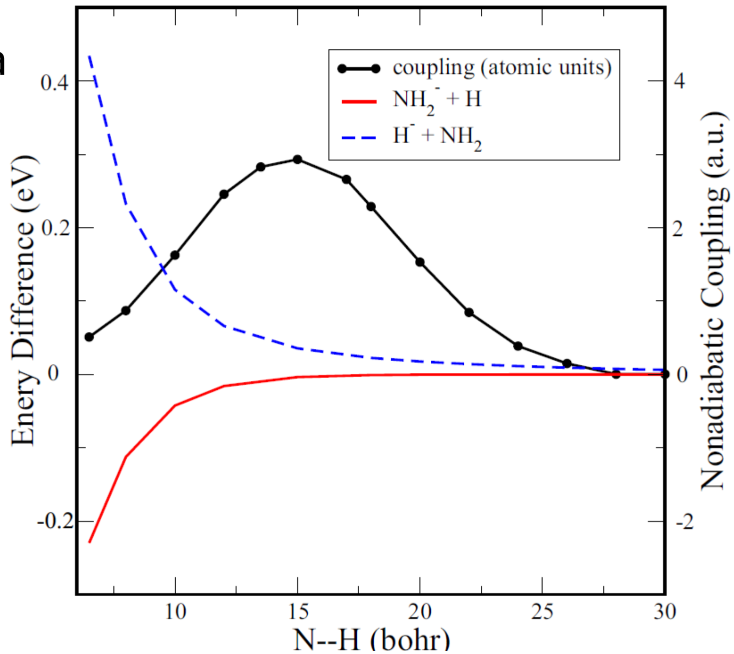




Summary & Outlook

5 eV dissociative electron attachment to ammonia produces NH_2^- by an indirect process of nonadiabatic charge transfer.





The higher-lying Feshbach resonance following electron attachment at 10 eV directly dissociates to H^- + NH_2* and produces NH_2^- via an unknown indirect process.

Investigations of transient anion dynamics in other small polyatomic systems will provide a more detailed understanding of fundamental non-adiabatic processes.

With deeper understanding of these fundamental processes, we can control chemistry of EUV photoresist materials at the level of individual electron-molecule interaction.