Anions 2007
Azolide Ion Chemistry

Park City, UT

July, 2007

Takatoshi Ichino, Shuji Kato, Stephanie Villano
John Stanton and Veronica M. Bierbaum
Carl Lineberger

JILA and Department of Chemistry
University of Colorado

Happy 59th, Ken!!

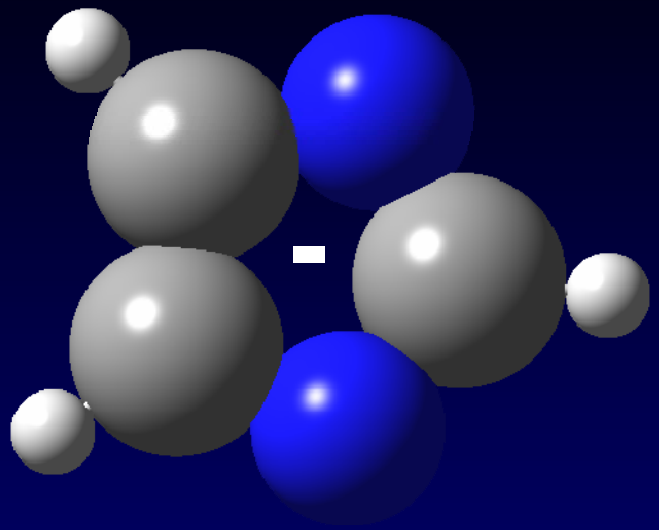
&

Thanks for everything, Jack!

Outline and Rationale

- Theory $\Longleftrightarrow$ experiment, synthesis,
- Selected ion flow tube (SIFT) and flowing afterglow
  - Gas phase synthesis of nitrogen-rich ions
  - Characterization of stability and structure
    - Reaction chemistry: acidity, collisional dissociation, structure
- Anion photoelectron spectroscopy
  - Electron binding energies, ground state surface properties
  - Low-lying excited states, structure, bond strengths
  - Simulations of spectra using calculated structures
  - Most B3LYP/6-311++G(d,p)
  - Most useful with small geometry changes
  - Can be problematic with moderate ones: CH_2^-, SF_6^-, . . .
  - Useful with very large changes: isomers, conformers, clusters
  - Vibronic coupling raises complex issues (ignored here today)

Azolides and related anions



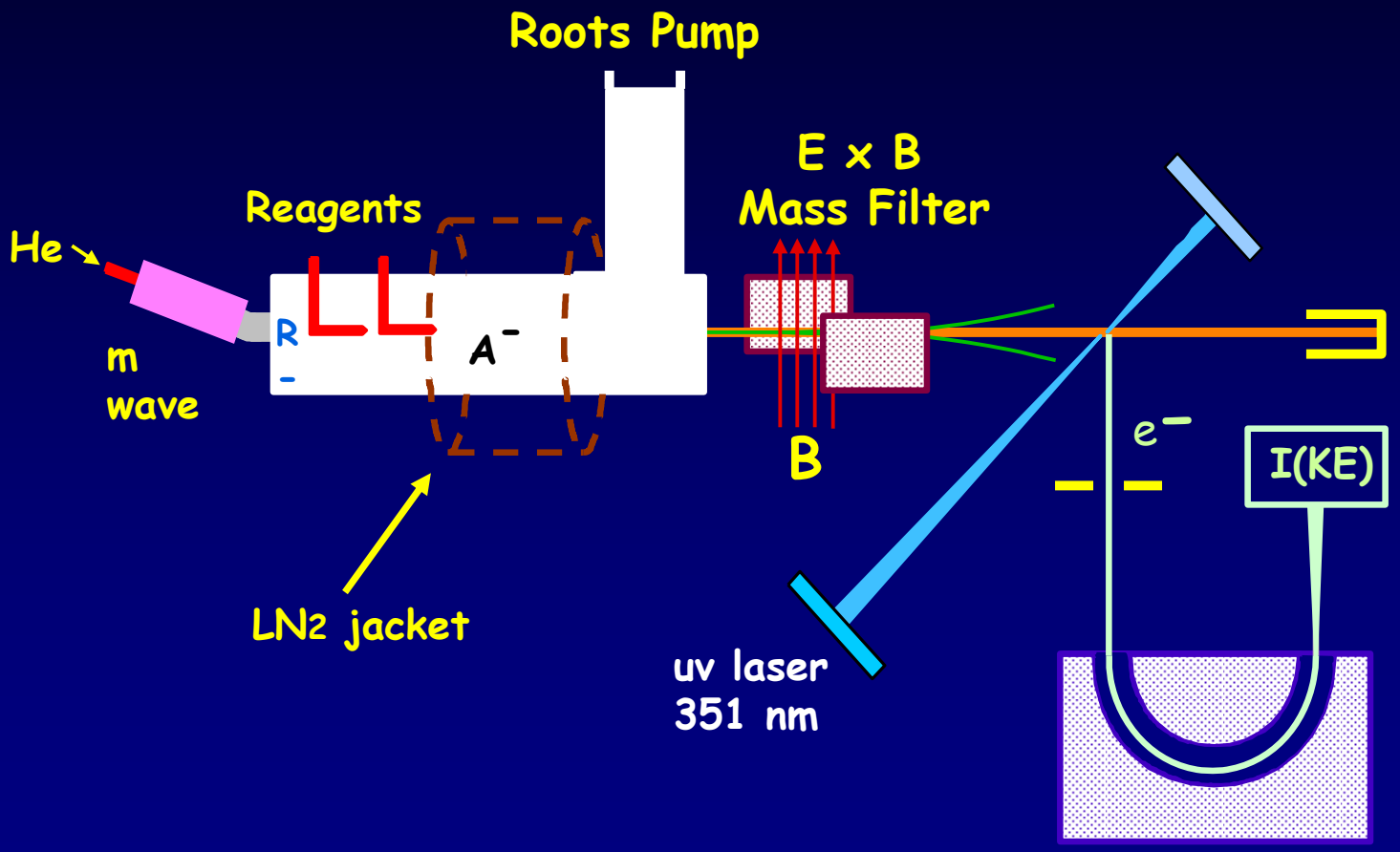
$C_{5-n}H_{5-n}N_n^-$

- Pyrazole (vibronic coupling)
- N-methyl pyrazole (deprotonation site ID)
- N-methyl imidazole (selective reactions)
- Vinyl diazomethyl anion (conformational selectivity)
- 1*H*-1,2,3 triazole (everything happens)

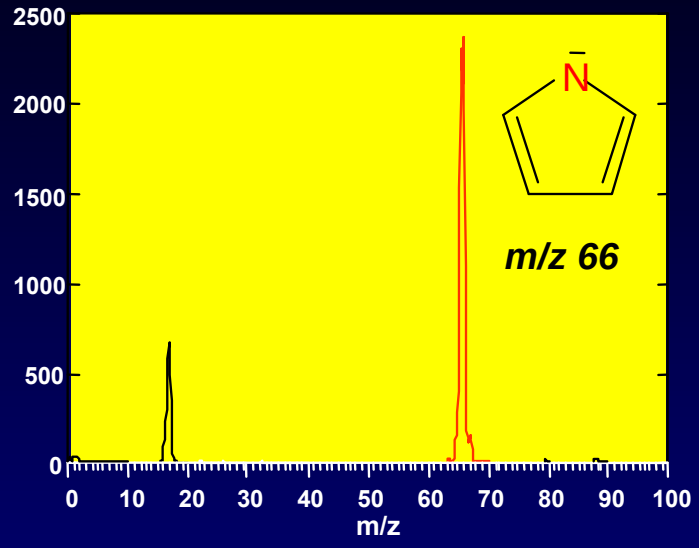
Azolides formed by OH^- deprotonation of azoles at known T

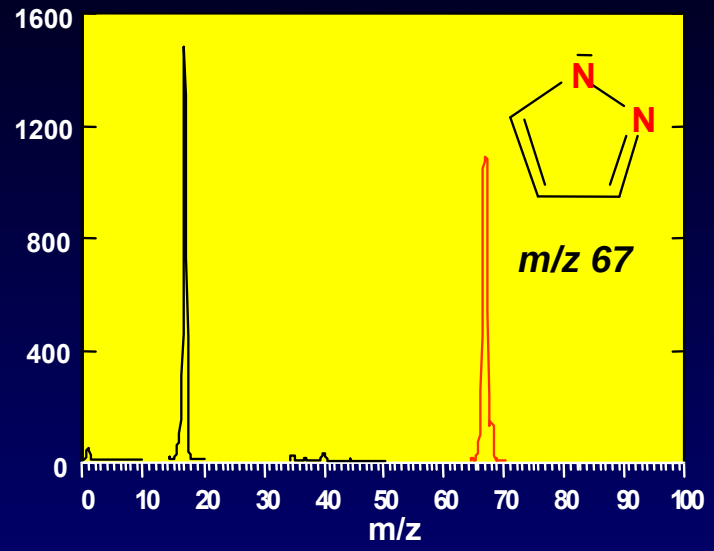
Negative Ion Photoelectron Spectrometer

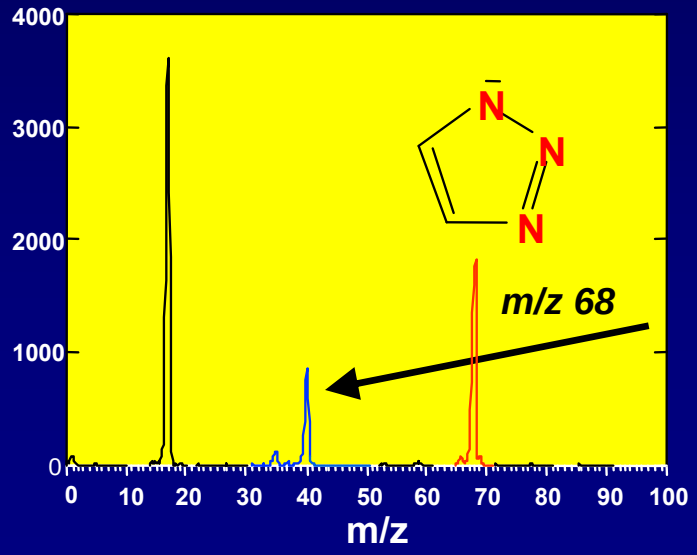
$$h\nu + A^- \rightarrow A + e^- \text{ (KE)}$$



Generation of M-1 Anions Via OH^- Deprotonation



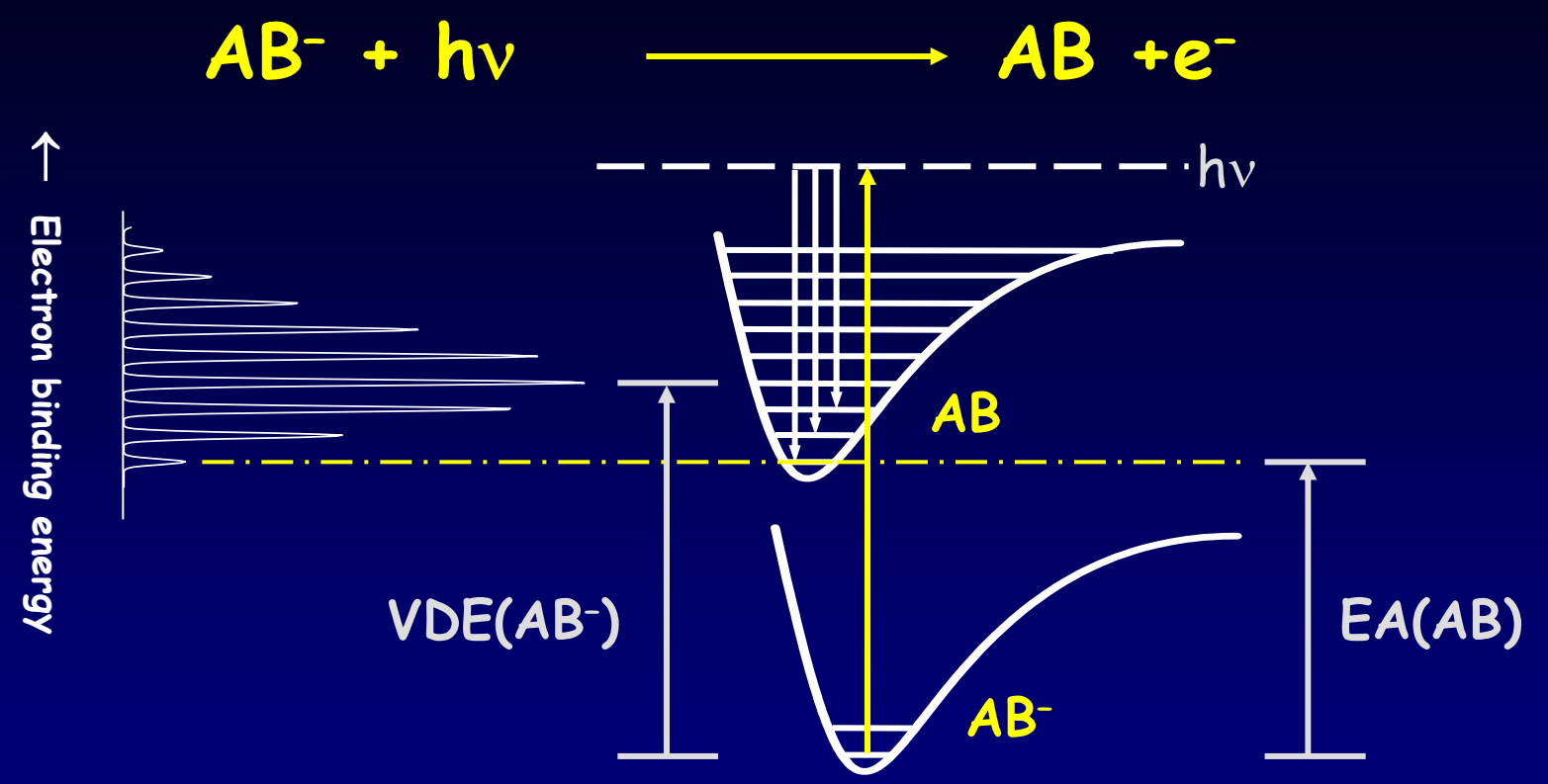




Note m/e = 40 second product

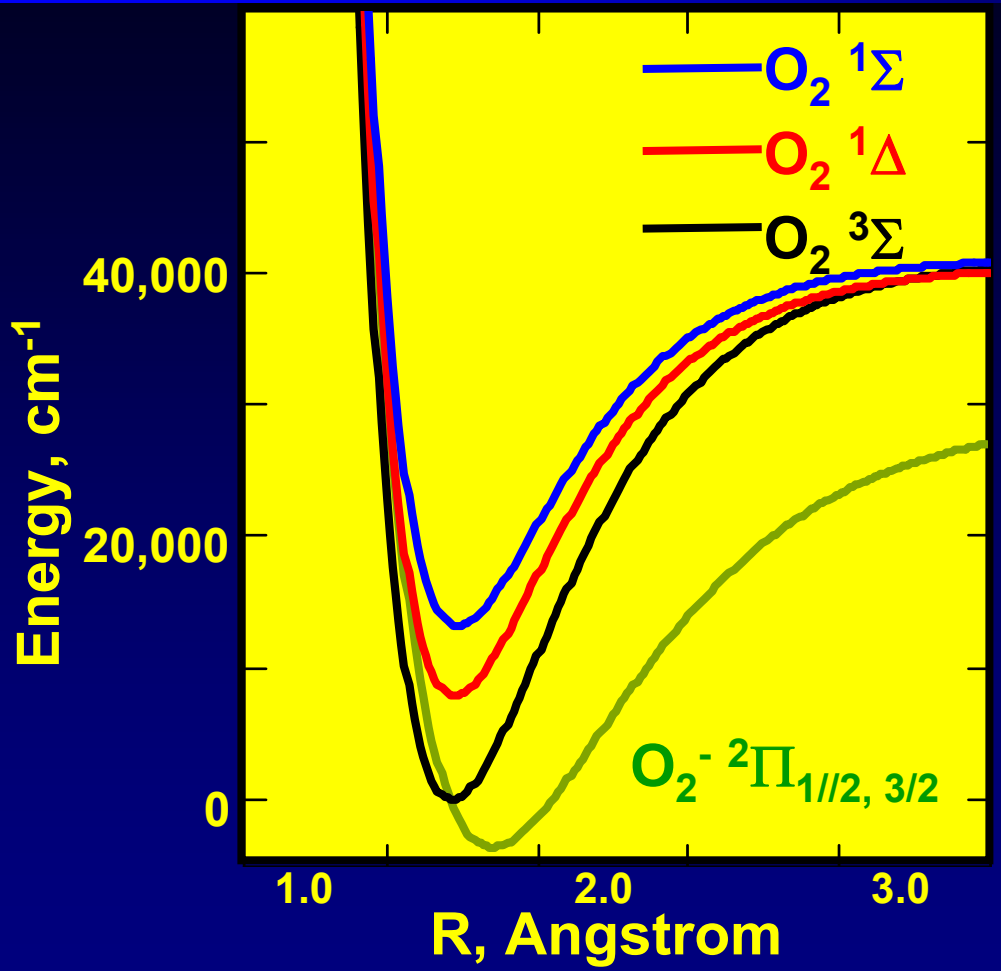
Other reactions appear to have only one ionic product.

Negative Ion Photoelectron Spectroscopy



- Intensities governed by Franck-Condon factors
- Instrument resolution is 5 meV (40 cm^{-1} or 0.1kcal/mol)
- $\Delta S = \pm 1$ selection rule
- Use DFT calculations and full FCF simulation to compare with exp.

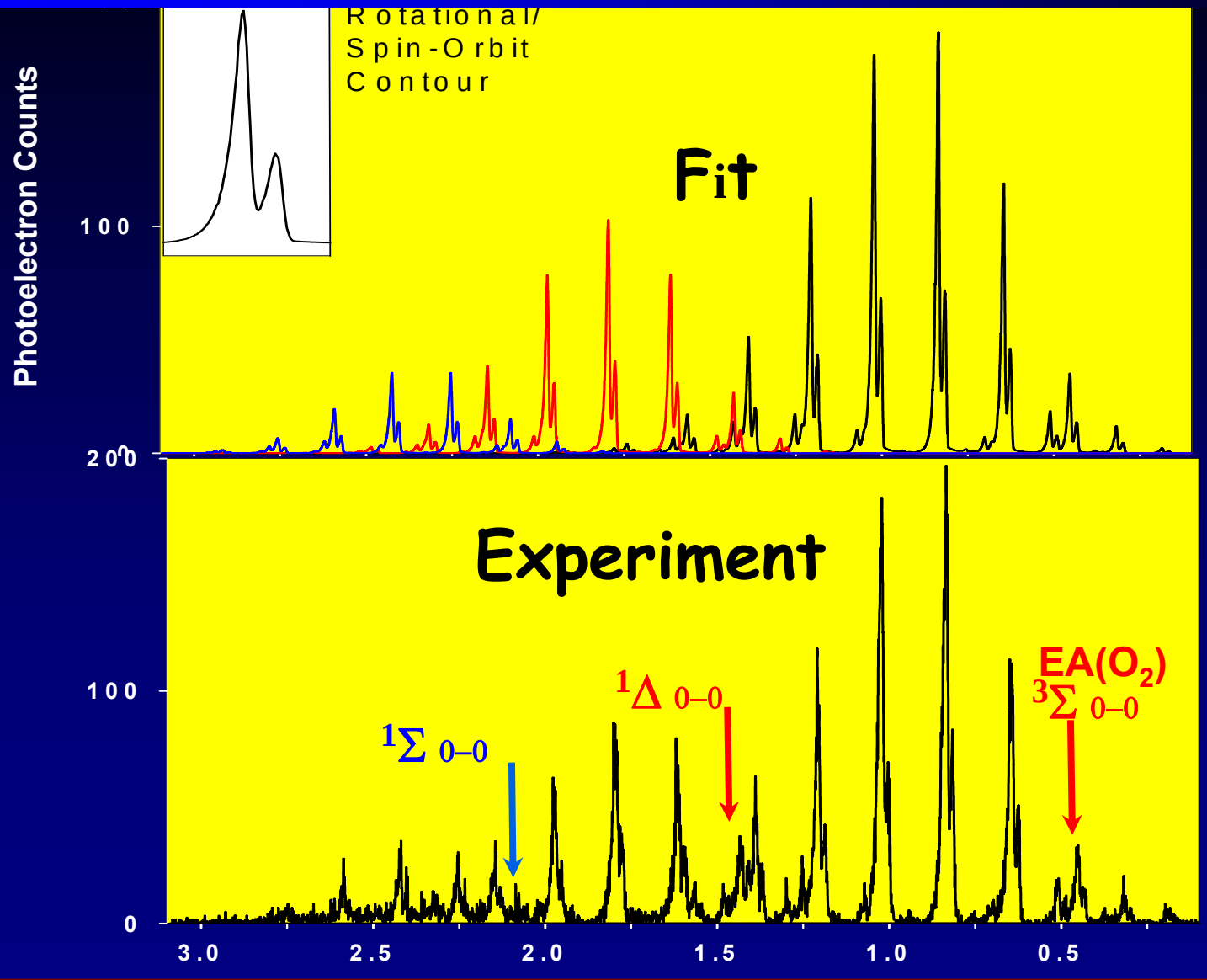
O_2^- and O_2 Electronic Potentials



How well can one fit the observed photoelectron spectrum by optimizing O_2^- properties: r_e, ω_e, S-O, and EA?

O_2^- photoelectron spectrum simulation

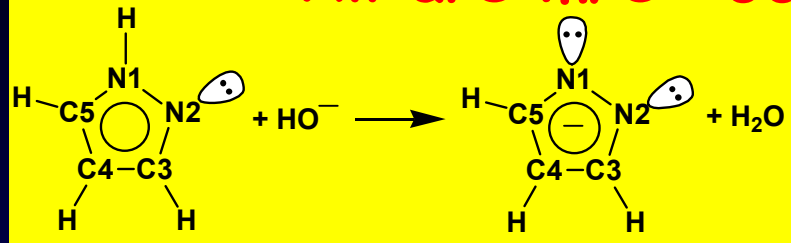
K. Ervin, I. Anusiewicz, P. Skurski, J. Simons and WCL,
J. Phys Chem. A 107, 8521 (2003)



Pyrazole reactions with hydroxide

All are m/e =66

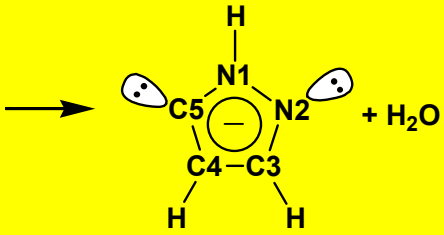
$\Delta_{rxn}H^{o}$



pyrazole

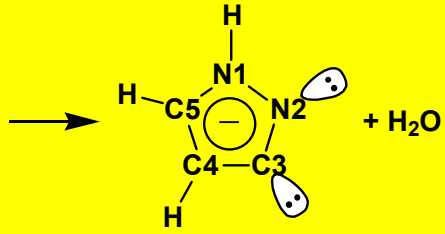
1-pyrazolide

-35 kcal/mol



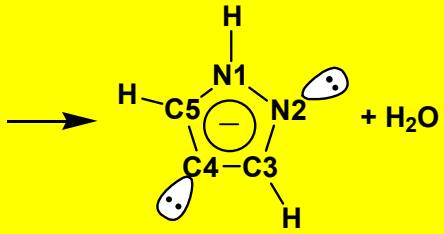
5-pyrazolide

-6 kcal/mol



3-pyrazolide

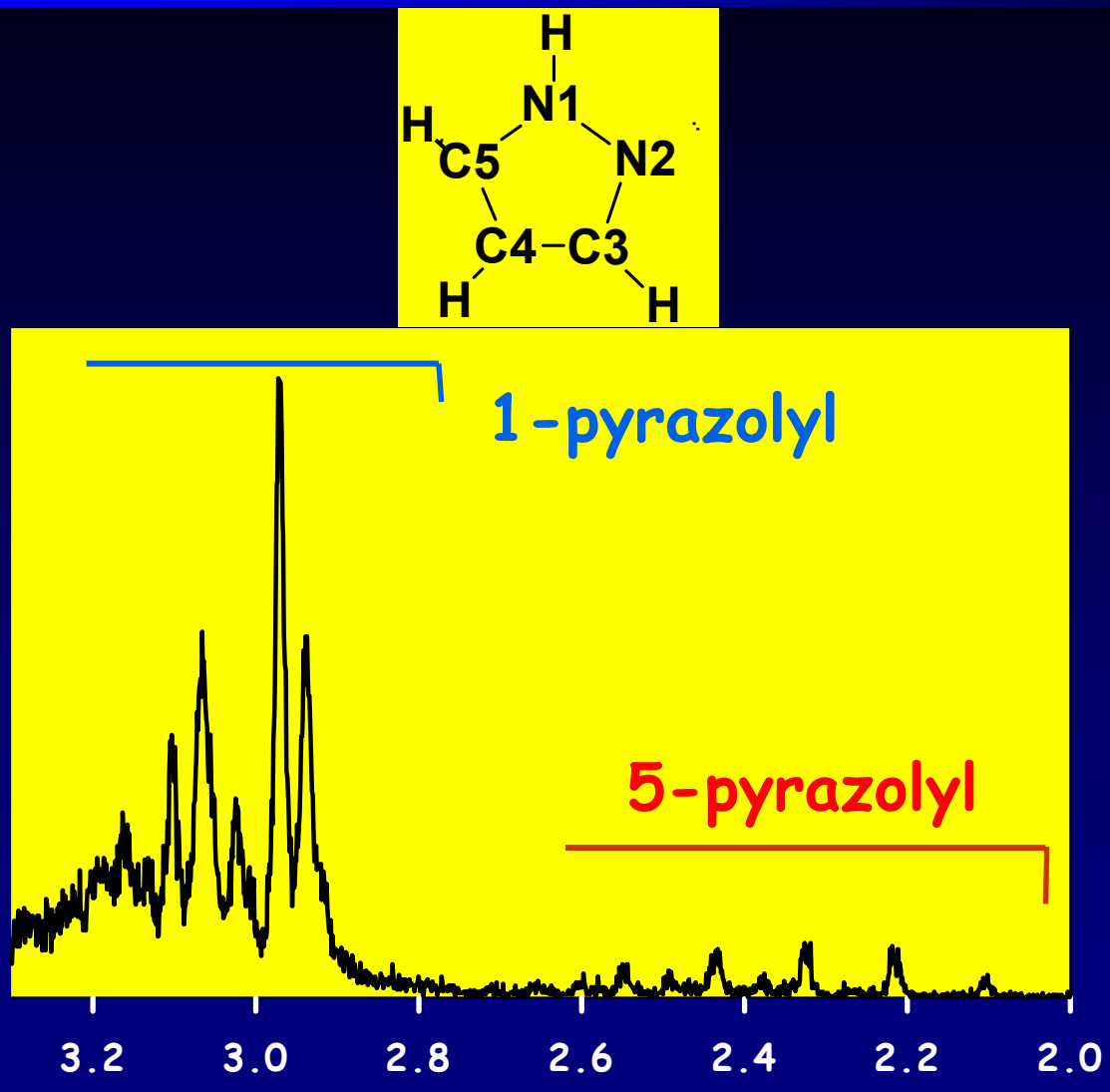
+ 9.9 kcal mol^{-1}



4-pyrazolide

+ 6.6 kcal mol^{-1}

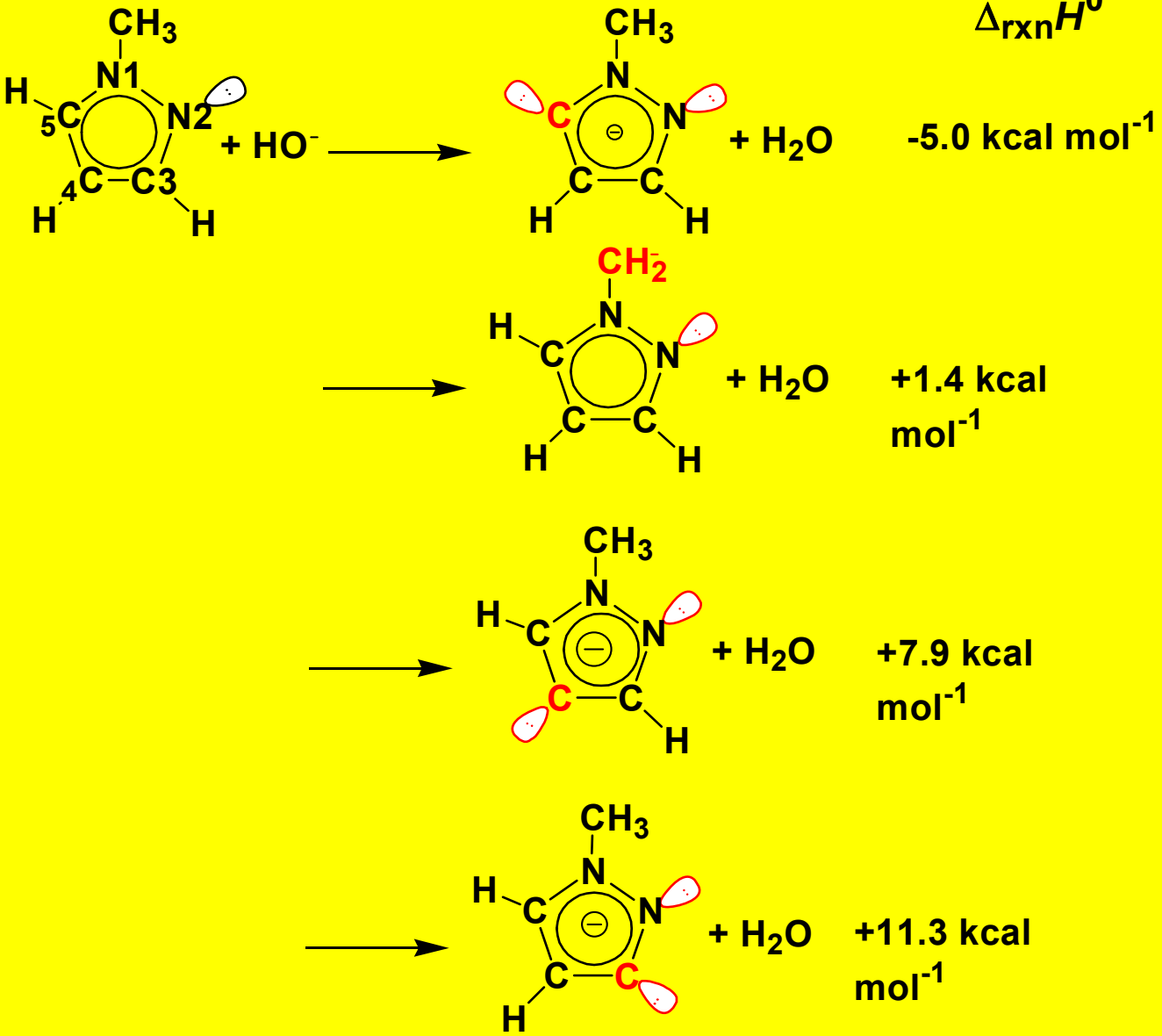
pyrazolide anions photoelectron spectrum



Test assignments by "blocking" N1 site with CH_3.

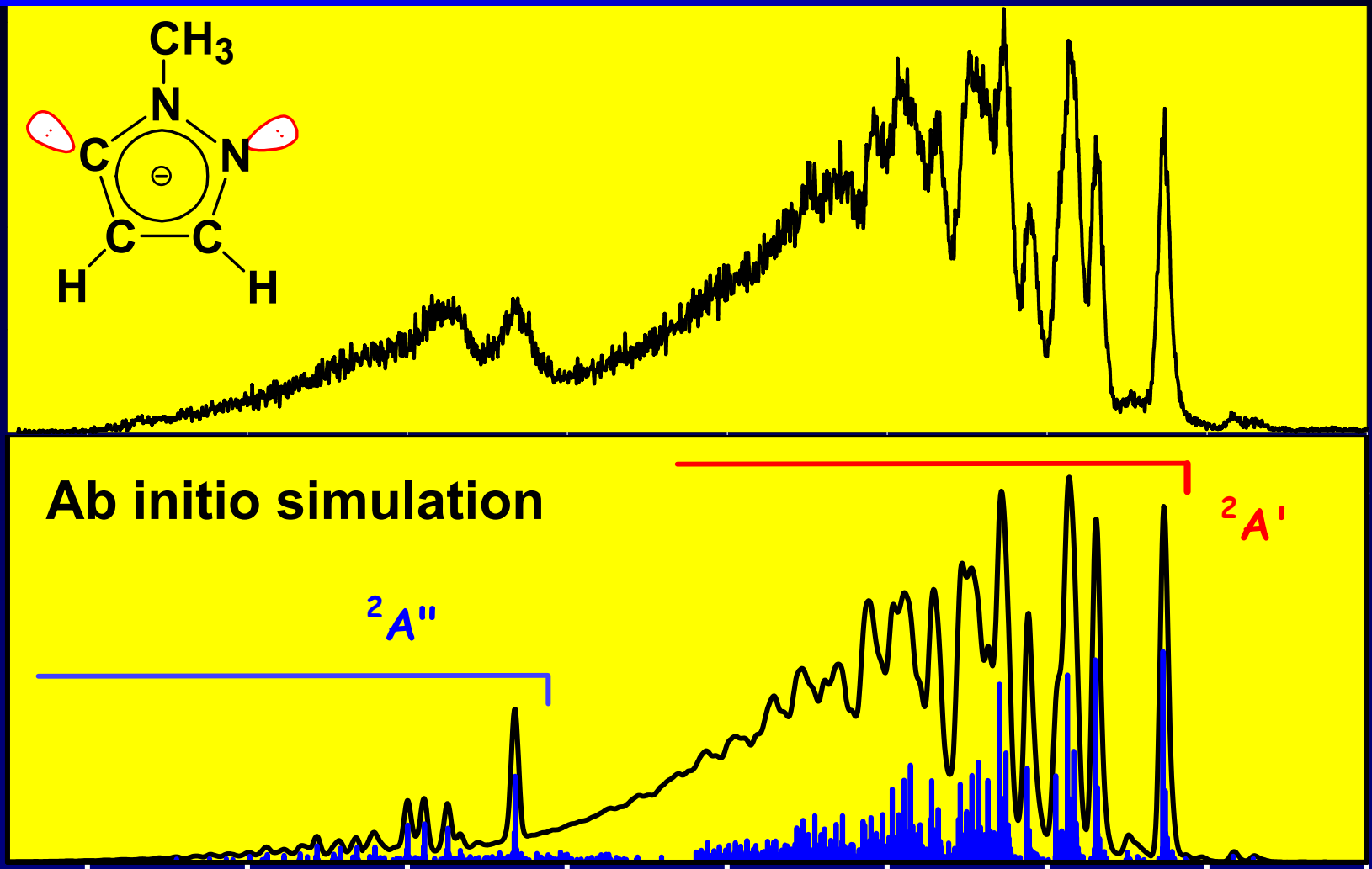
N-methyl-pyrazole reactions with OH^-

All are m/e =71



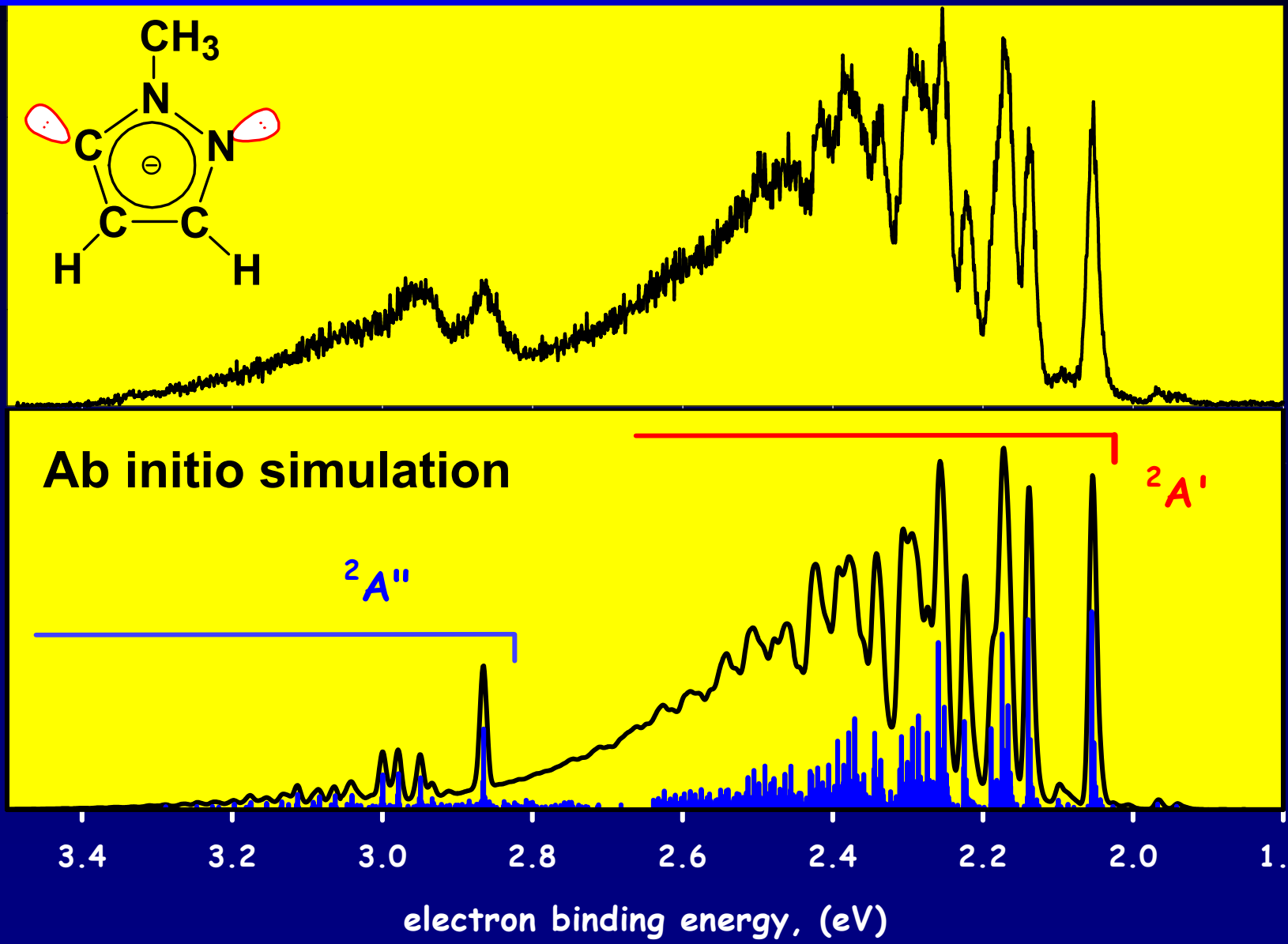
$\Delta_{rxn}H^0$

N-methyl-5 -pyrazolide photoelectron spectrum



Simulation is convincing confirmation of C5 deprotonation.

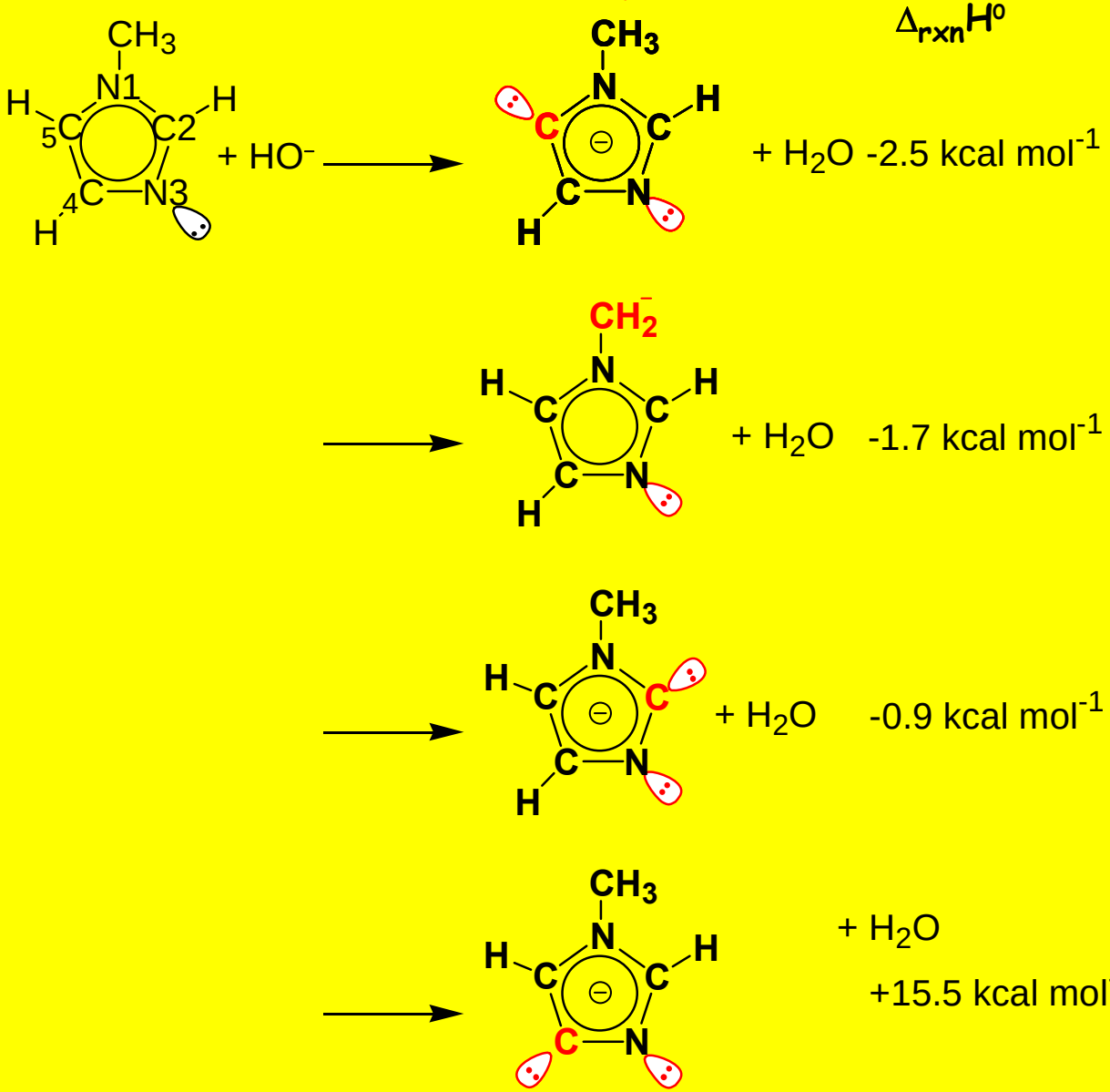
N-methyl-5 -pyrazolide photoelectron spectrum



What will happen when more reaction channels are open?

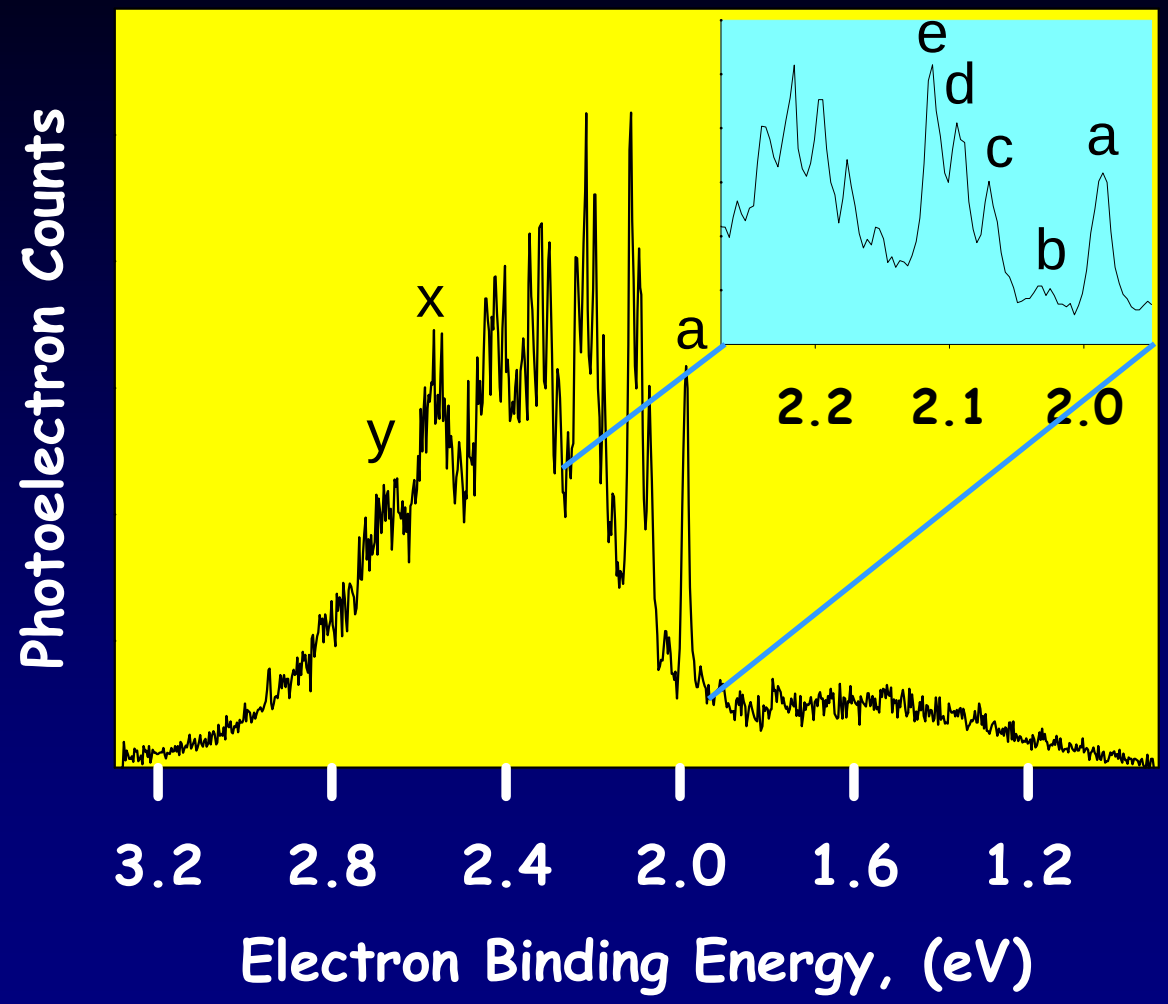
N-methyl-imidazole reactions with OH^-

All are m/e =71



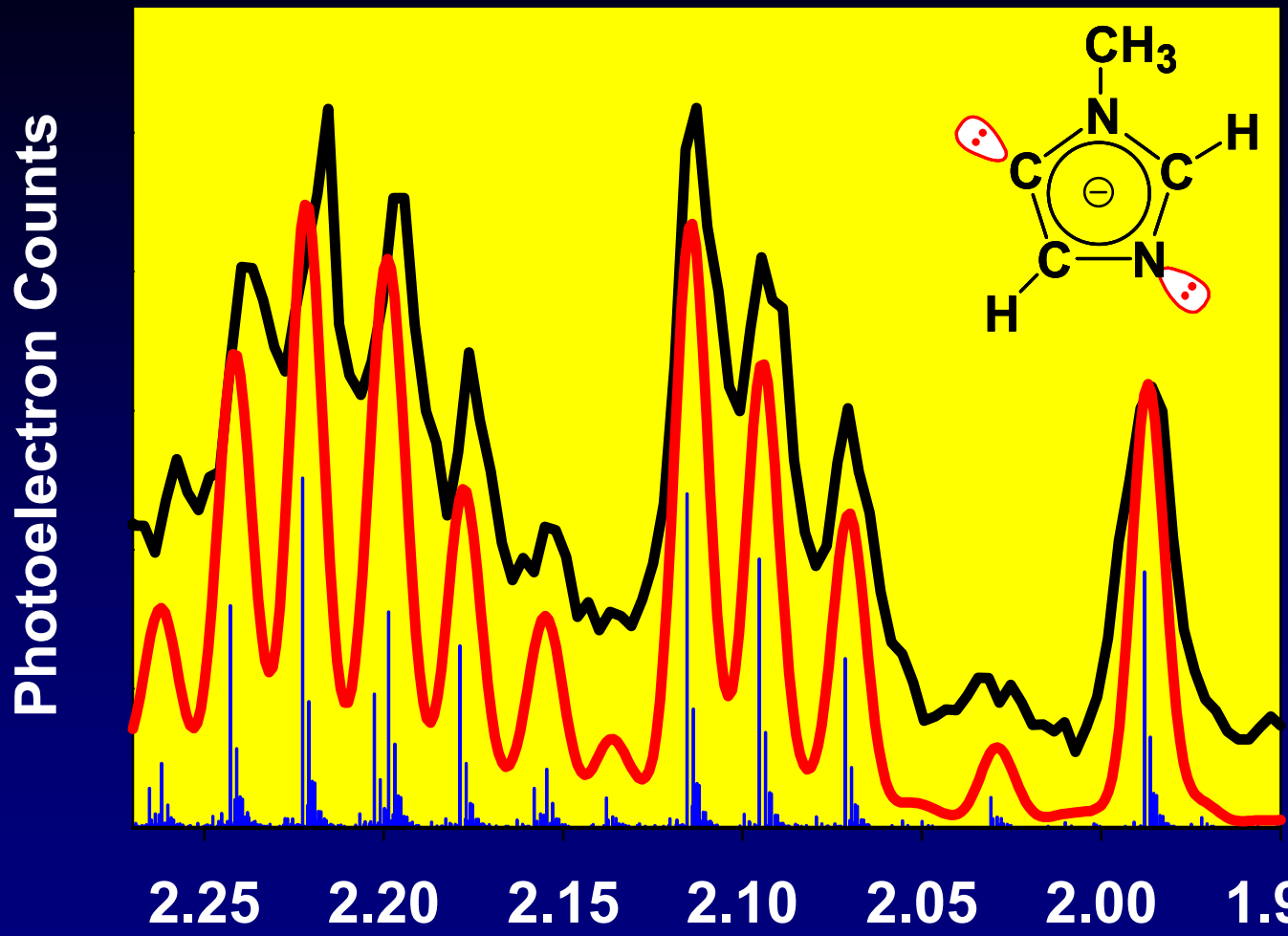
$\Delta_{rxn}H^o$

N-methyl imidazolide pe spectrum



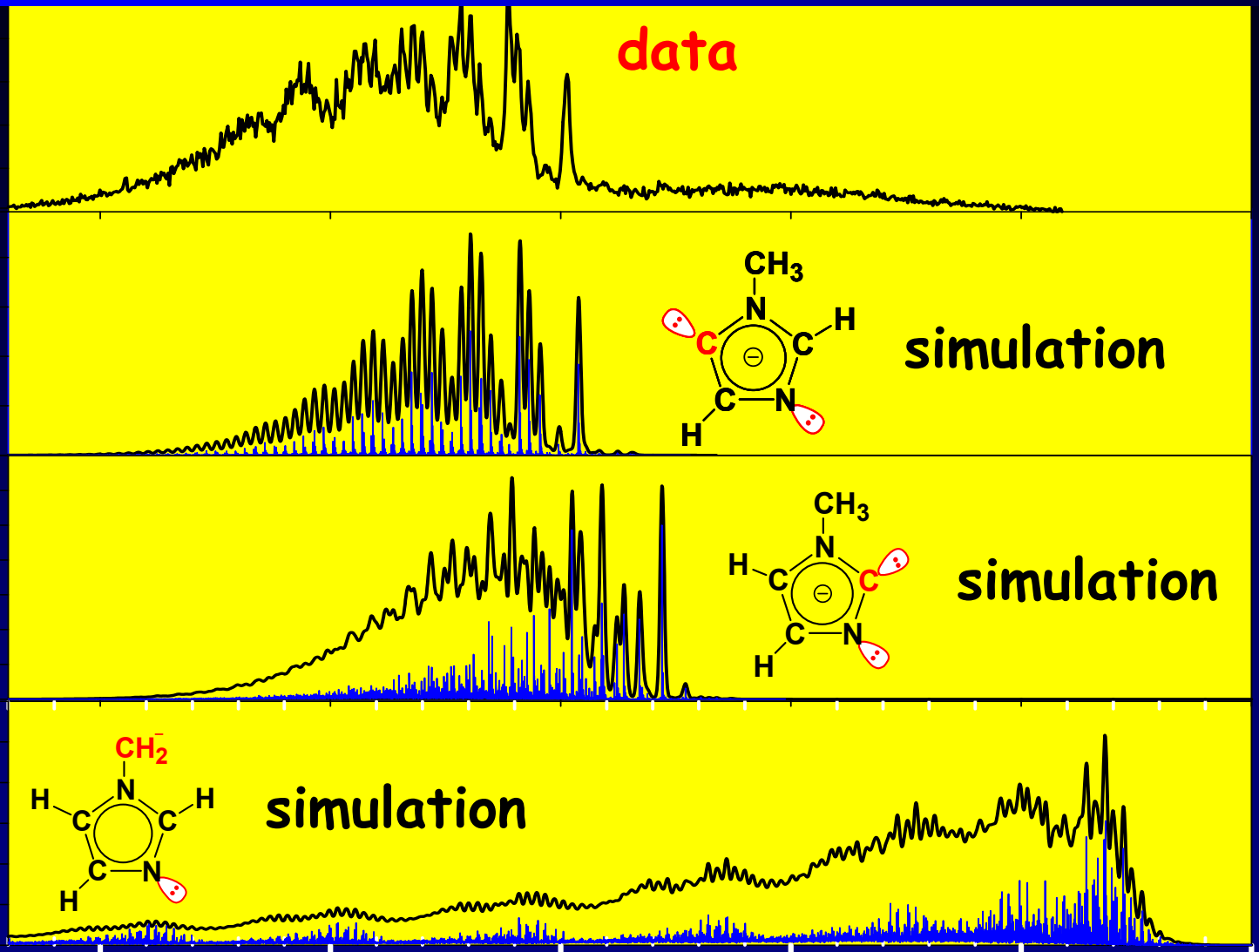
How well does the simulation reproduce the detailed structure?

N-methyl imidazolide
expanded view of simulation & experiment

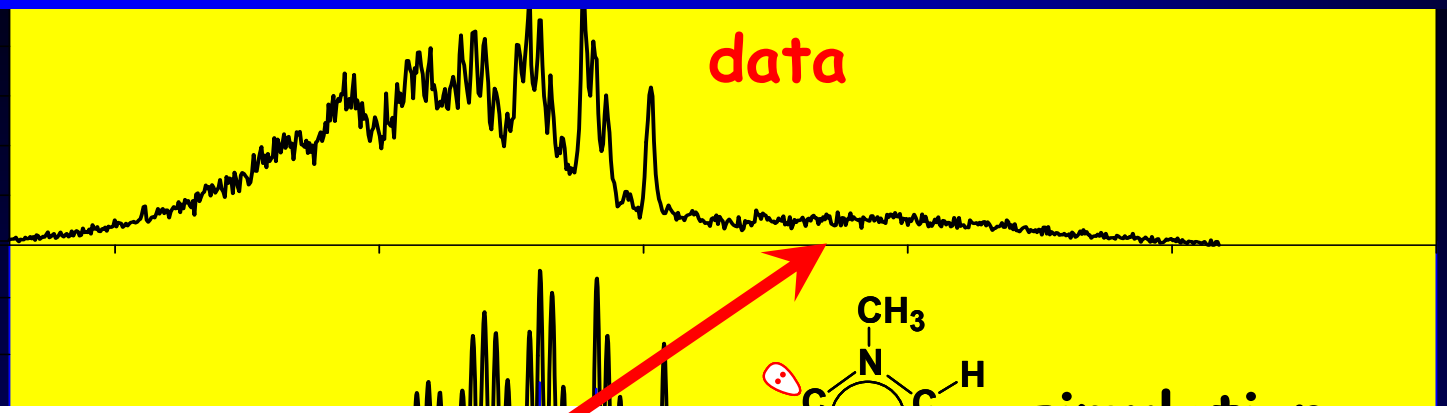


But which anion structure(s) are present?

N-methyl imidazolide pes simulations

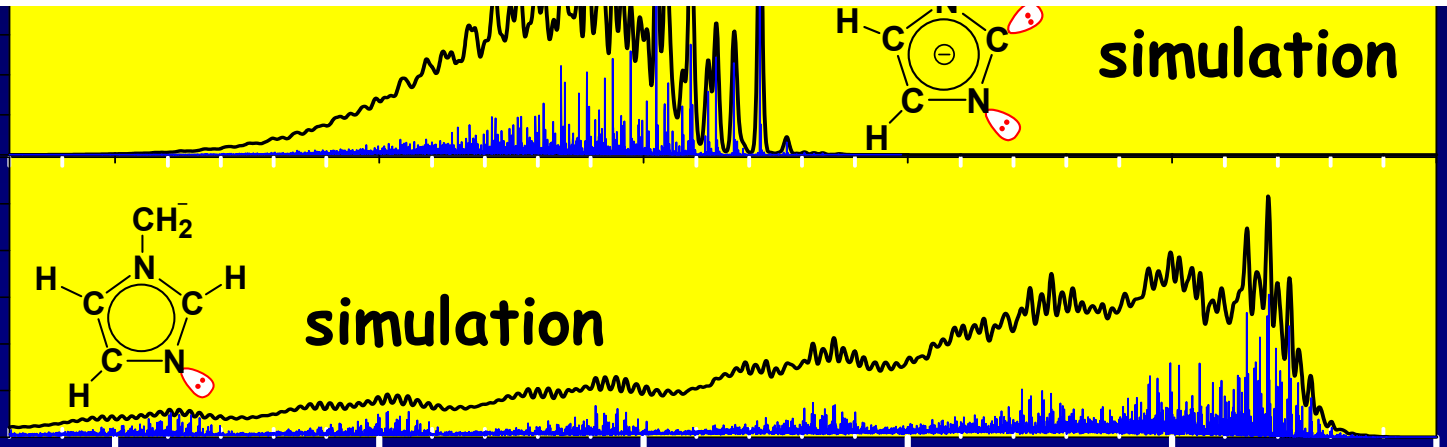


N-methyl imidazolide pes simulations

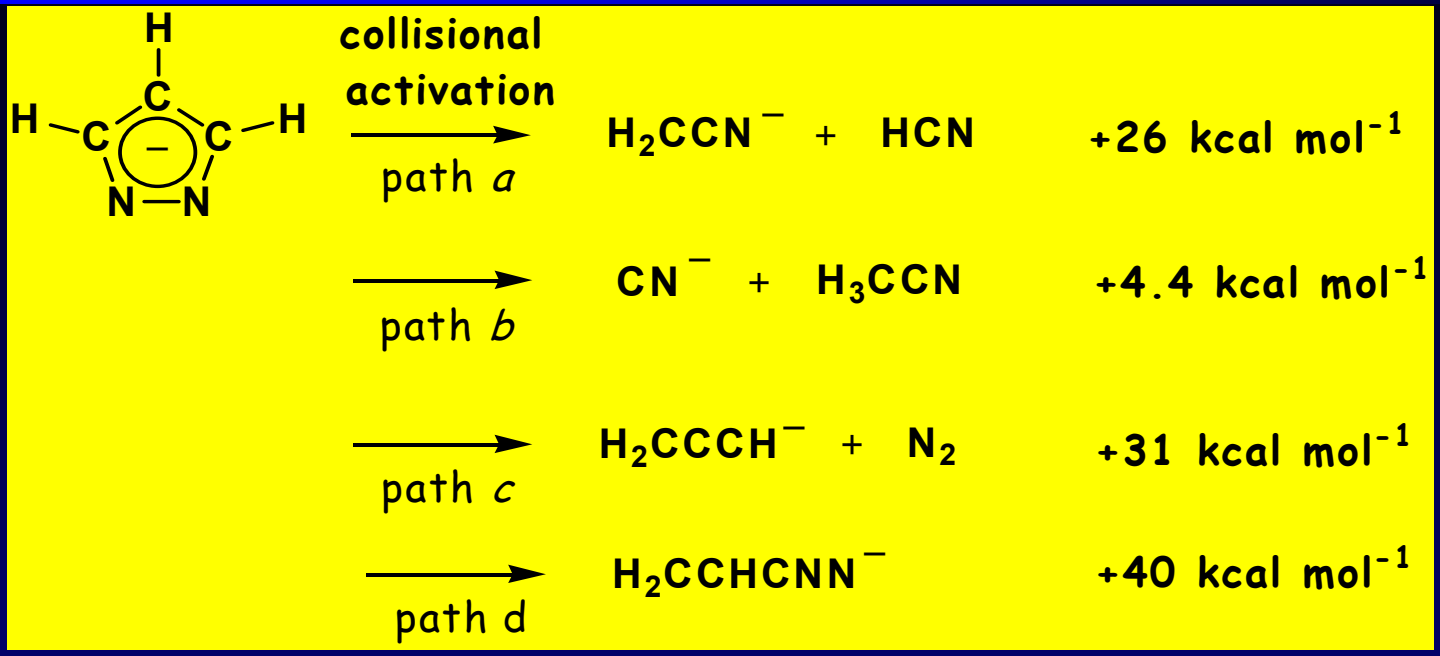


Only the C5 deprotonation product is present in significant yield, although all three isomers are energetically accessible

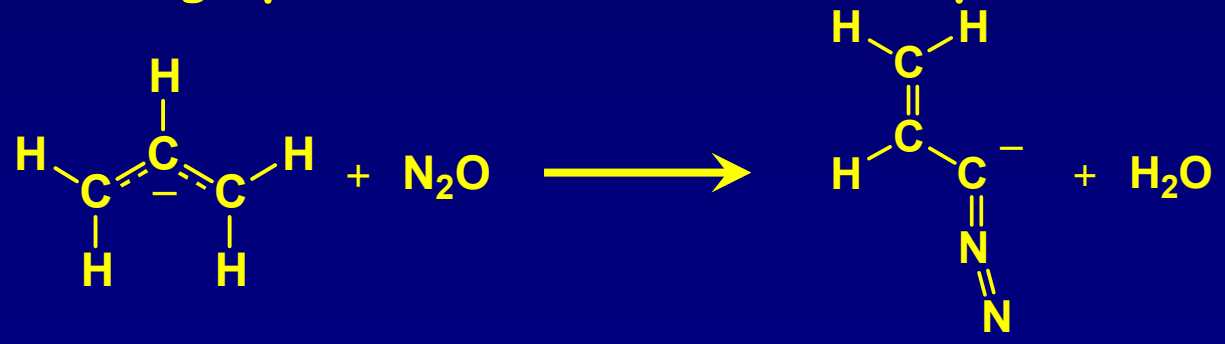
What is the "blob" at lower eBE? Same mass. Ring open?



Vinyldiazomethyl (vdm) anion chemistry

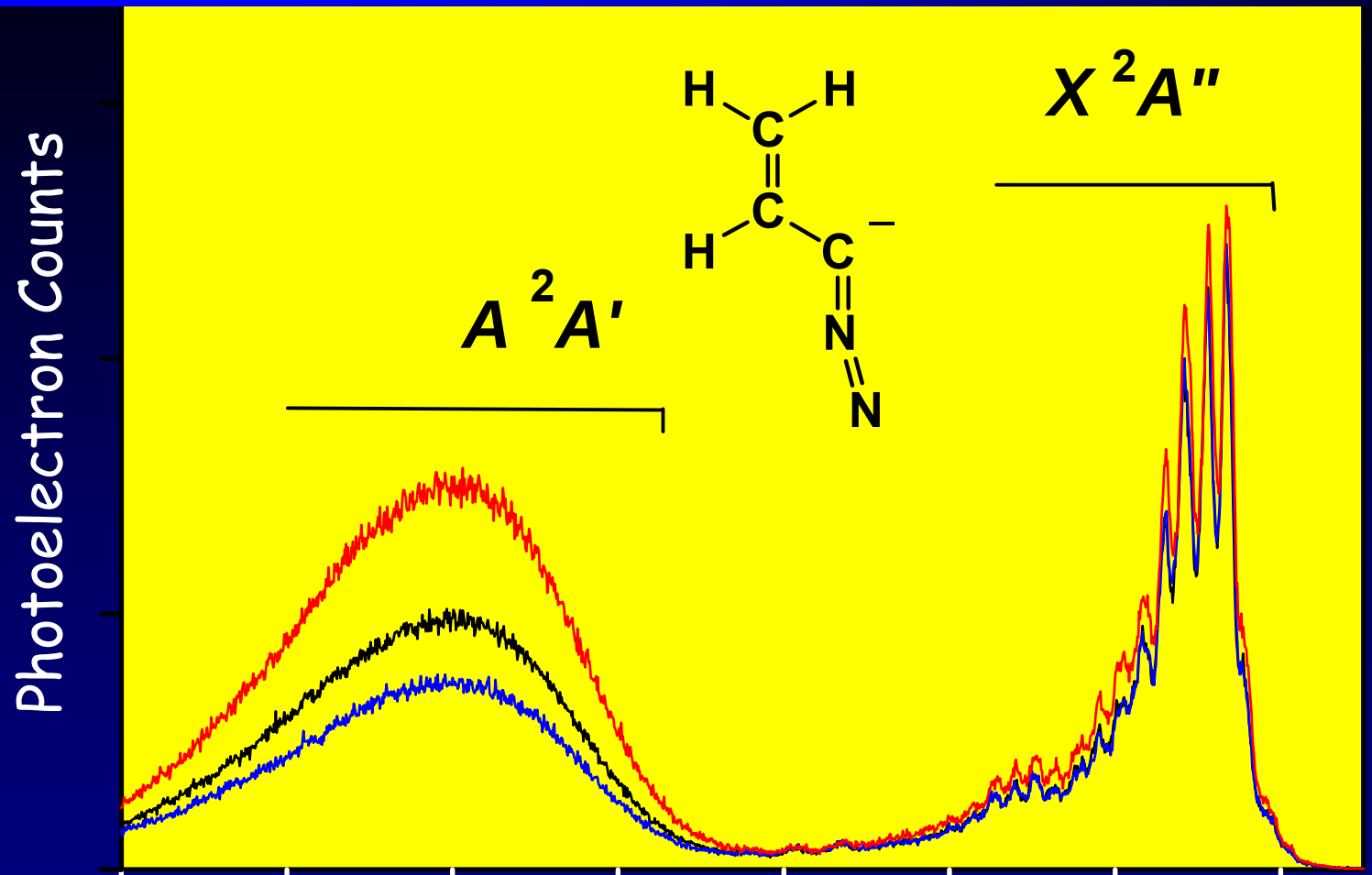


Produce the ring open form in reaction of allyl anion with N_2O.



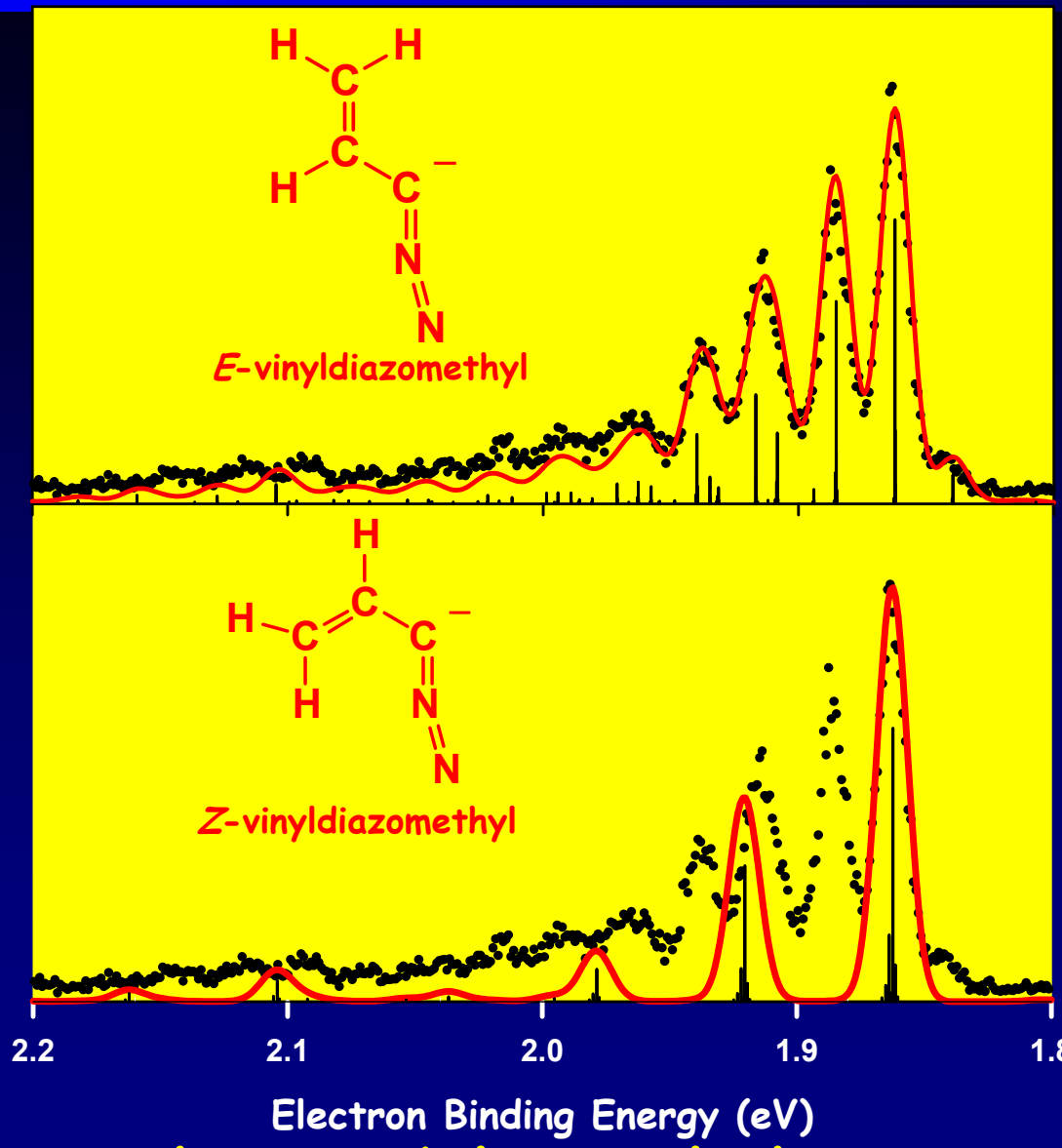
Both *E*- and *Z*- conformations of vdm$^-$ may be present

Vinyldiazomethyl anion pes



Can simulations differentiate between *E*- and *Z*- conformers?

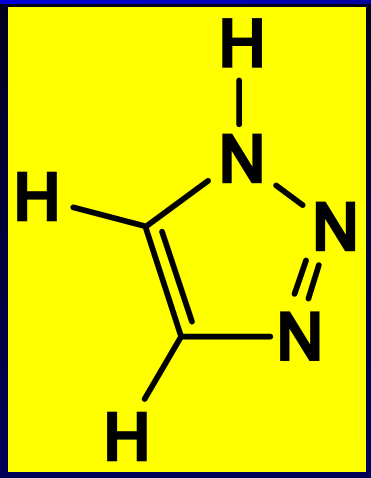
Vinyldiazomethyl anion chemistry



☑ Yes!

So we will use this capability to look at a complex reaction.

1*H*-1,2,3 triazole reaction with OH^-



$OH^- + C_2N_3H_3 \rightarrow (m/e\ 68)^- + H_2O$ major product

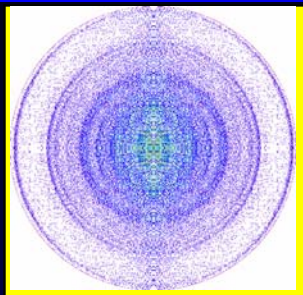
$\rightarrow (m/e\ 40)^- +$ neutral(s) smaller

Gentle CID on m/e 68 gives extensive m/e = 40 anion(s)

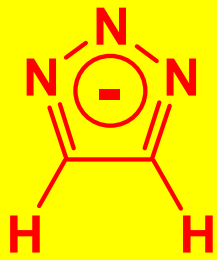
What are the identities, structures and energetics of these anions?

Can we infer plausible reaction mechanisms?

1,2,3,triazolide imaging pe spectrum



actually
m/e = 68

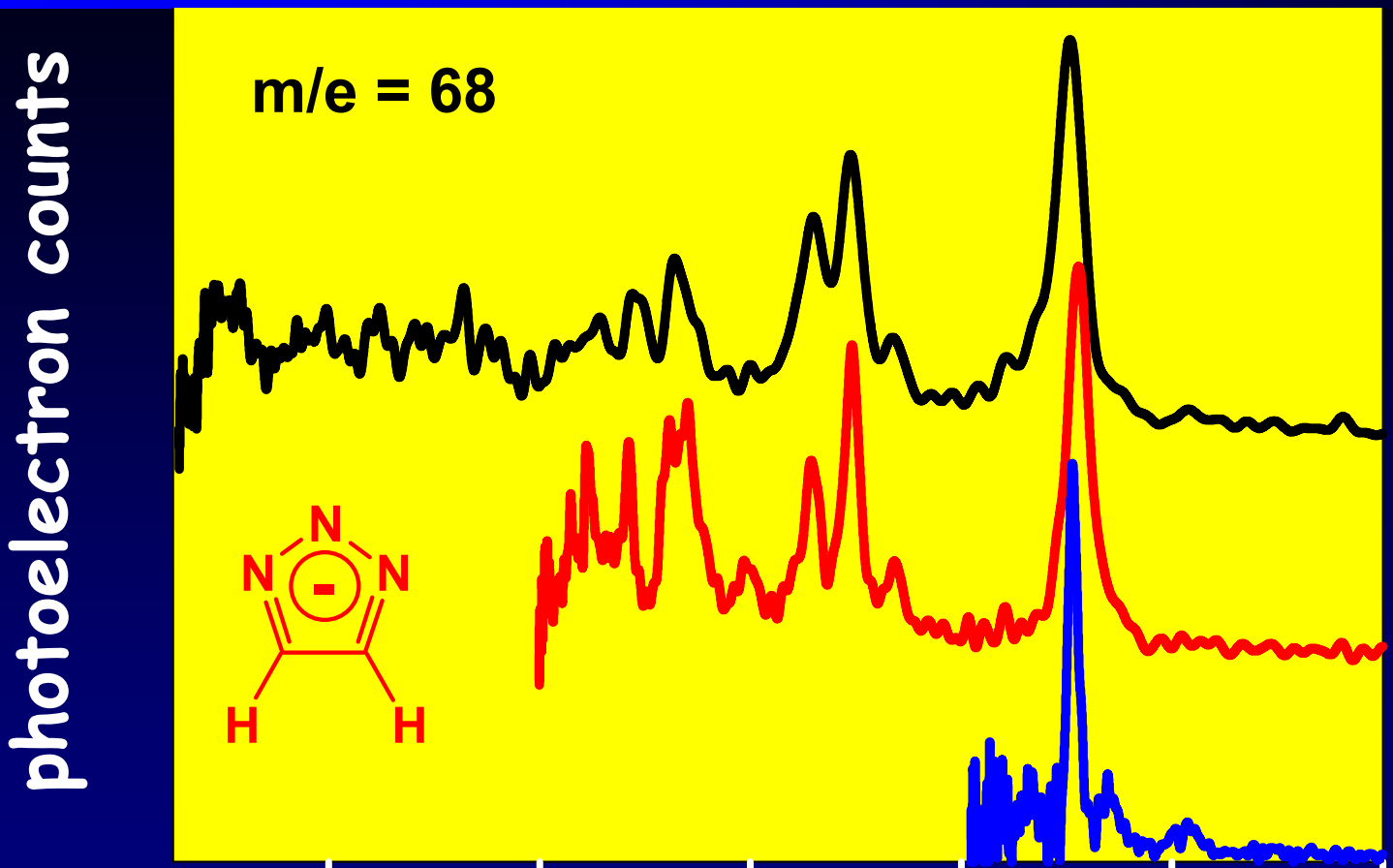


Photoelectron counts

3.70 3.65 3.60 3.55 3.50 3.45 3.40

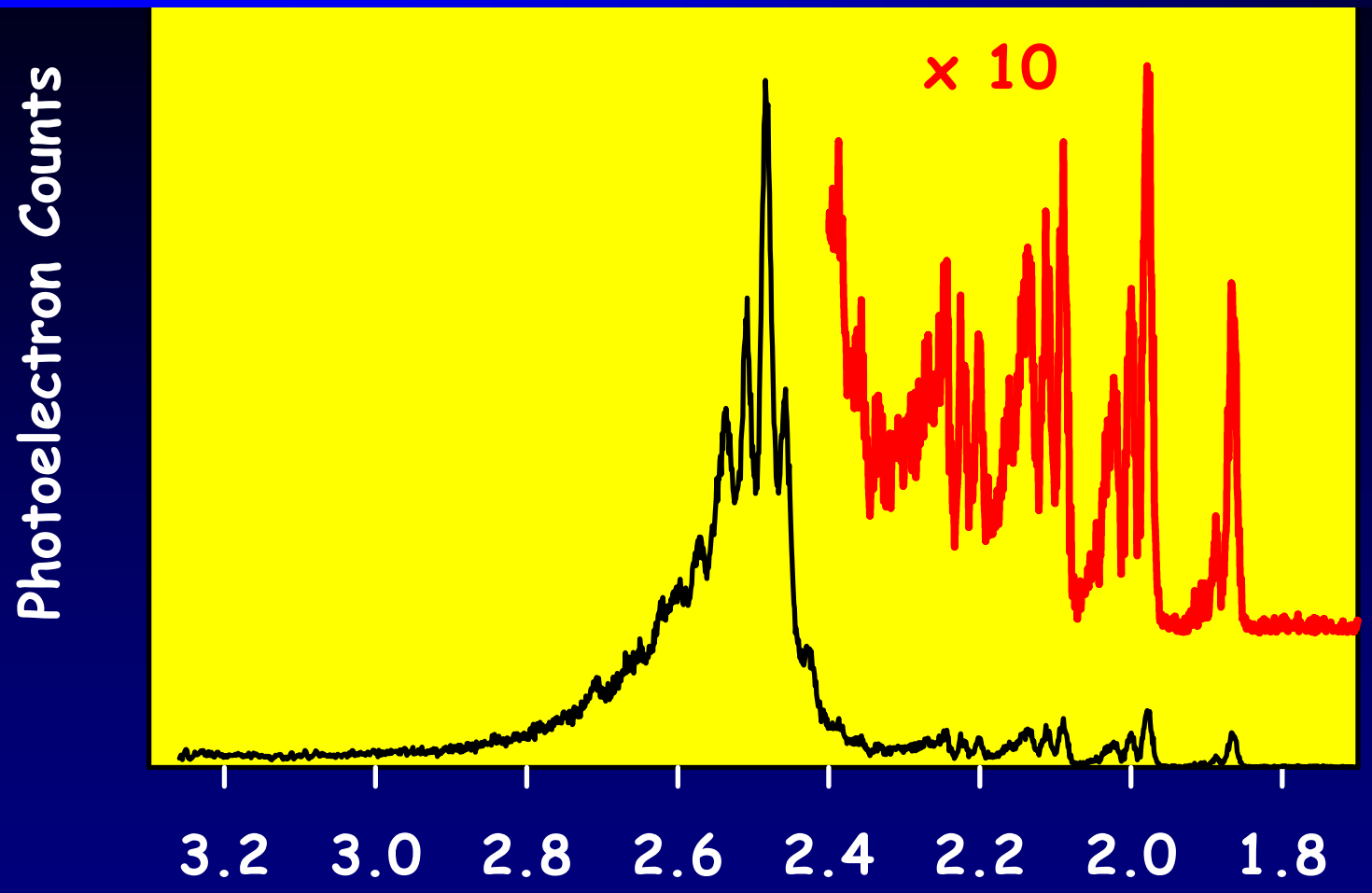
electron binding energy (eV)

355, 335, 320 nm images



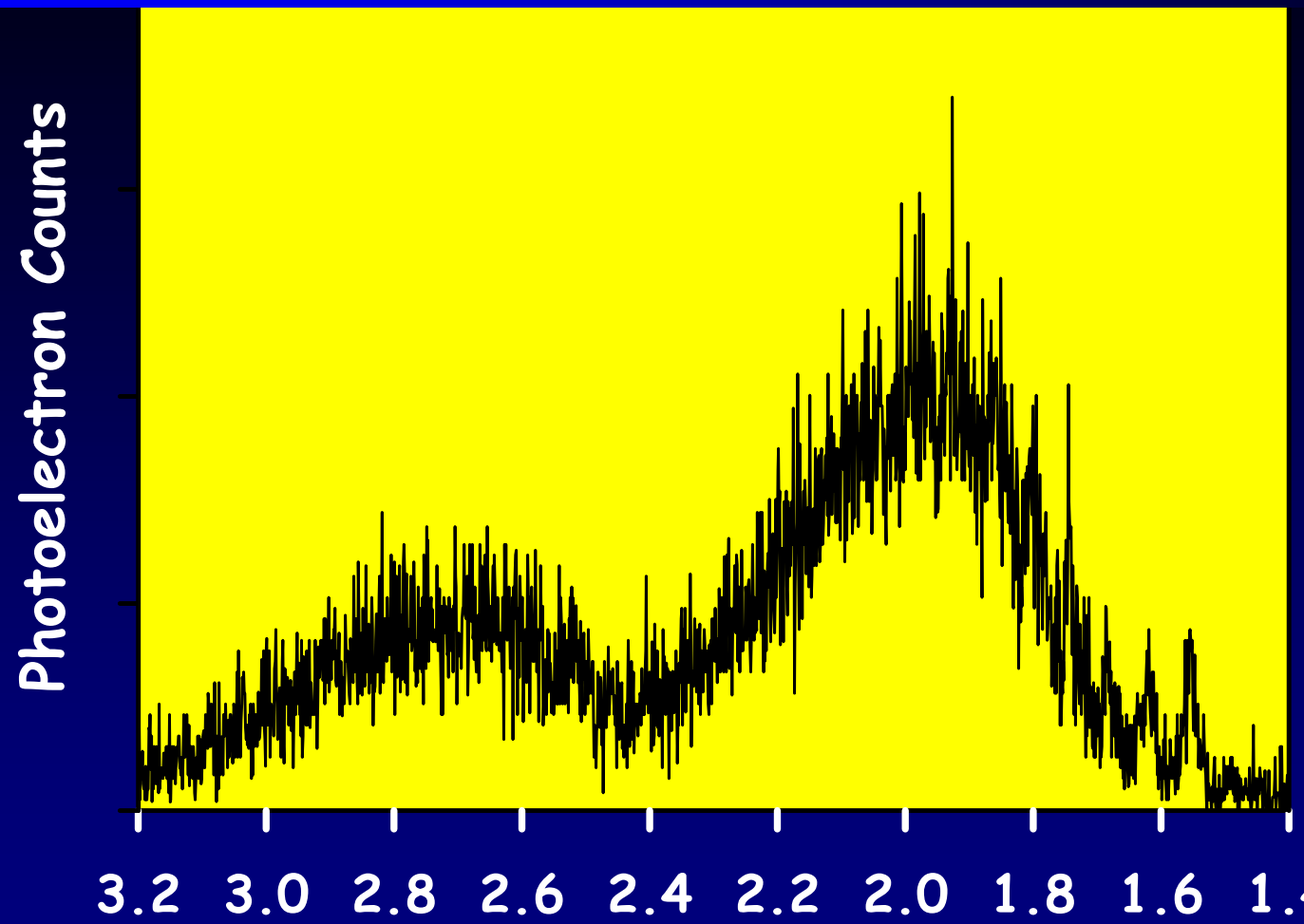
But there is photoelectron signal at lower binding energies.

m/e = 68 photoelectron spectrum



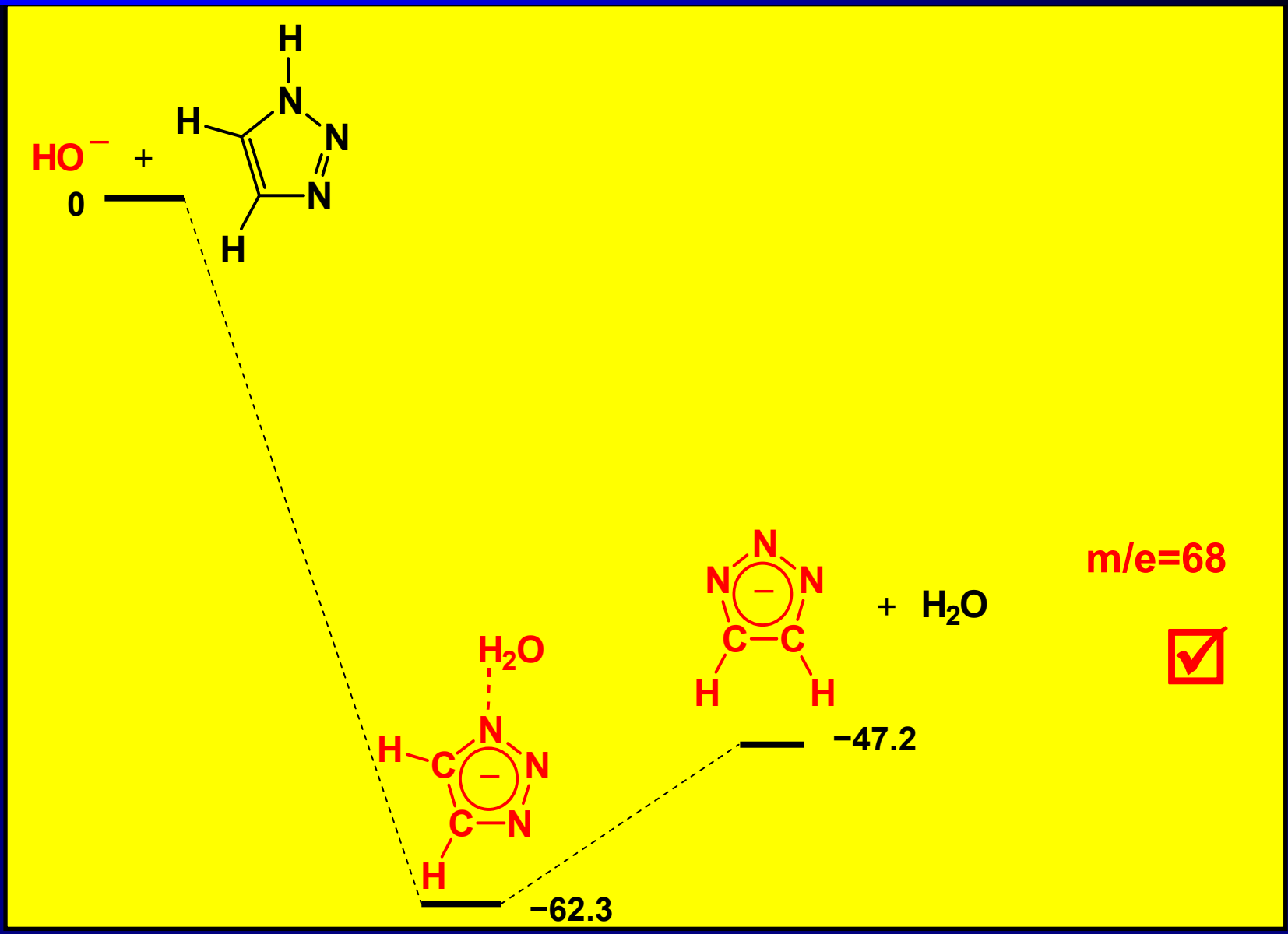
And there is the other m/e = 40 reaction product:

m/e = 40 photoelectron spectrum

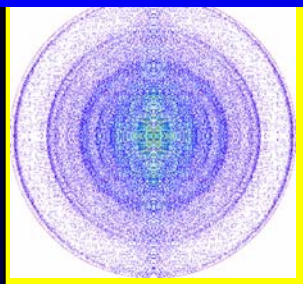


So how do we rationalize all these data?

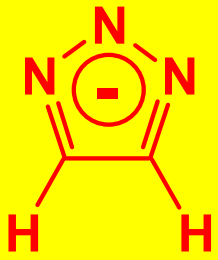
Triazole N1 deprotonation by OH^-



1,2,3,triazolide imaging pe spectrum



EA = 3.447(4) eV



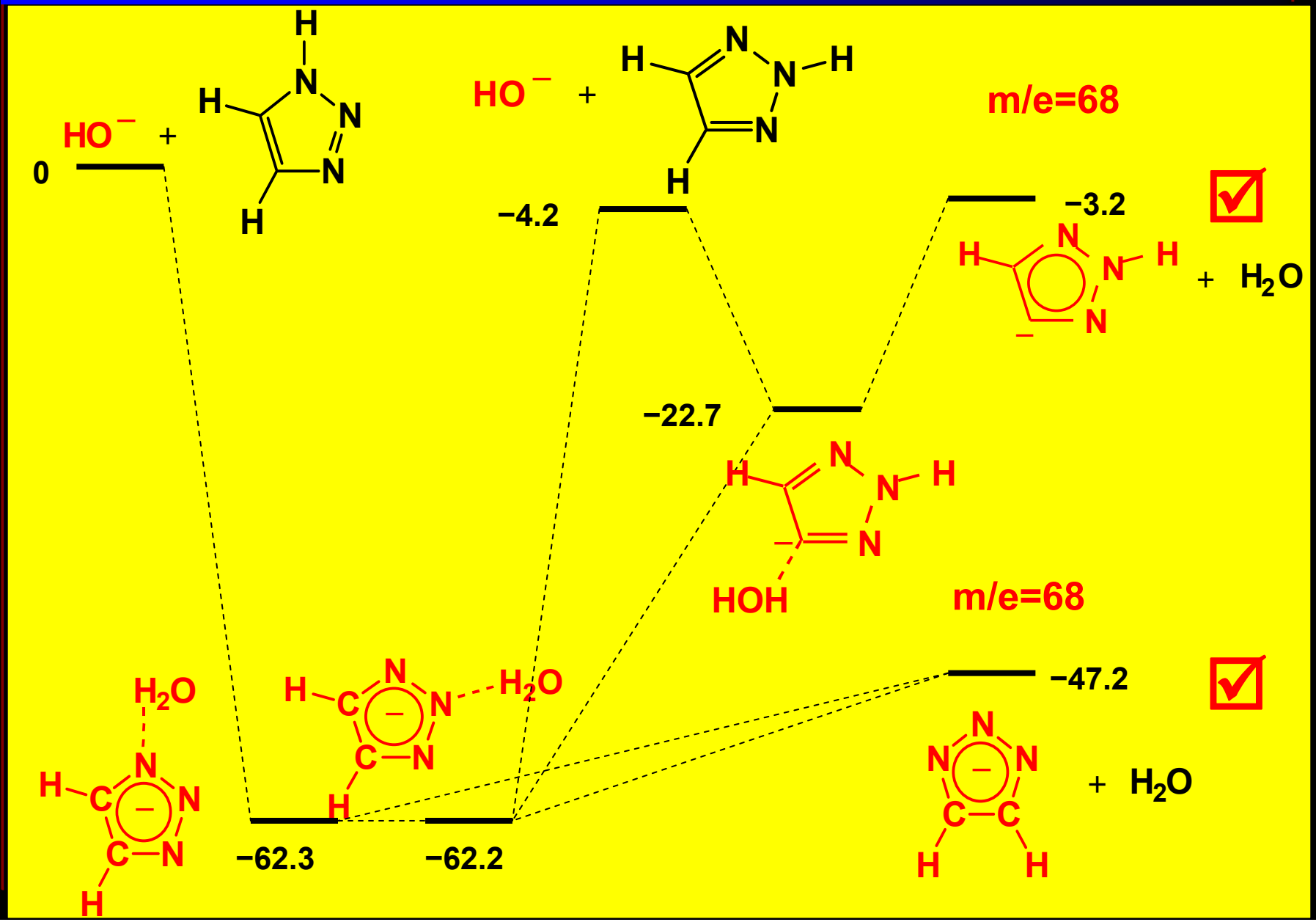
Photoelectron counts

3.70 3.65 3.60 3.55 3.50 3.45 3.40

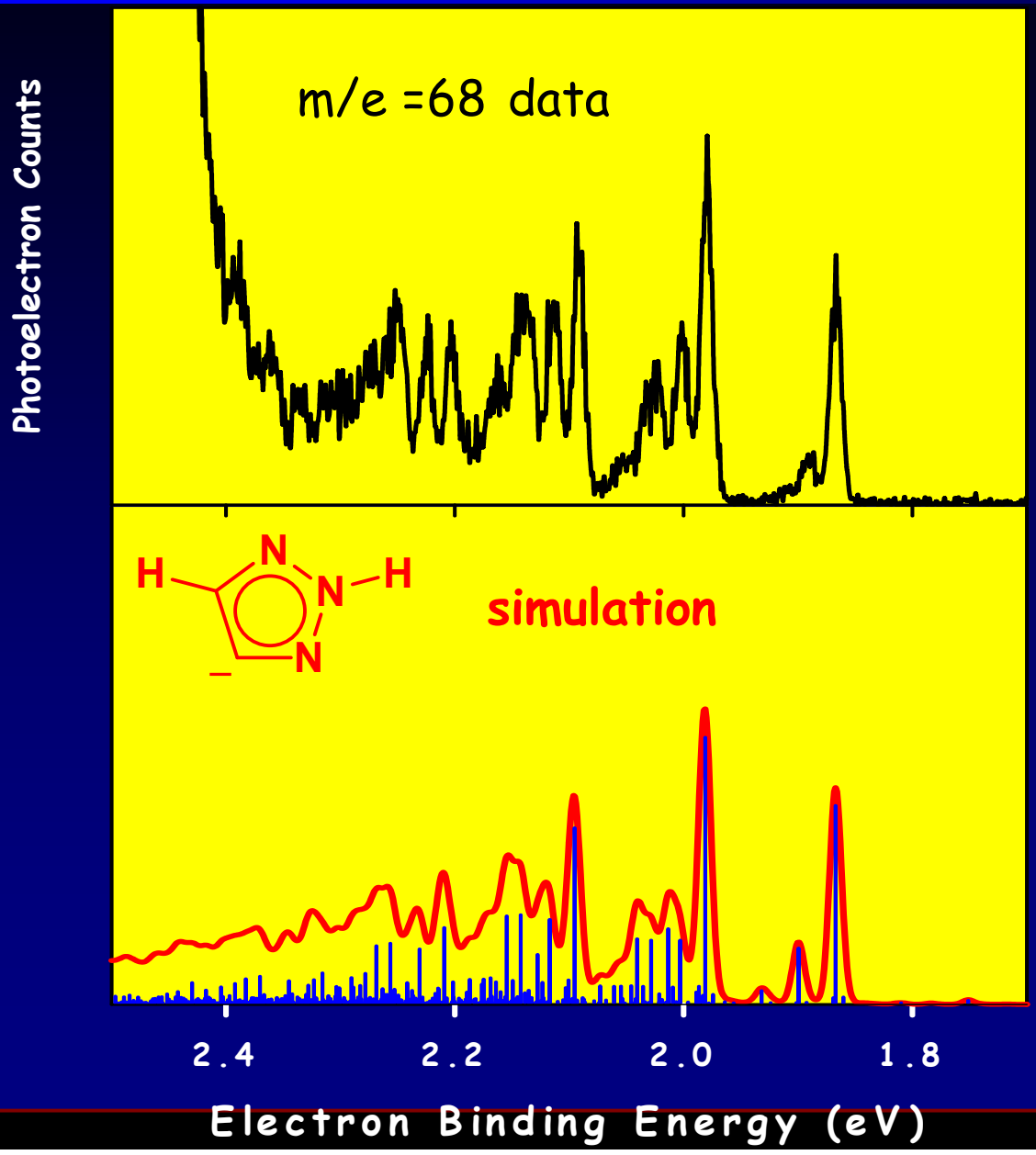
electron binding energy (eV)

What are the identities, structures and formation mechanisms for the minor reaction products?

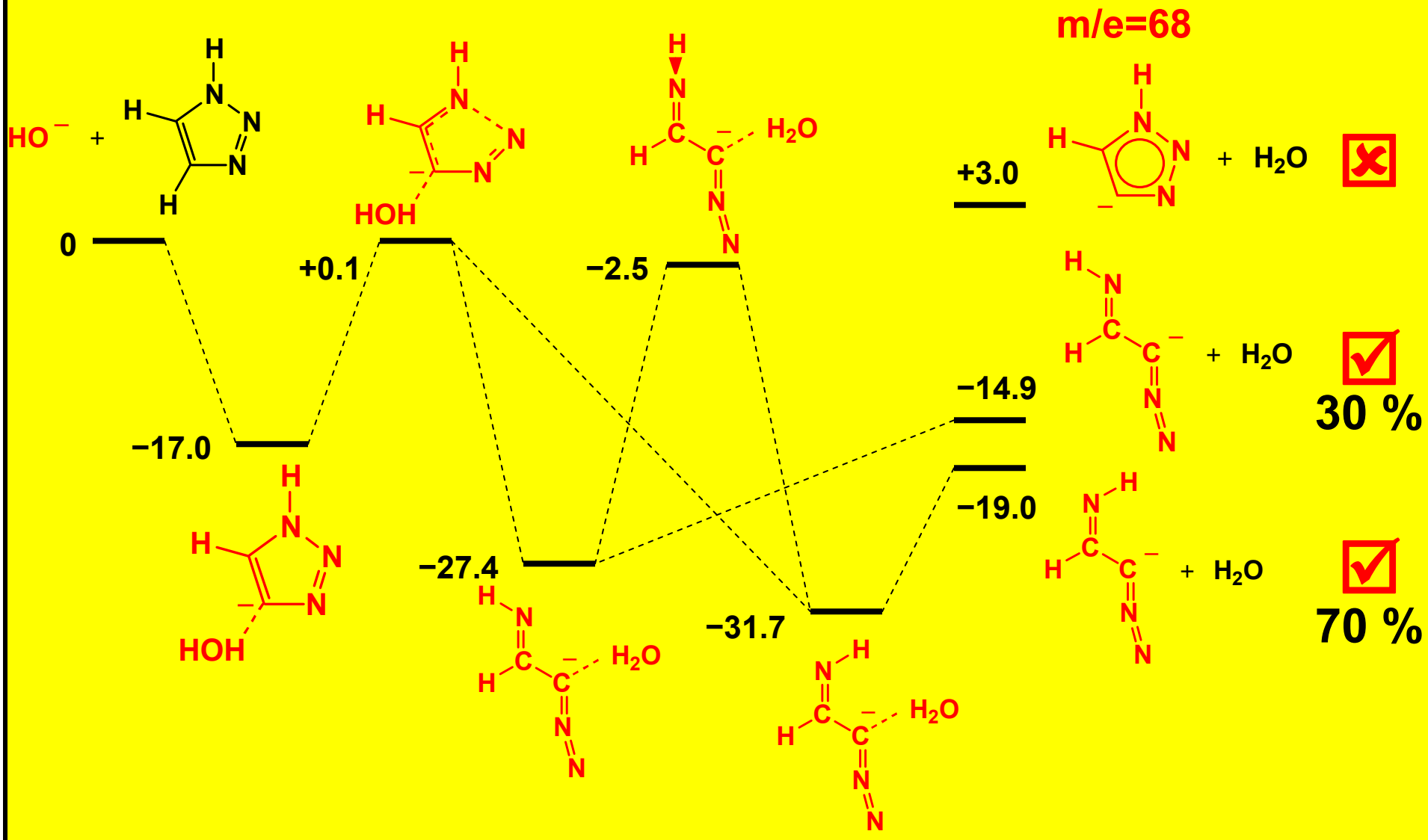
Indirect C4 deprotonation within complex



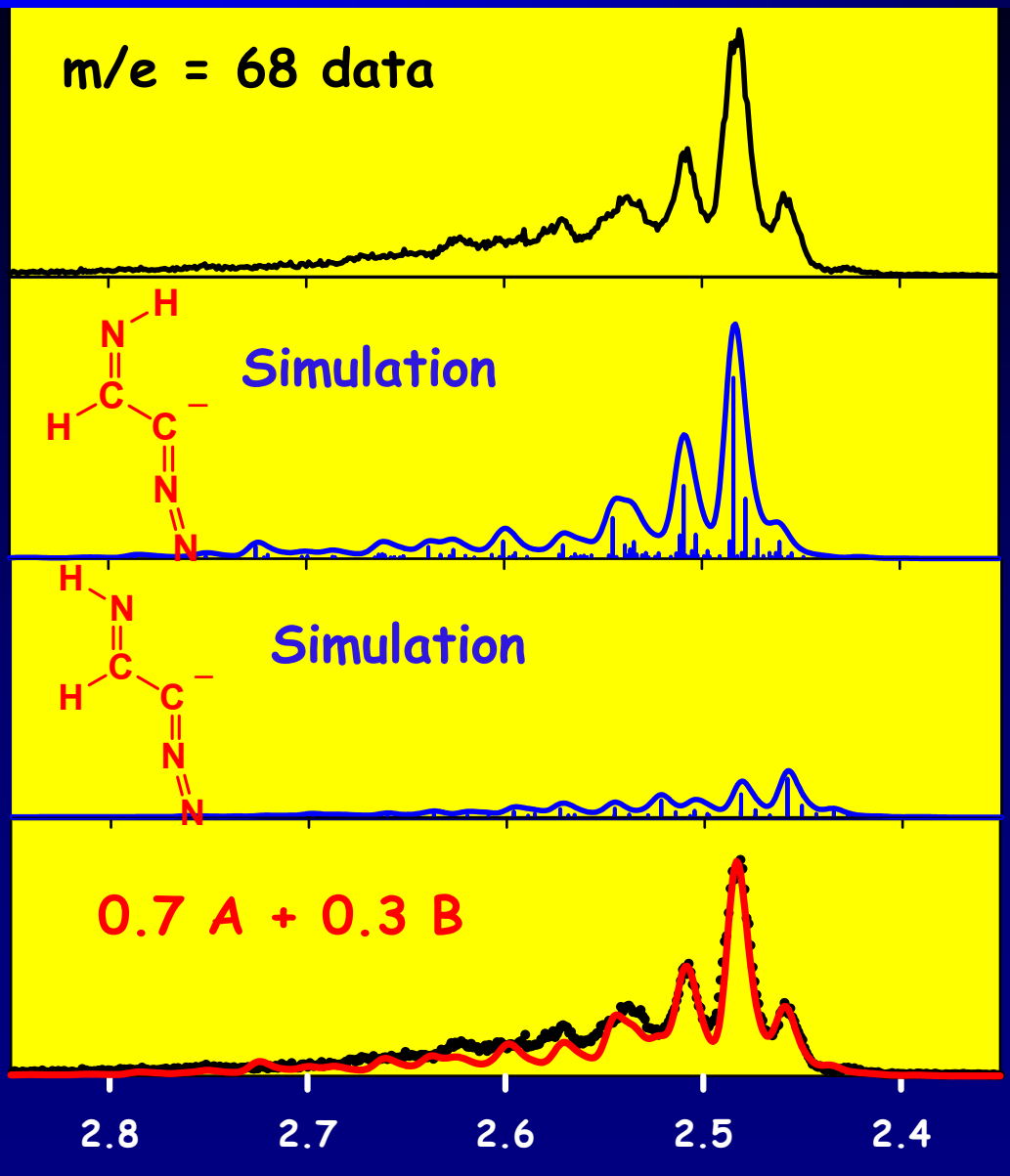
C4 deprotonated product observed



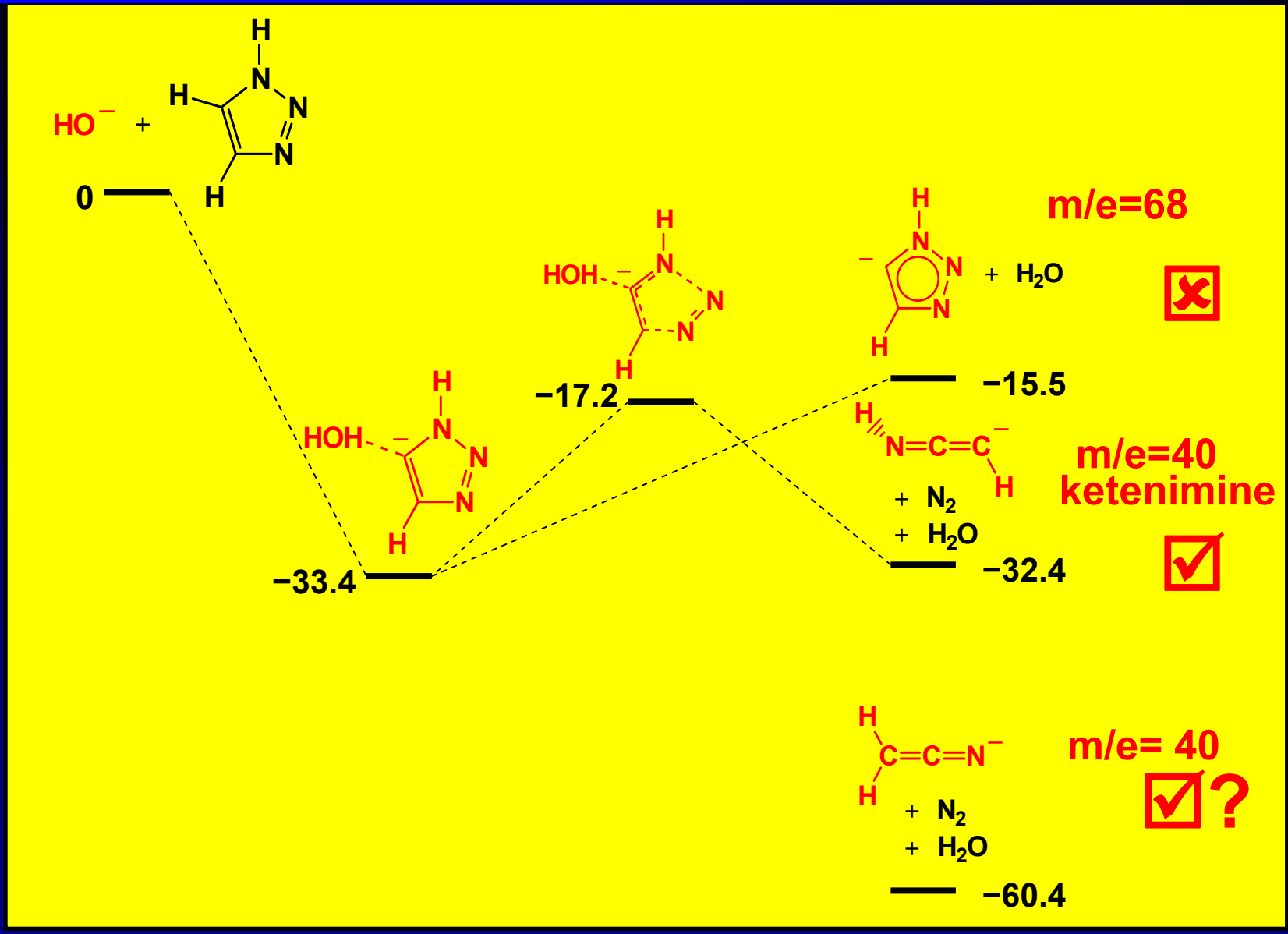
C4 attack by OH^- leads to ring opening



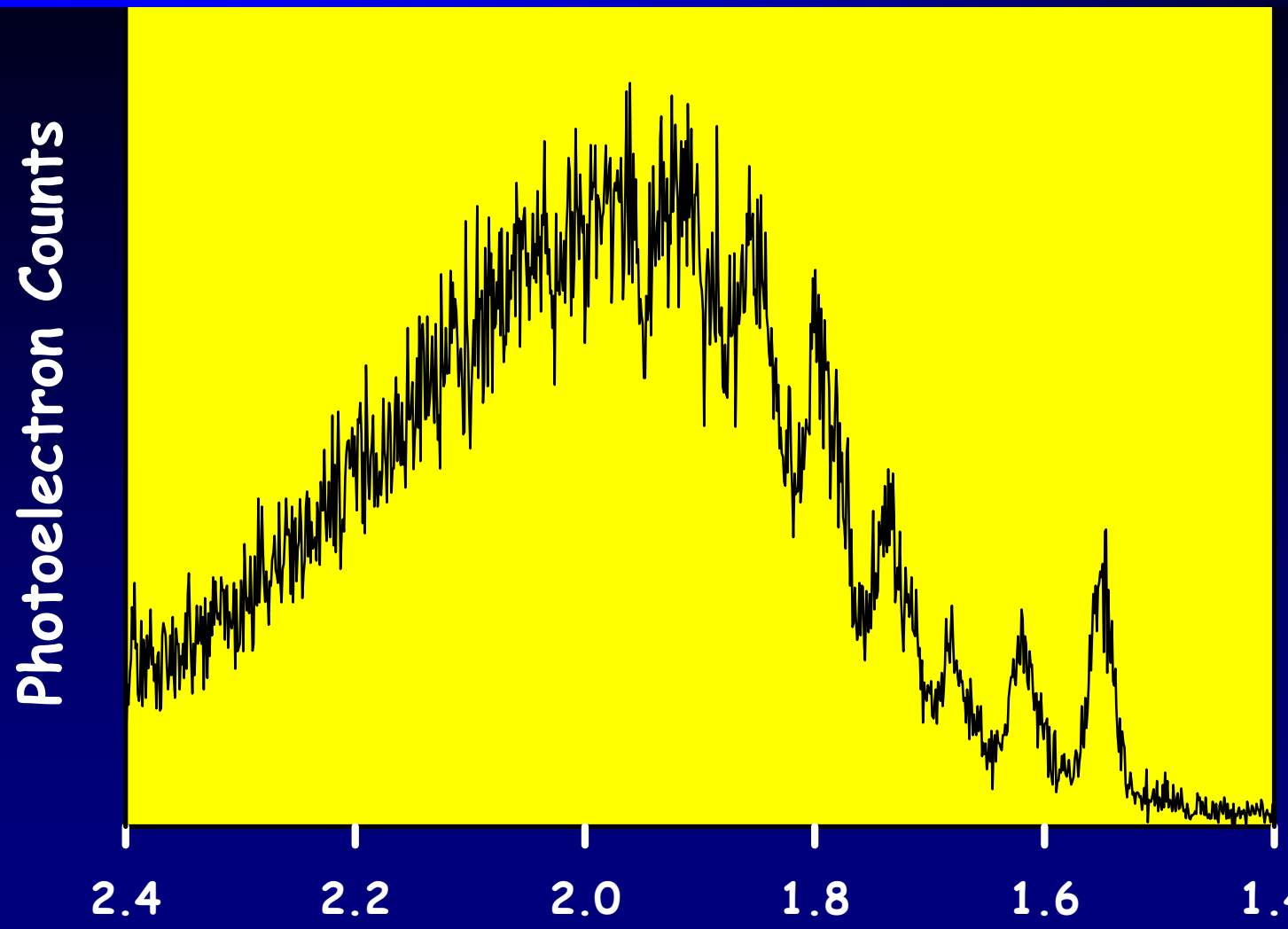
Both conformers are present



C5 attack also leads to ring opening

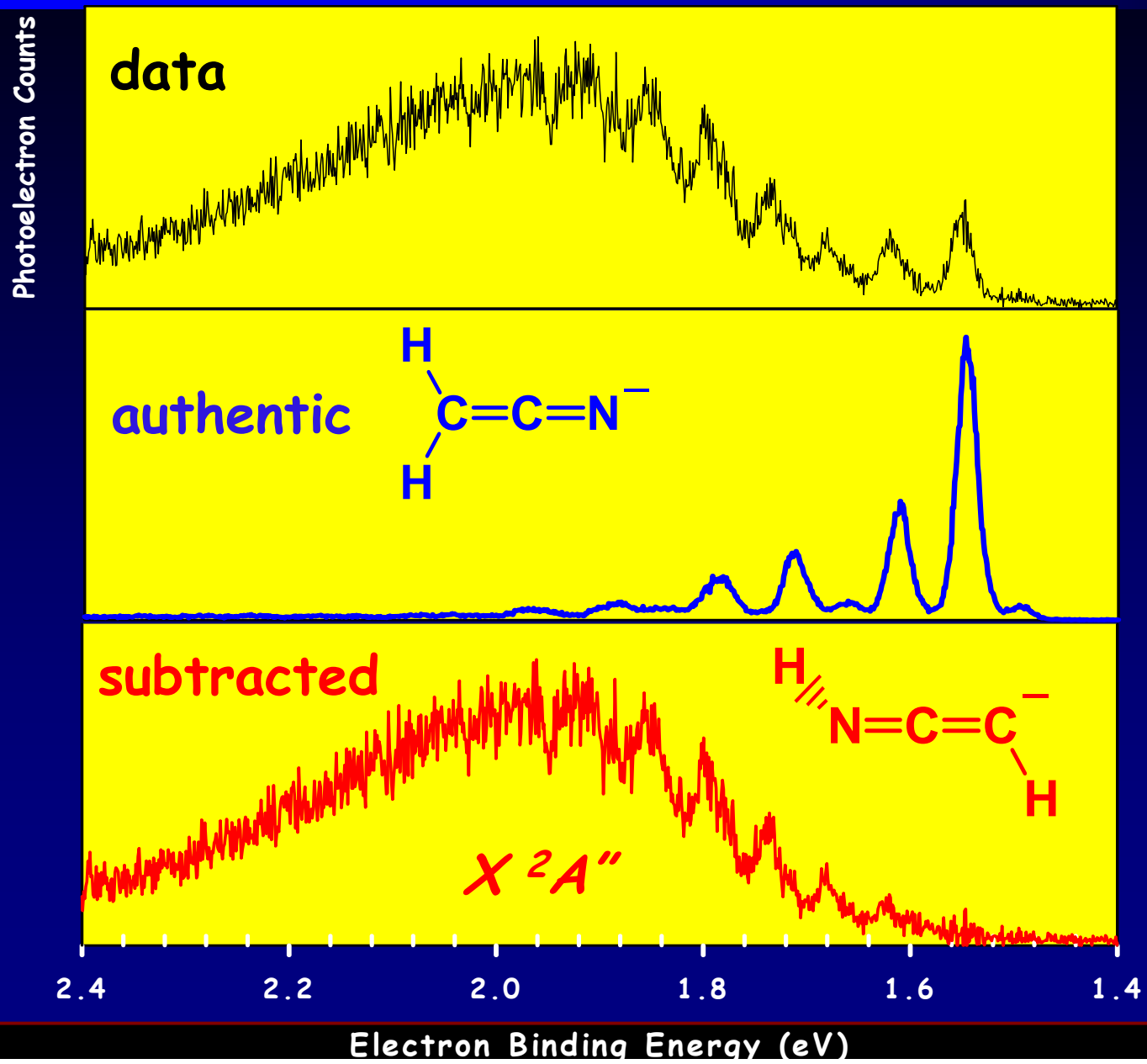


Improved m/e = 40 data



Very likely two species in spectrum. Try to model them.

Both m/e = 40 products are present



In Conclusion . . .

- The combination of flowing afterglow ion chemistry and anion photoelectron spectroscopy can provide unique data on the structure, energetics and reactions of highly unstable species.

- **HAPPY BIRTHDAY, KEN!!!!**