Institut für Ionenphysik and Angewandte Physik
Leopold-Franzens-Universität Innsbruck

Molecular data for biological applications

Interactions of electrons with molecules of biological relevance

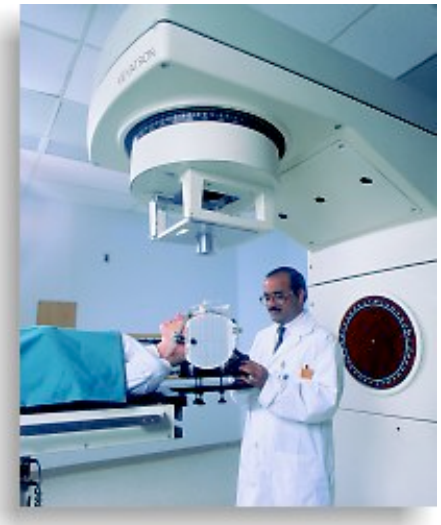
Verena Grill

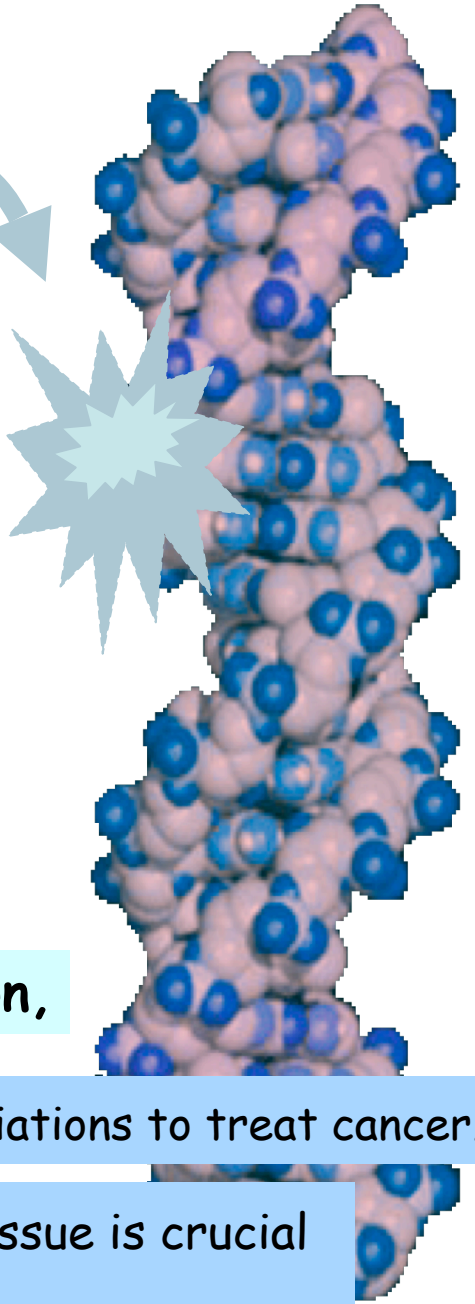
5th International Conference on Atomic and Molecular Data and Their Applications Meudon, France, Oktober 15-19, 2006

Outline

- Interactions of electrons with molecules of biological relevance:
  - Dissociative Electron Attachment (DEA) to nucleobases: site selectivity for hydrogen ablation (isolated in the gas phase, and –recently- in a cold helium matrix)
  - DEA to nitroaromatic compounds: site selectivity for NO_2^- ablation
  - Dissociative Electron Impact Ionization: appearance energy measurements for nucleobases, comparison of the absolute cross section for positive and negative ion formation.

Radiation





Ionizing radiation produces a variety of damage:

mutagenic

recombinogenic

and other lethal DNA lesion,

but **radiotherapy** benefits from the lethal properties of radiations to treat cancer.

►Understanding the mechanisms of radiation action on tissue is crucial for improving radiotherapy and estimating radiation risk.

DNA

A large number of secondary electrons with kinetic energies below about 20 eV are produced along the radiation track.

Electrons are efficient at transfering energy, i.e.

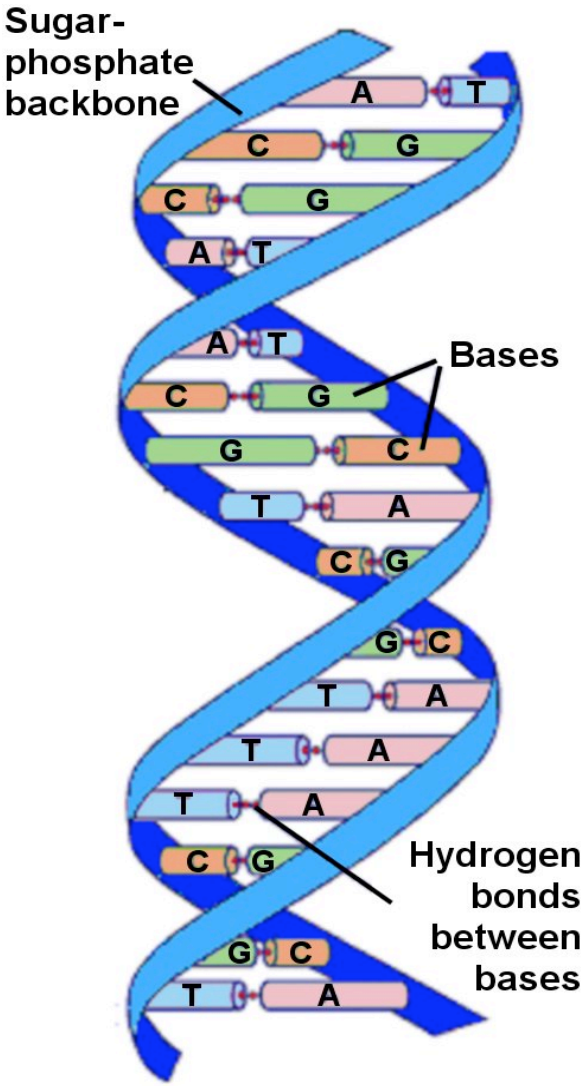
$$e + DNA/RNA \rightarrow DNA/RNA^{+} + 2e$$

$$e + DNA/RNA \rightarrow DNA/RNA^{*} + e$$

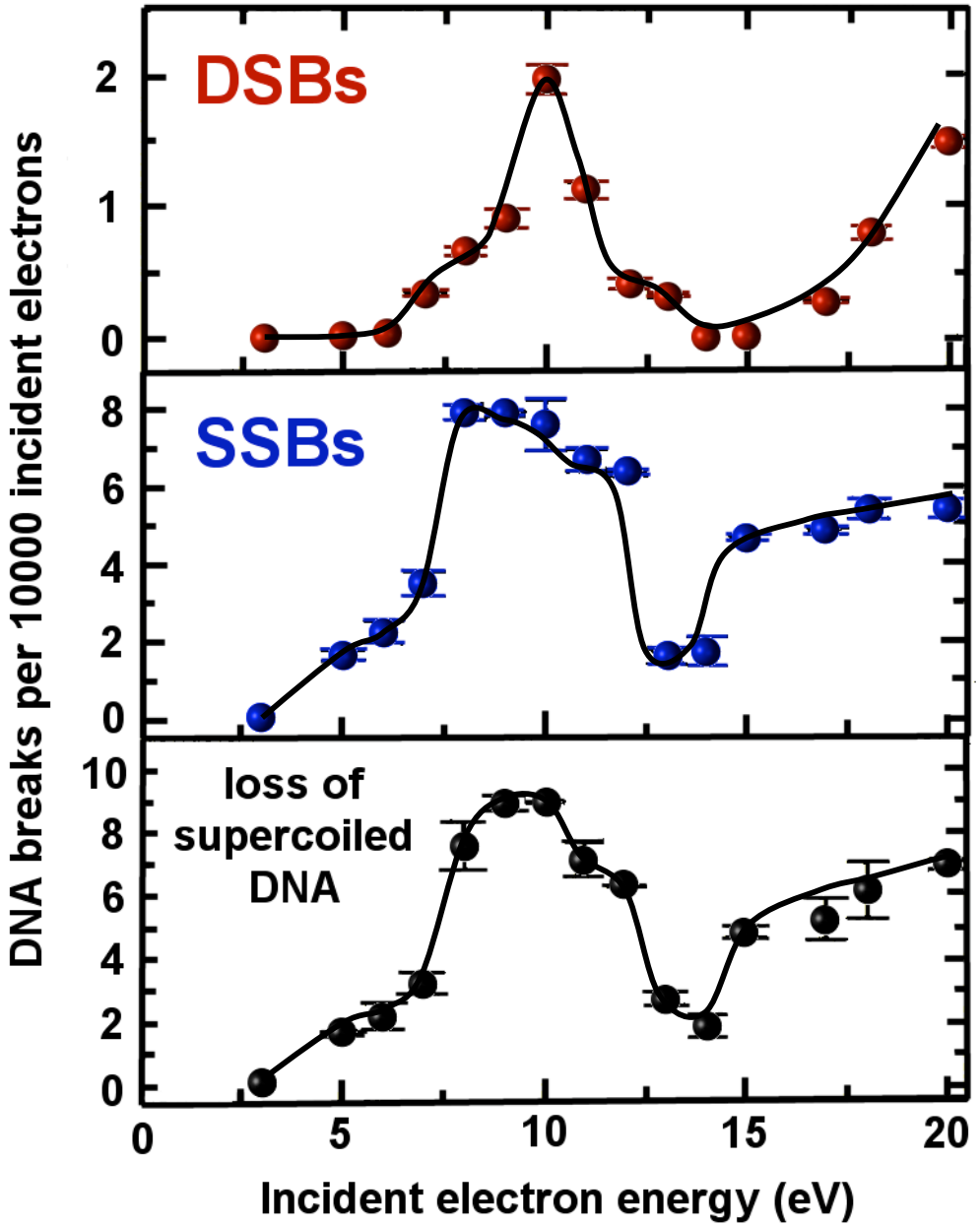
$$e + DNA/RNA \rightarrow DNA/RNA^{-}$$

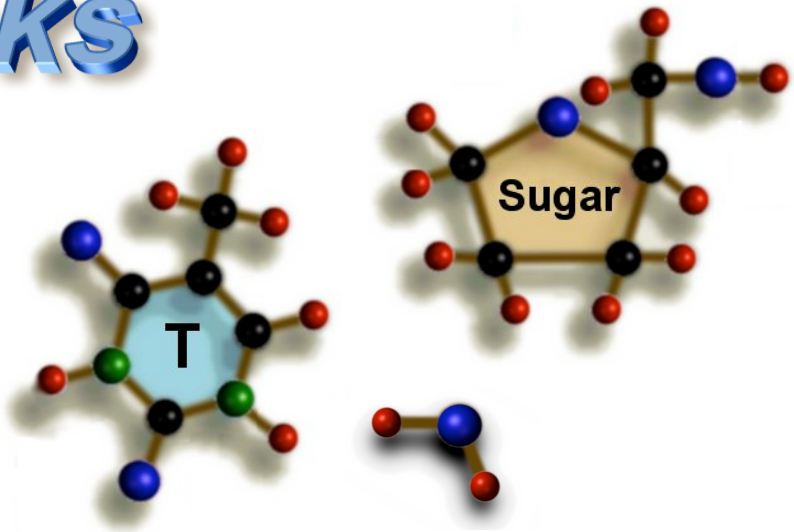
need to be considered.

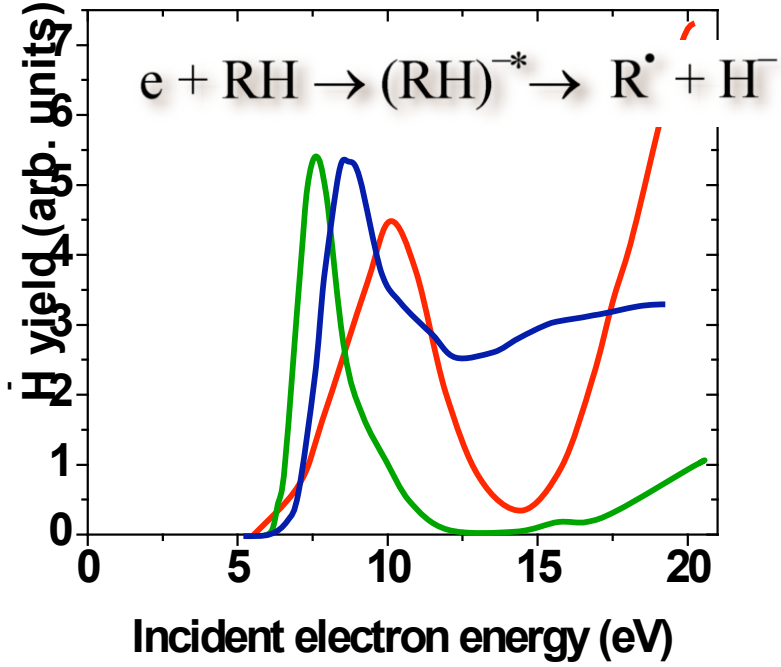
Single and double strand breaks may be induced by ***secondary species*** !



DNA-strand breaks







Sanche a.c. Science, 287 (2000) 1658

Interaction of low energy electrons

Formation of negative ions:

$e^- + AB \rightarrow (AB)^{-*}$ Transit negative ion (TNI)

$\rightarrow AB^-$

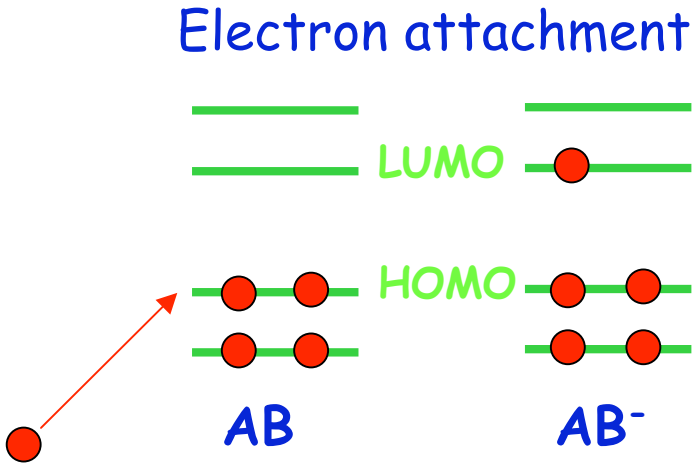
molecular anion

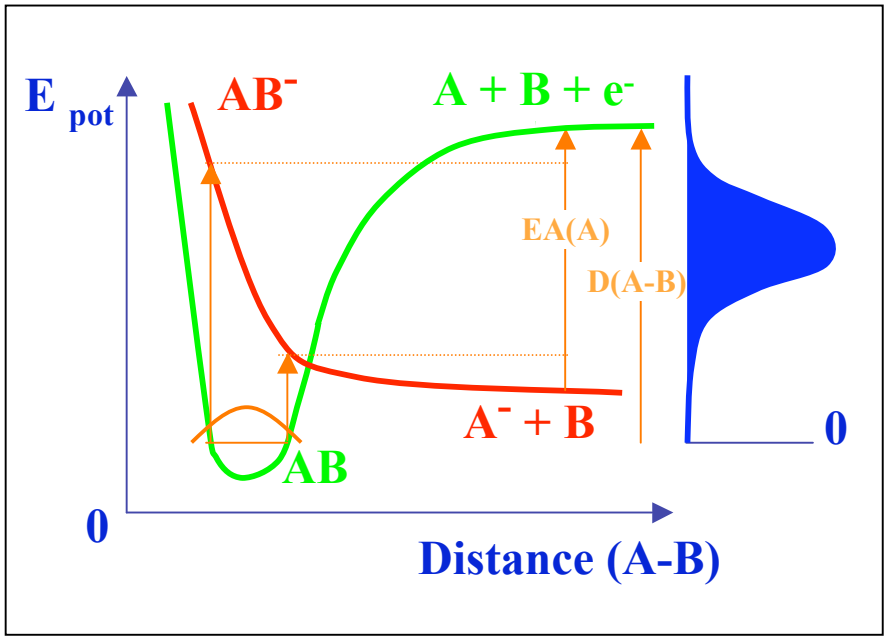
$\rightarrow AB + e^-$

autodetachment

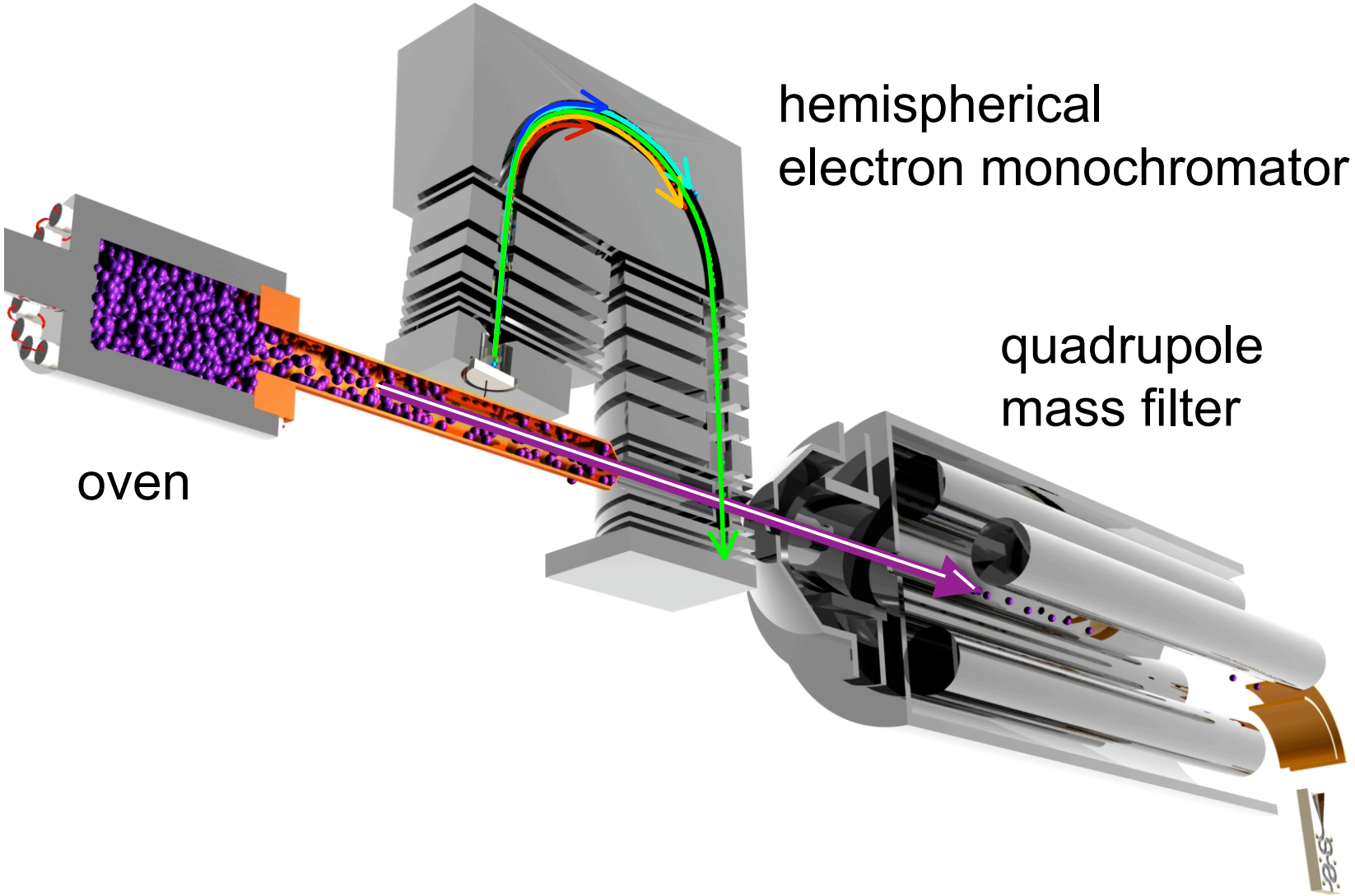
$\rightarrow A^- + B$

dissociative electron attachment (DEA)

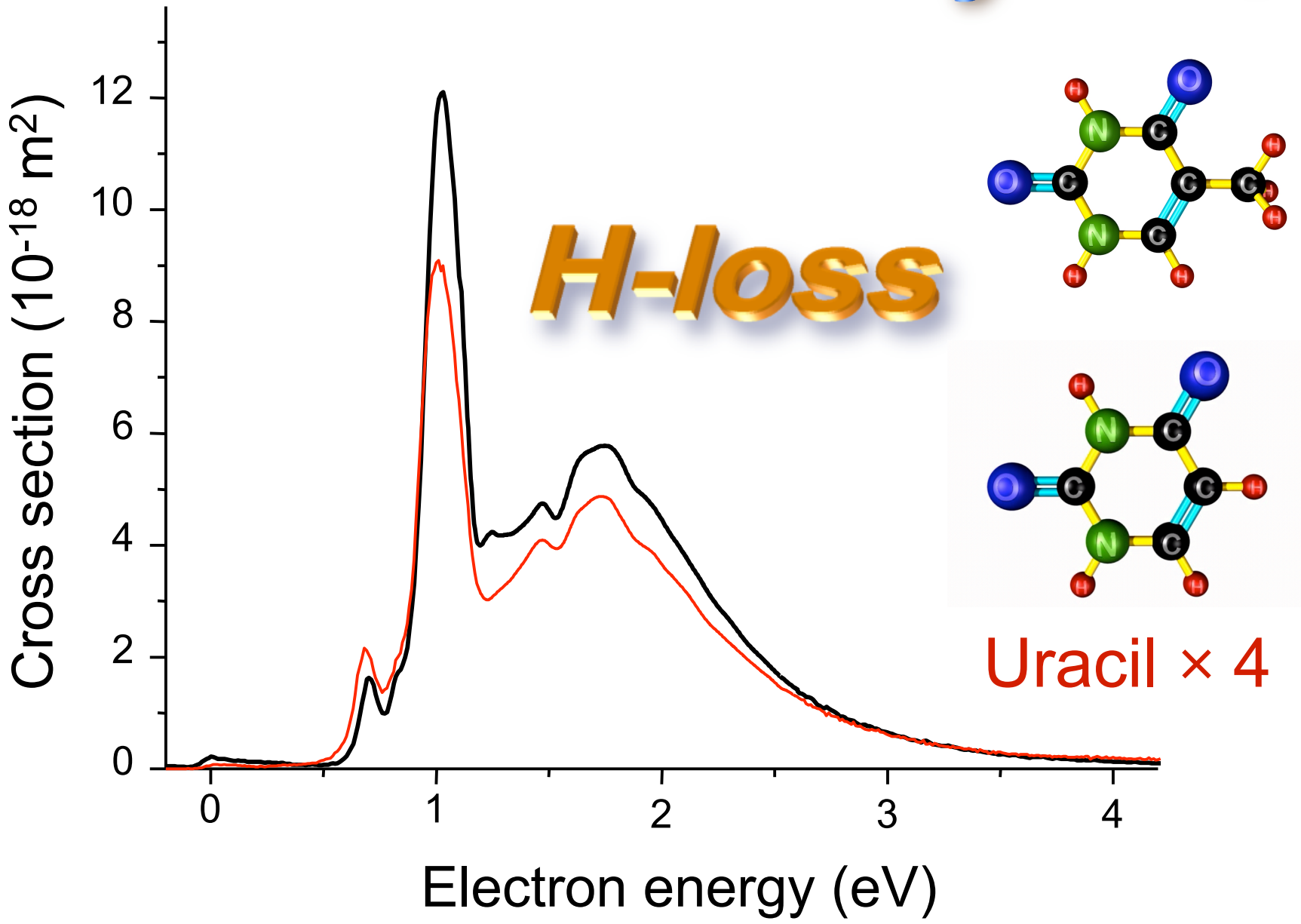




Apparatus


hemispherical
electron monochromator
quadrupole
mass filter
oven
channeltron SEM

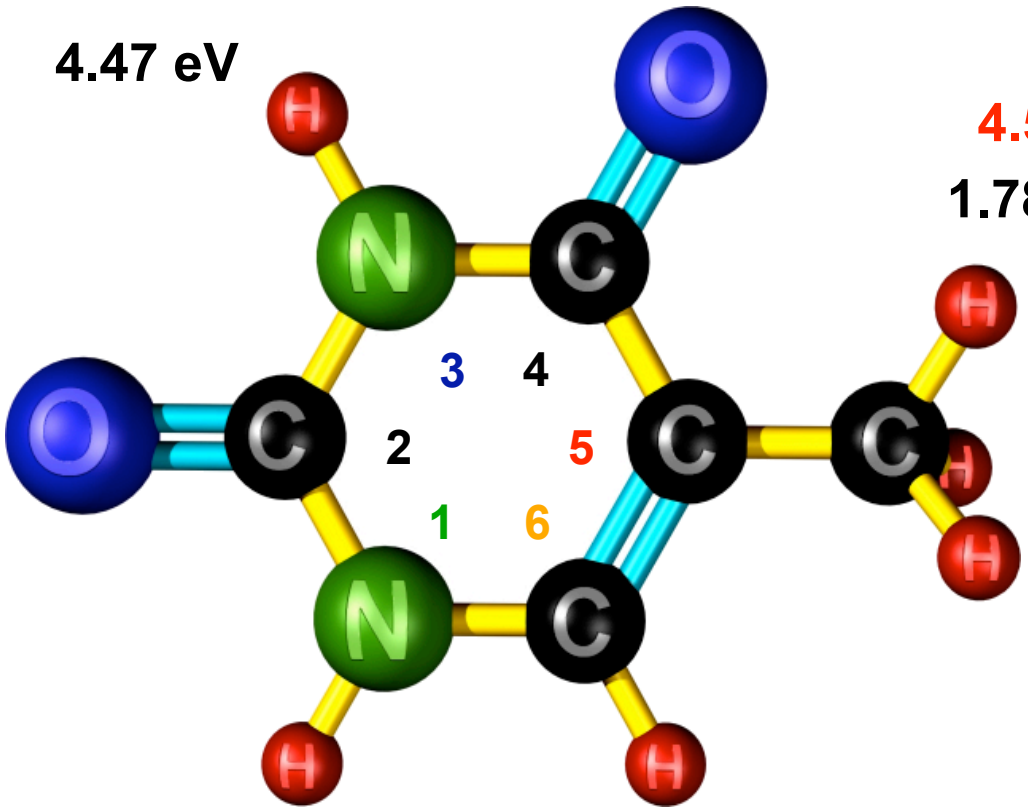
$T + e^- \rightarrow (T\text{-}H)^- + H$ Thymine



G2MP2 electron affinities of the 4 isomers of the ´Thymine minus´ radical

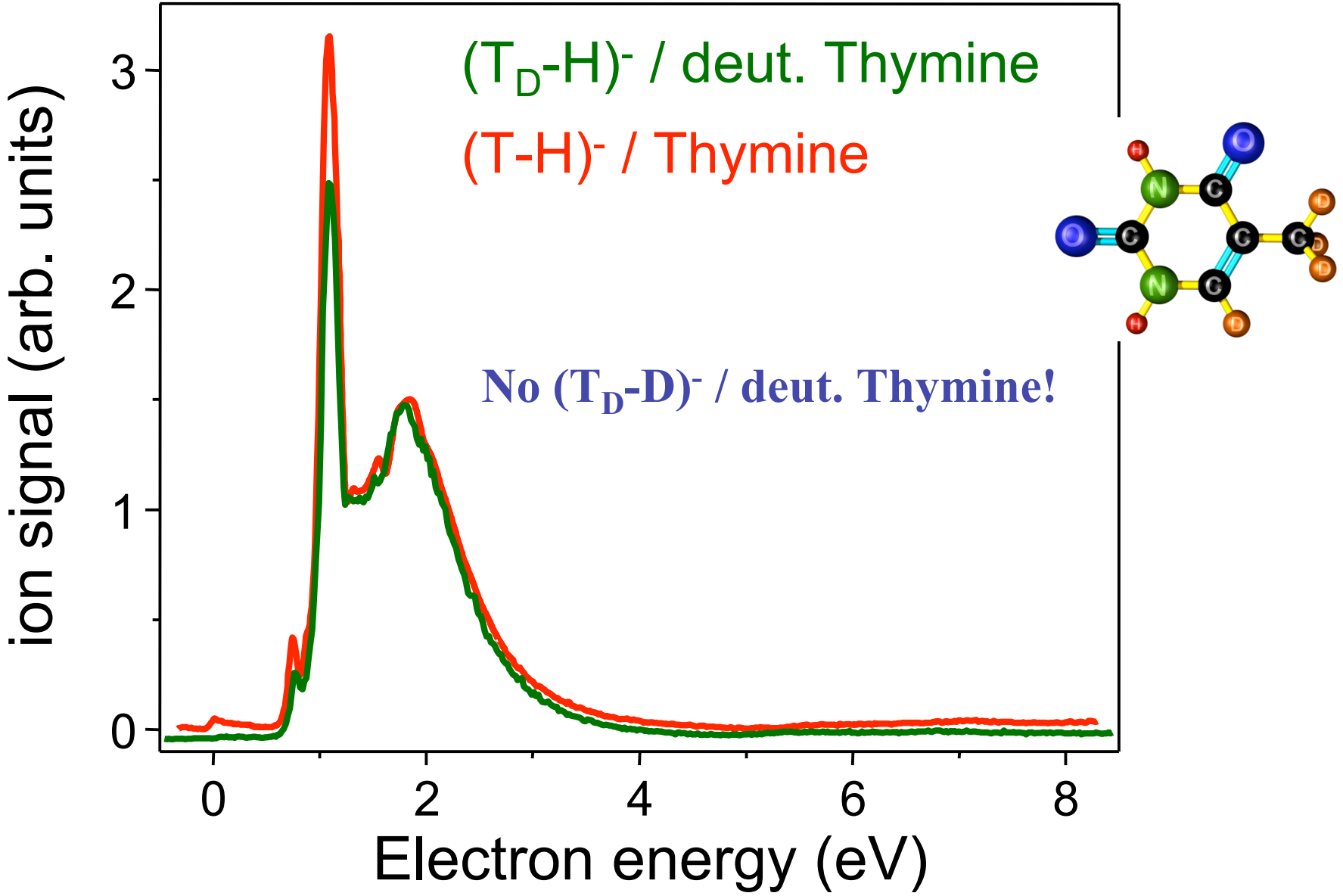
(positive values mean: formation of anion is exothermic)

binding energies of C-H and N-H bonds



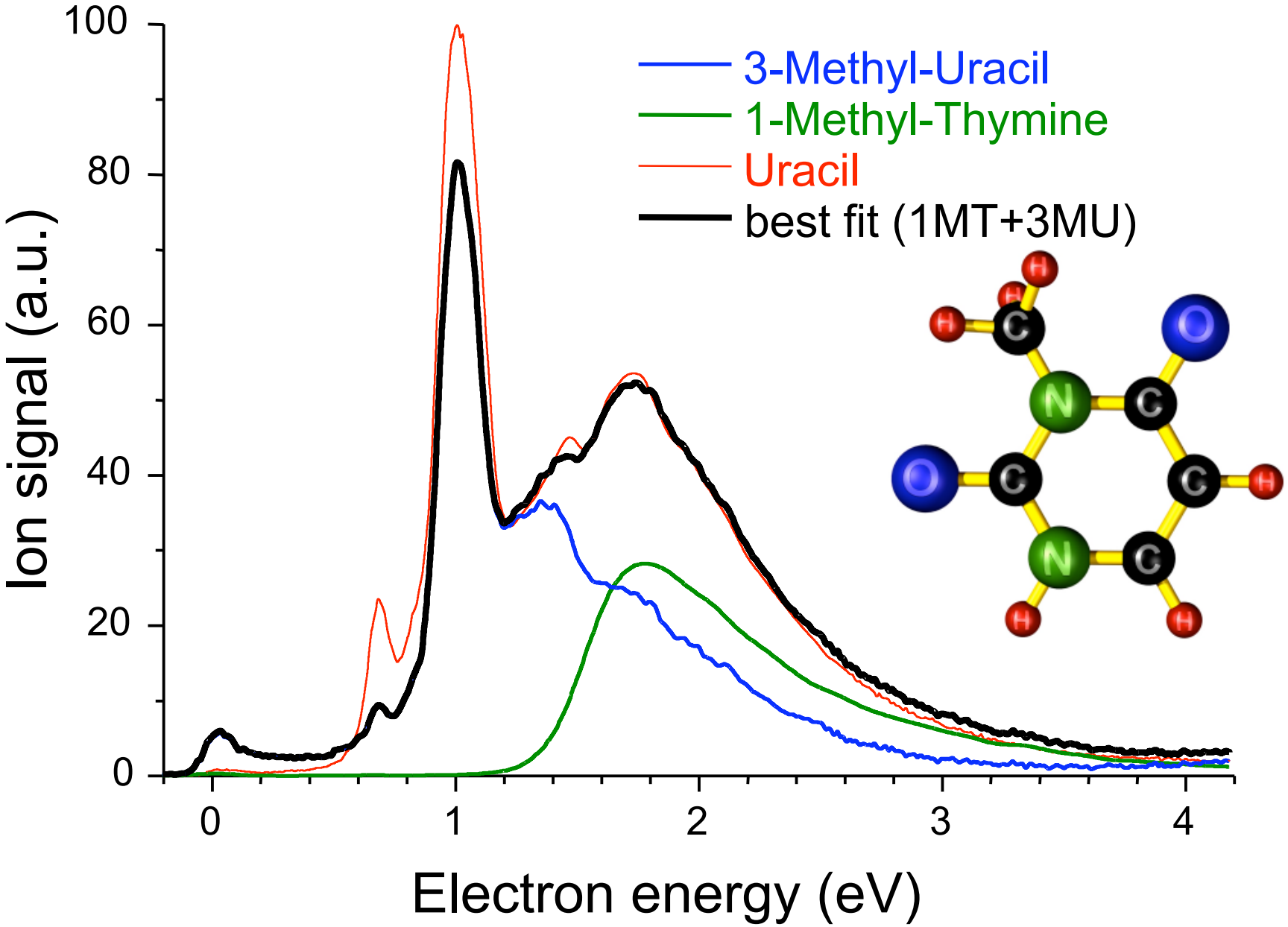
#	BE-EA (eV)
1	0.9
3	1.3
5	2.7
6	2.2

Partially deuterated thymine

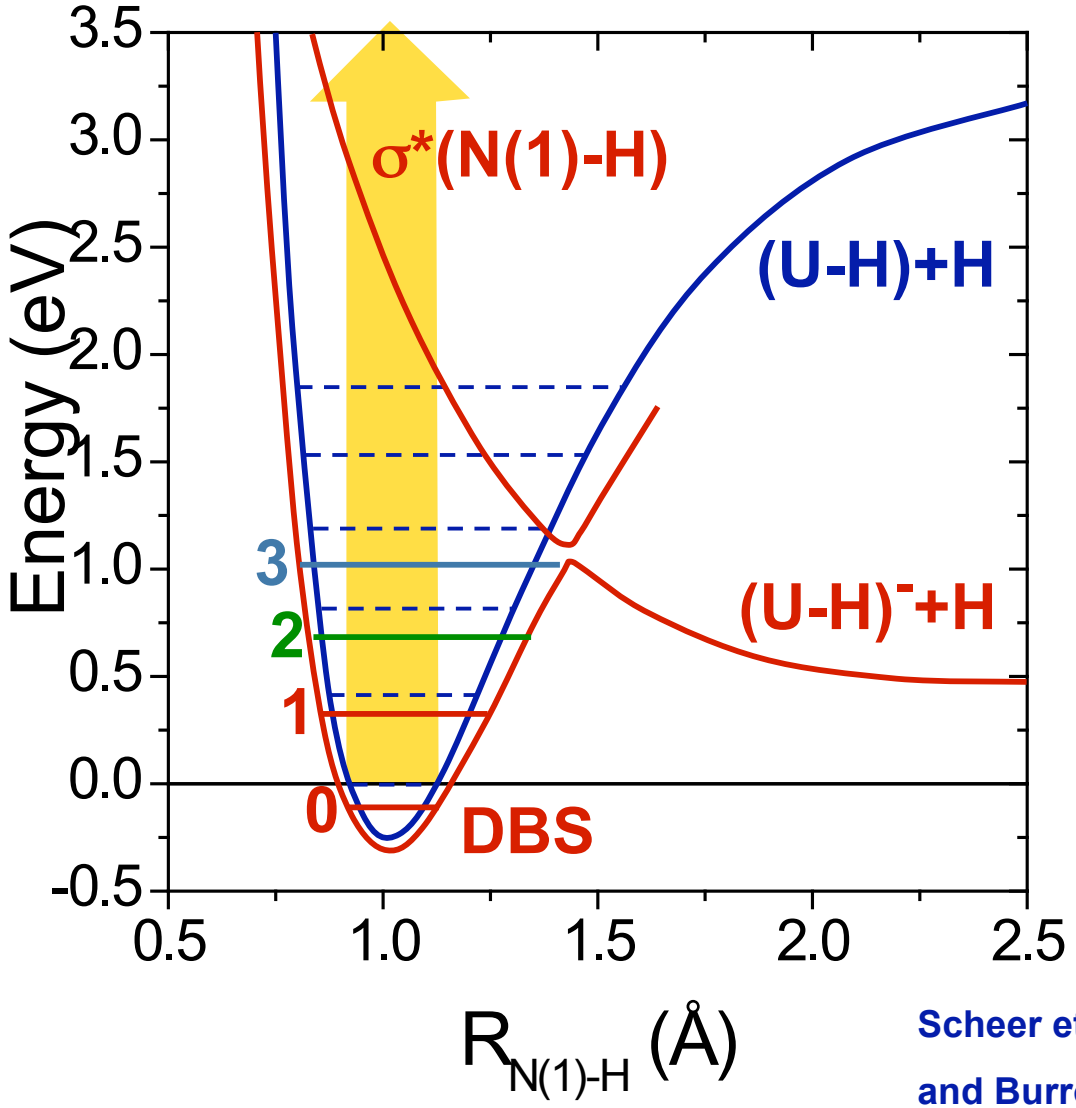


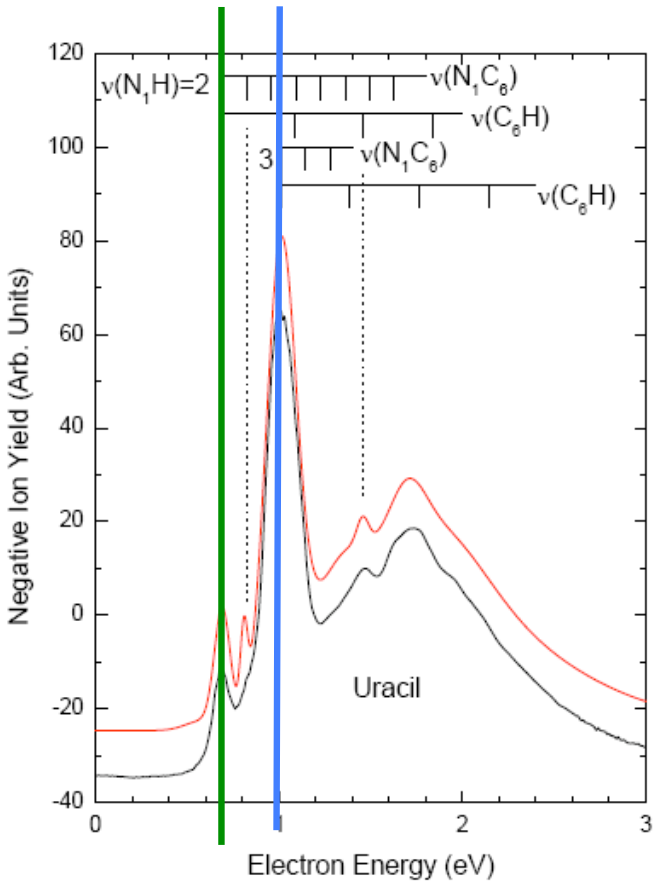
S. Ptasinska et al., *J. Chem. Phys.* 12/**123** (2005), 124302-8

S. Ptasinska et al. *Angew. Chem. Int. Ed.* 44 (2005) 6941



Vibrational structures

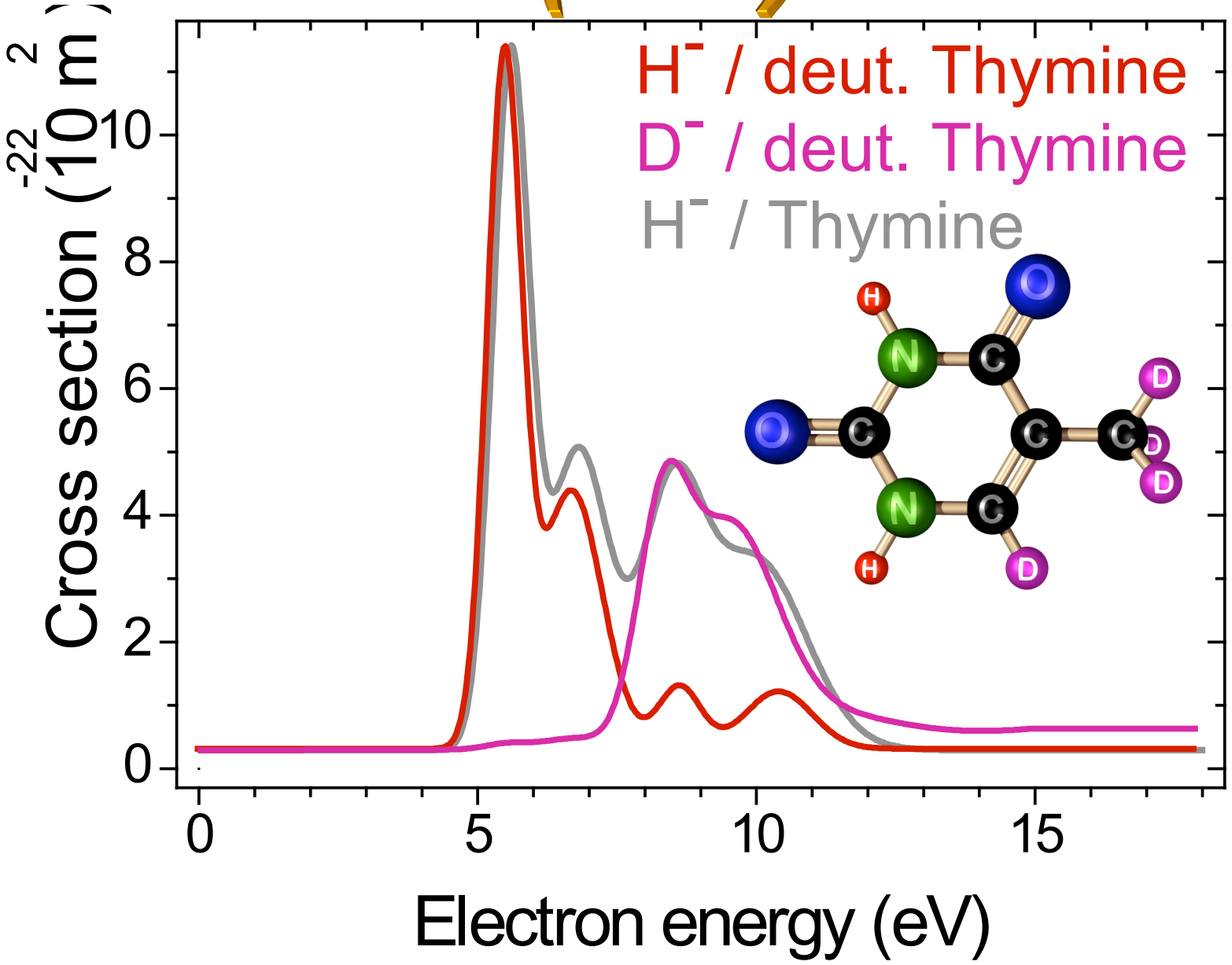




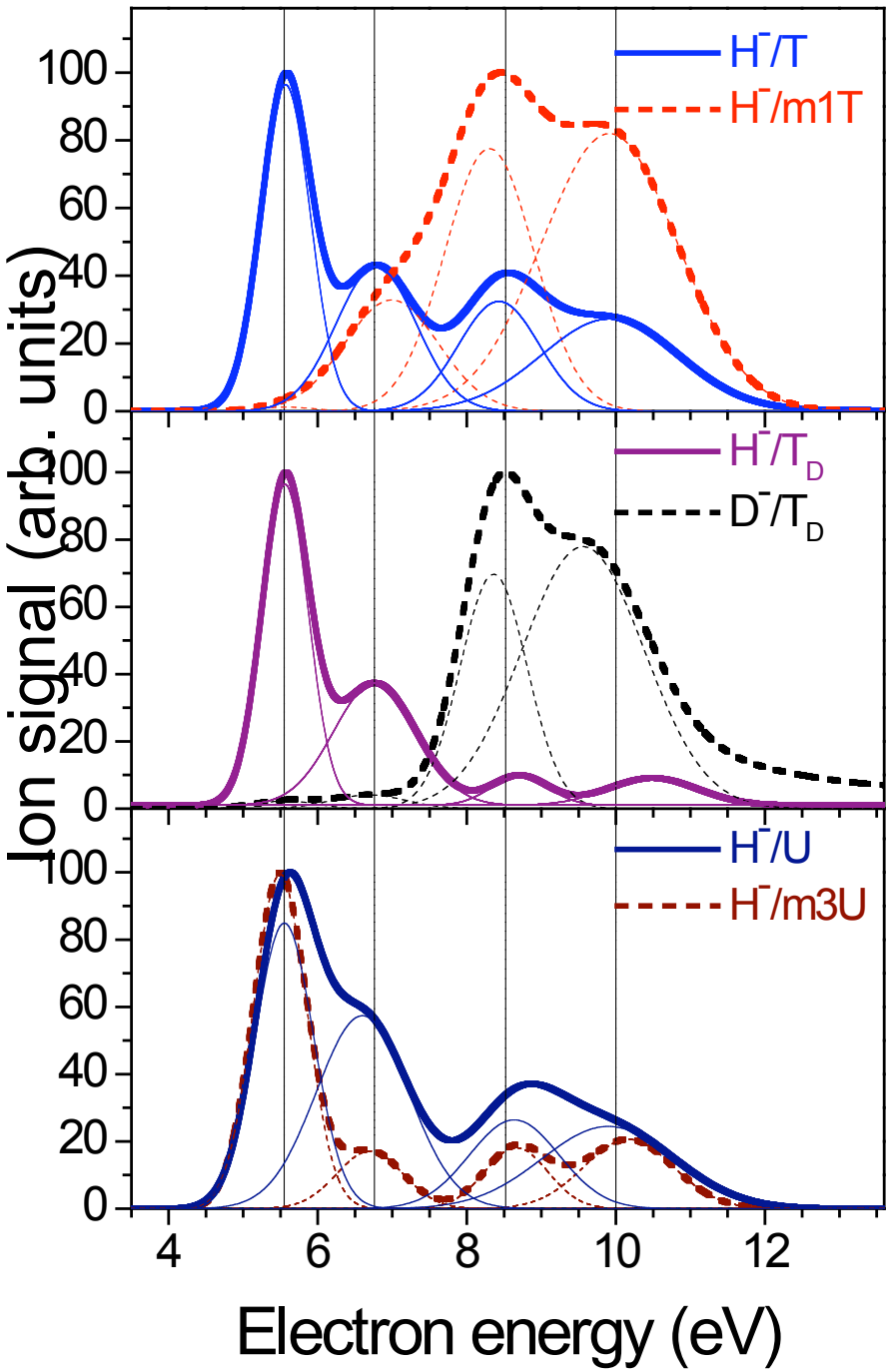
Scheer et al. PRL, 92 (2004) 068102

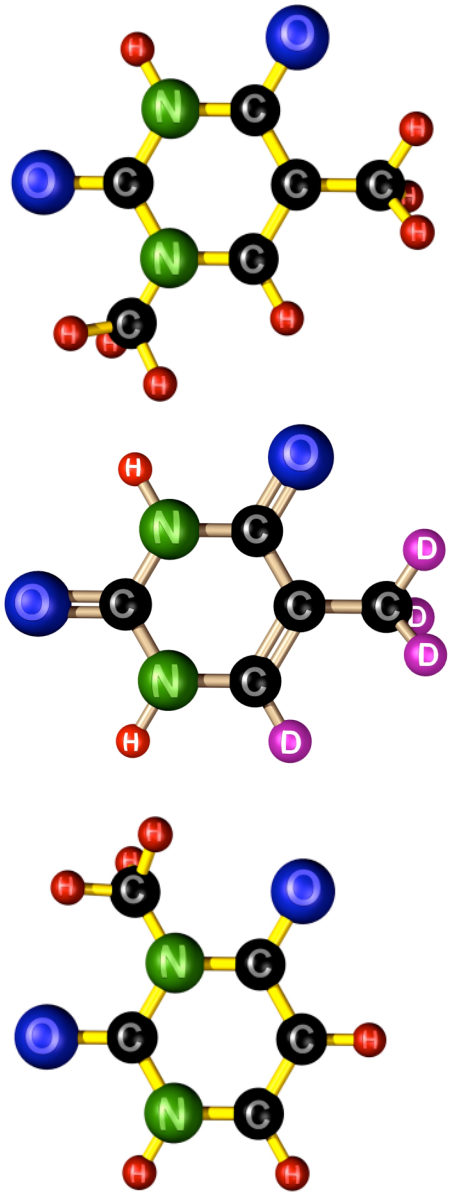
and Burrow et al. J. Chem. Phys. 124 (2006) 124310

$T + e^- \rightarrow H^- + (T\text{-}H)$

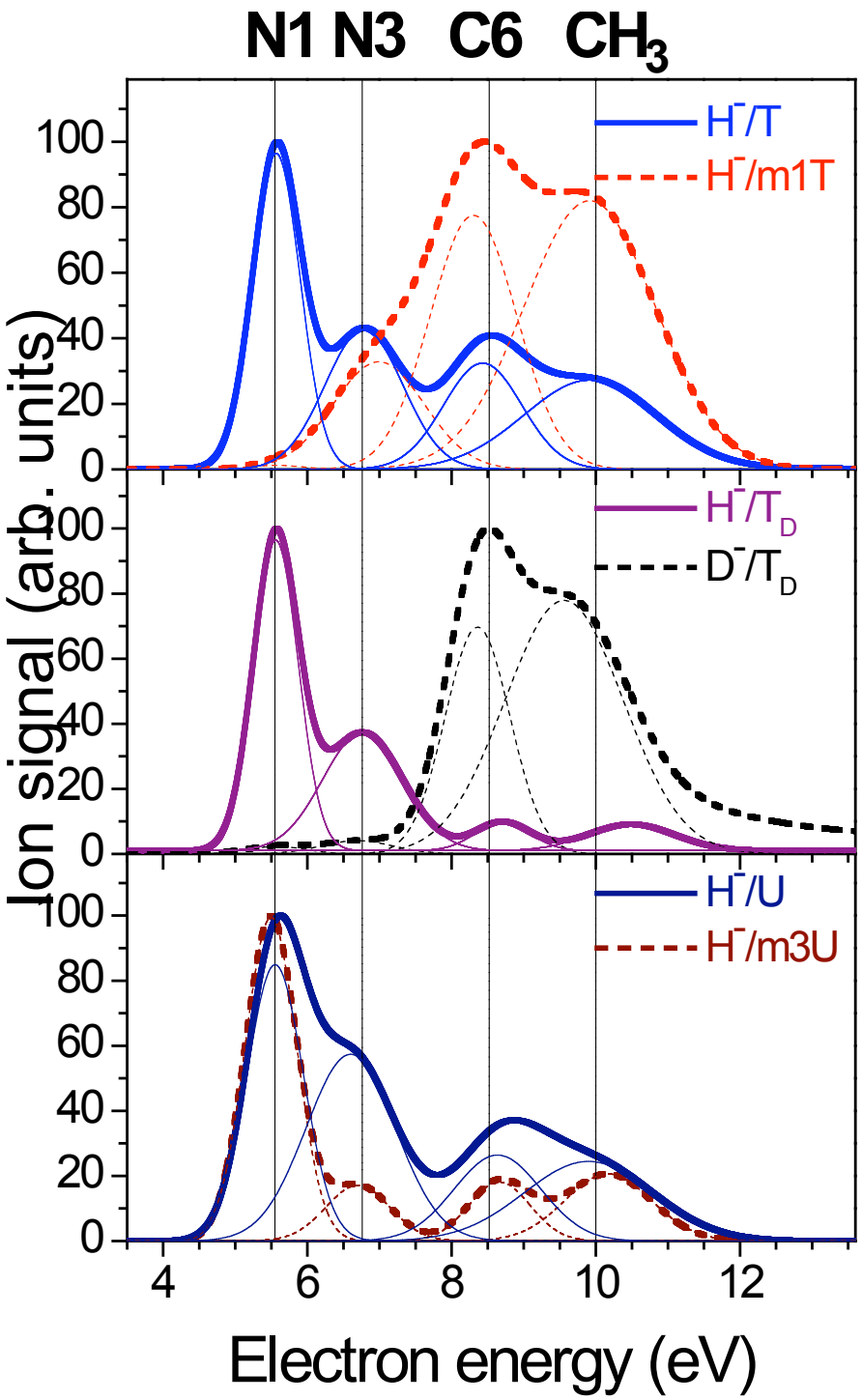


S. Ptasinska et al. *Angew. Chem. Int. Ed.* **44** (2005) 1647





S. Ptasinska et al. *Phys. Rev. Lett.* **95** (2005) 093201



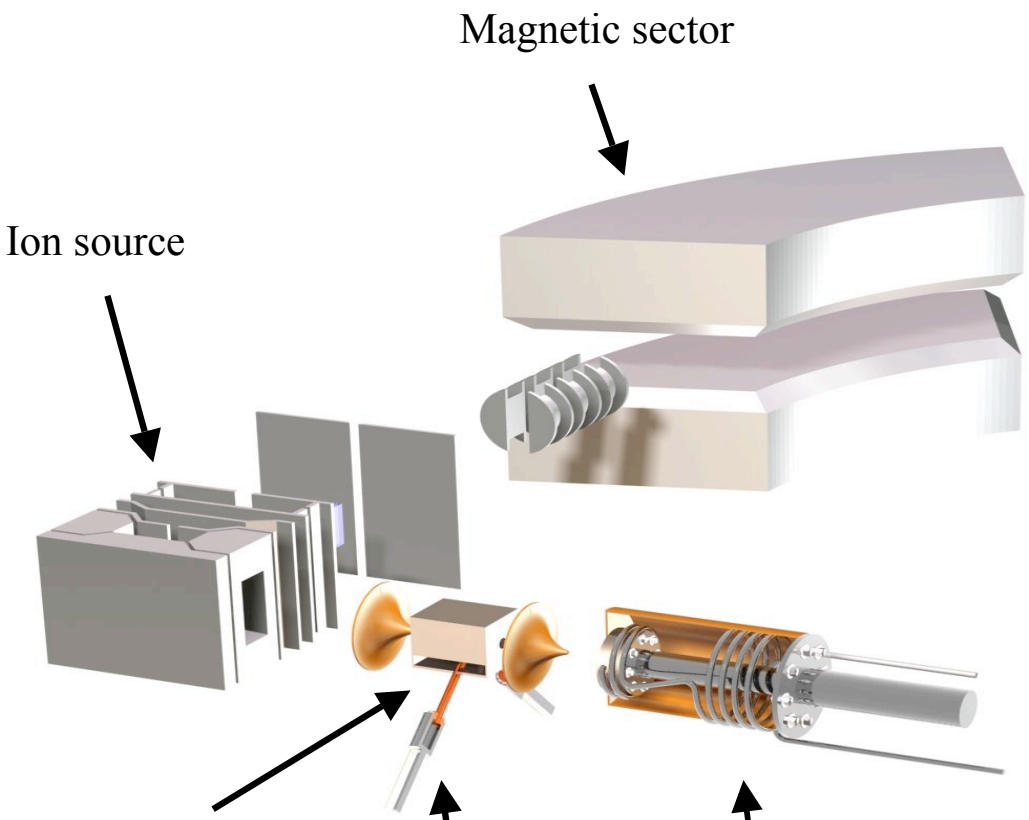
- All anions have 4 common resonances that have the same position and width
- The resonance at 5.5 eV leads exclusively to H^- loss from the N1 position
- The 6.8 eV resonance leads to loss from N3
- At 8.5 and 10 eV H^- loss from C positions whereas CH_3 groups contribute mainly to the 10 eV peak.

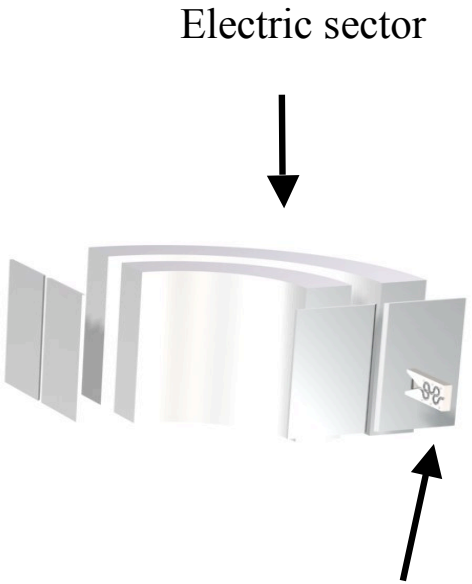
S. Ptasinska et al. *Phys. Rev. Lett.* **95** (2005) 093201

Thymine pickup by He

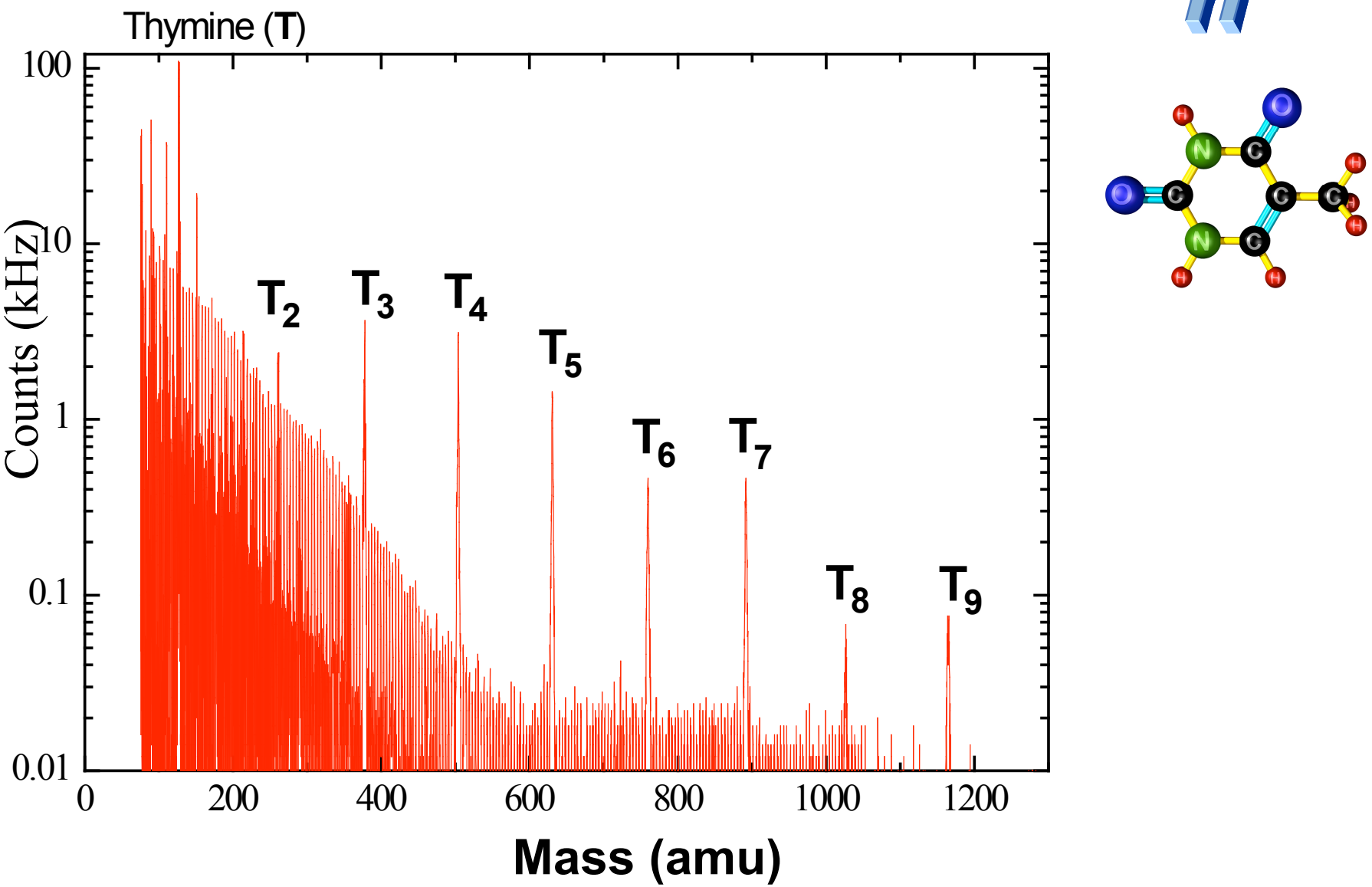
- Interactions of electrons with molecules of biological relevance:
  - Dissociative Electron Attachment (DEA) to nucleobases: site selectivity for hydrogen ablation (isolated in the gas phase, and –recently- in a cold helium matrix)
  - DEA to nitroaromatic compounds: site selectivity for NO_2^- ablation
  - Dissociative Electron Impact Ionization: appearance energy measurements for nucleobases, comparison of the absolute cross section for positive and negative ion formation.

Apparatus


Magnetic sector
Ion source
Pick-up cell
Oven
T ≈ 420 K
Helium cluster source
10-15 bar
10 K
N ≈ 10^4

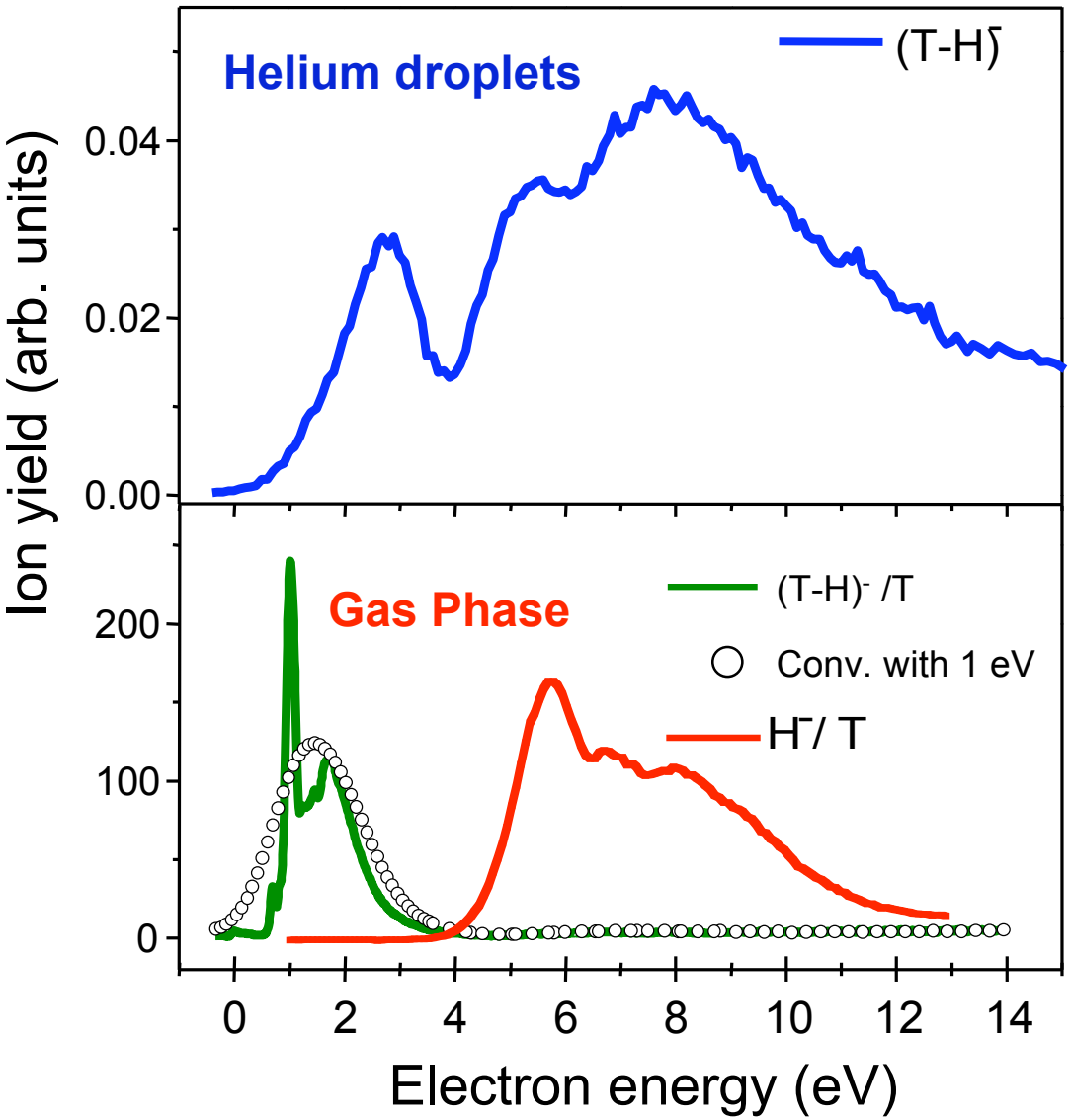

Electric sector
Channeltron

Thymine pickup by He_n

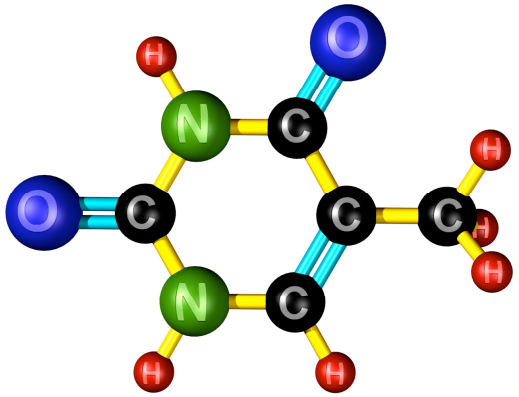


Electron energy: 150 eV

Thymine pickup by He_n



$(T\text{-}H)^-$ /T

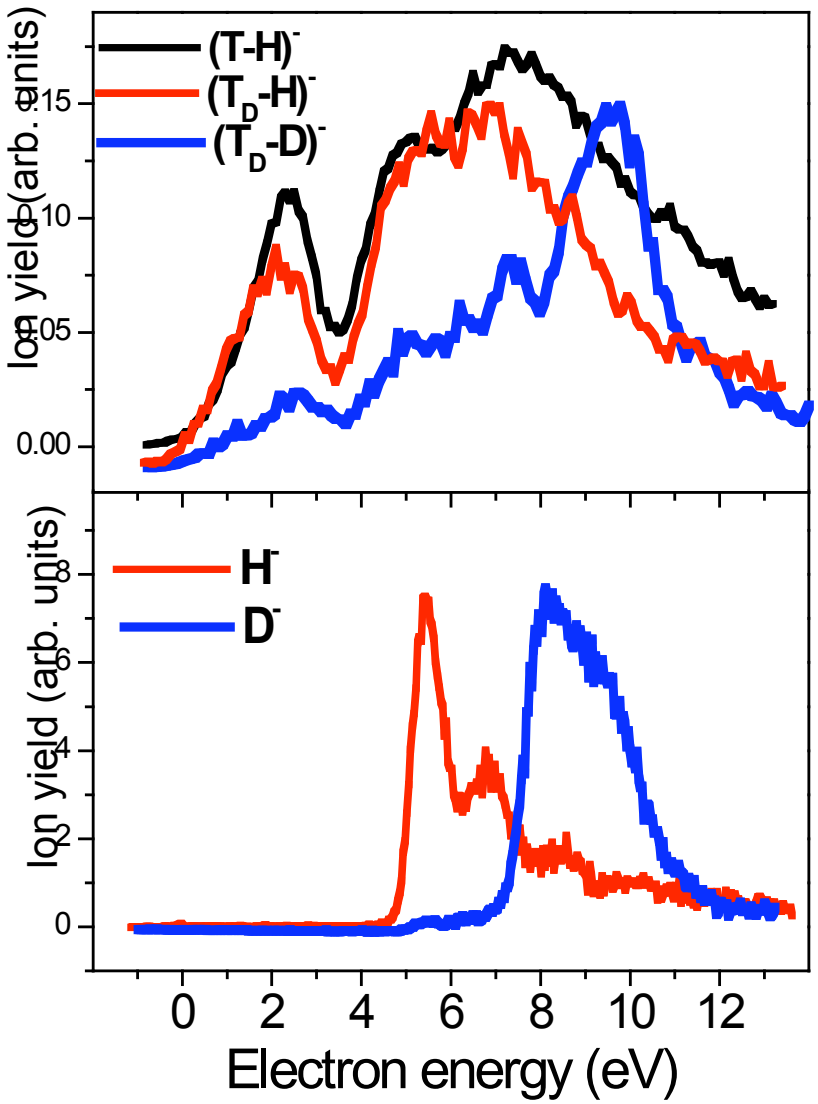


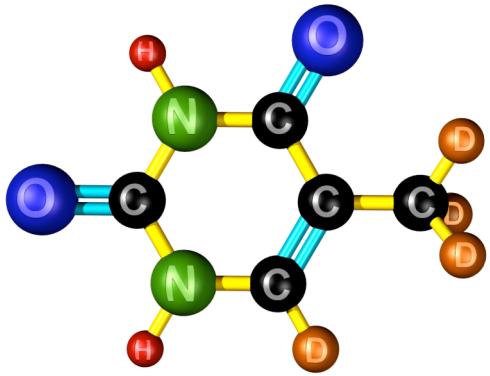
Electron transfer reaction

$e + T \leftrightarrow (T)^{-*} \rightarrow H^- + (T\text{-}H)^{\bullet}$

$H^- + (T\text{-}H)^{\bullet} \rightarrow (T\text{-}H)^- + H^{\bullet}$

Part. deuterated Thymine pickup by He_n



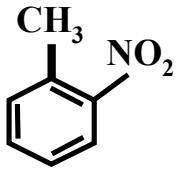


DEA to nitroaromatic compounds

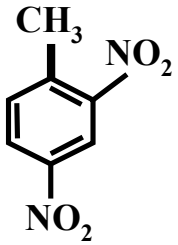
- Interactions of electrons with molecules of biological relevance:
  - Dissociative Electron Attachment (DEA) to nucleobases: site selectivity for hydrogen ablation (isolated in the gas phase, and –recently- in a cold helium matrix)
  - DEA to nitroaromatic compounds: site selectivity for NO_2^- ablation
  - Dissociative Electron Impact Ionization: appearance energy measurements for nucleobases, comparison of the absolute cross section for positive and negative ion formation.

DEA to nitroaromatic compounds

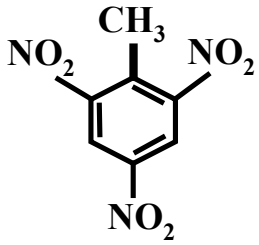
2-Nitrotoluene



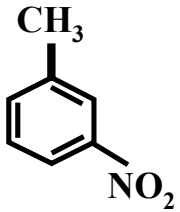
2,4-Dinitrotoluene (DNT)



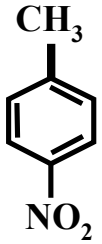
2,4,6-Trinitrotoluene (TNT)



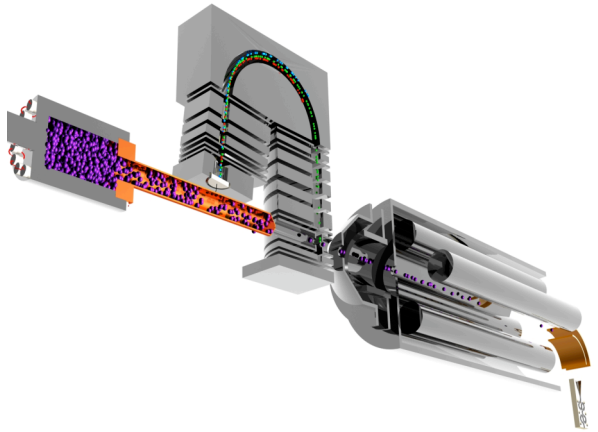
3-Nitrotoluene



4-Nitrotoluene



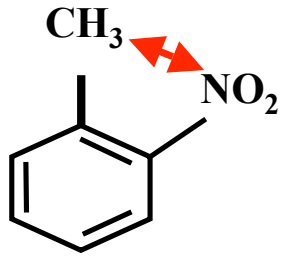
Apparatus

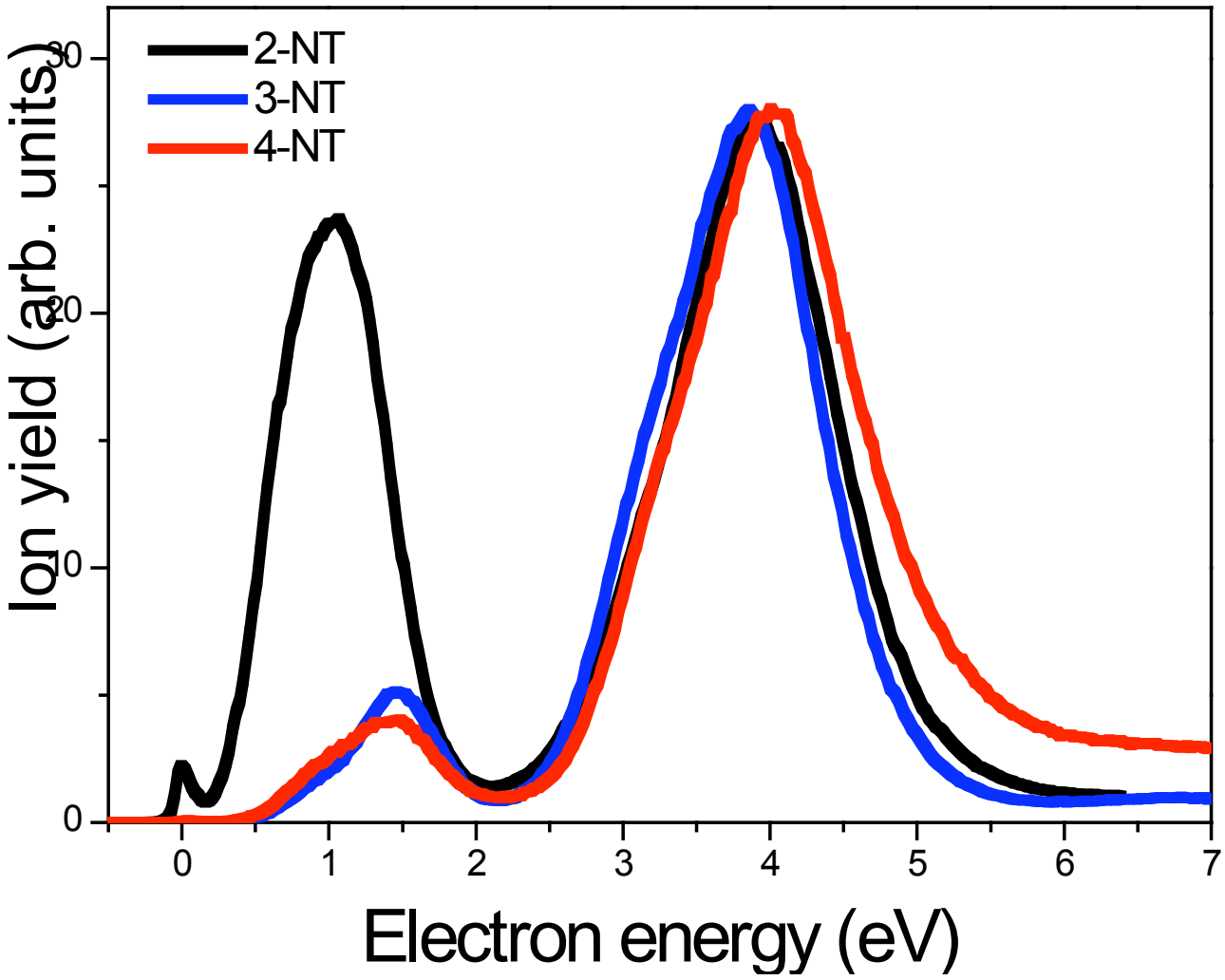


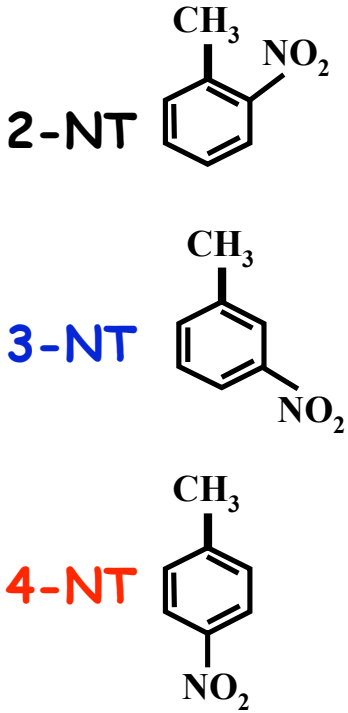
Nitrotoluenes

NO_2^- formation

$$NT + e^- \rightarrow NO_2^- + (NT\text{-}NO_2)$$





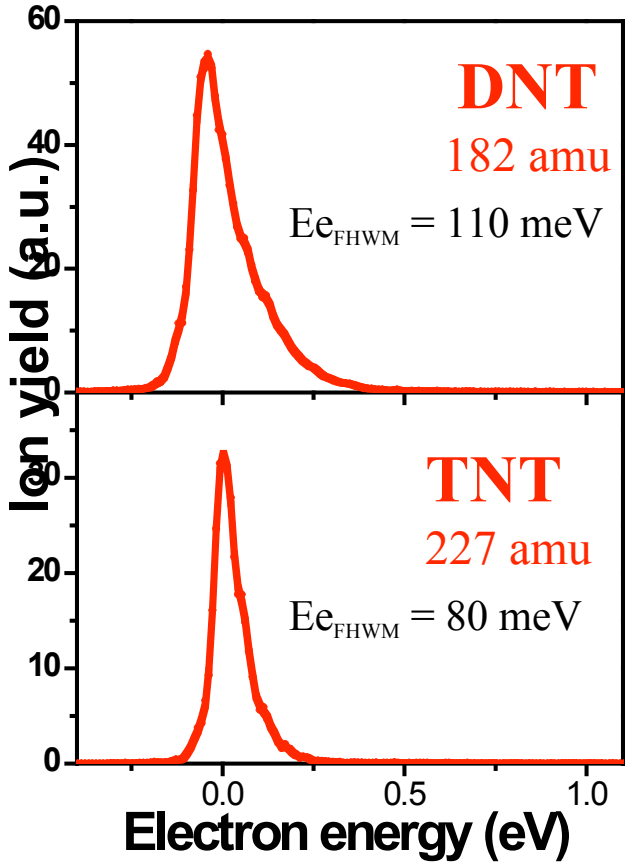


Di- and Trinitrotoluenes

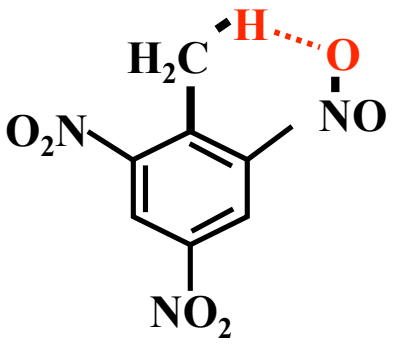
Negative ion formation

TNT + e⁻ → TNT⁻

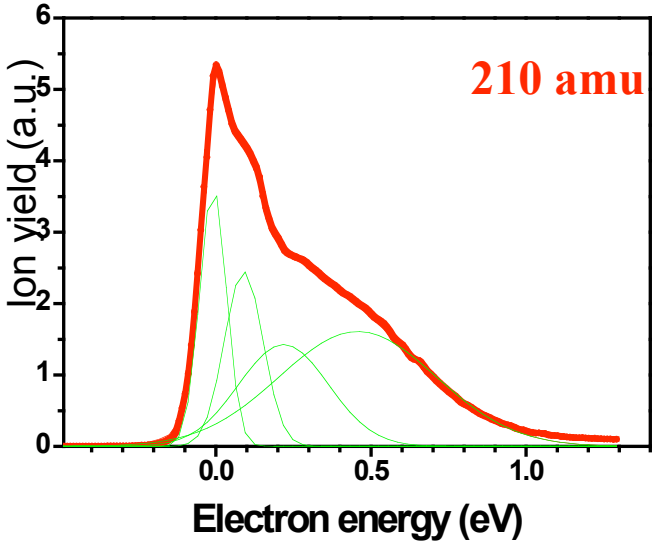
molecular anion



TNT + e⁻ → (TNT-OH)⁻ + OH•



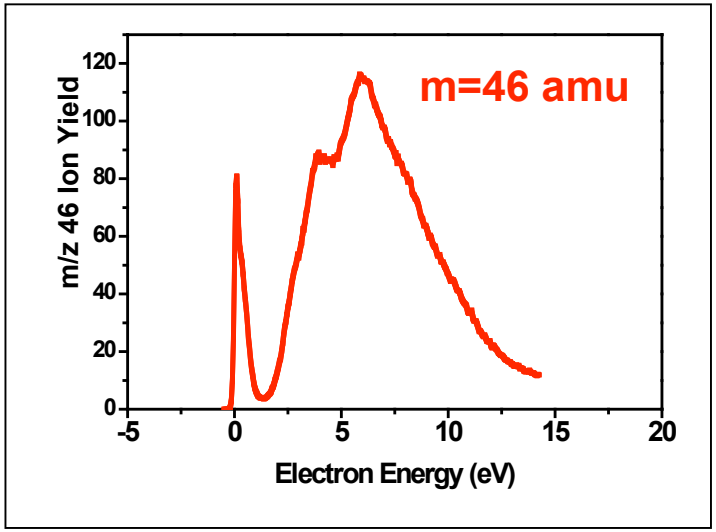
Hydroxyl radical



Trinitrotoluenes

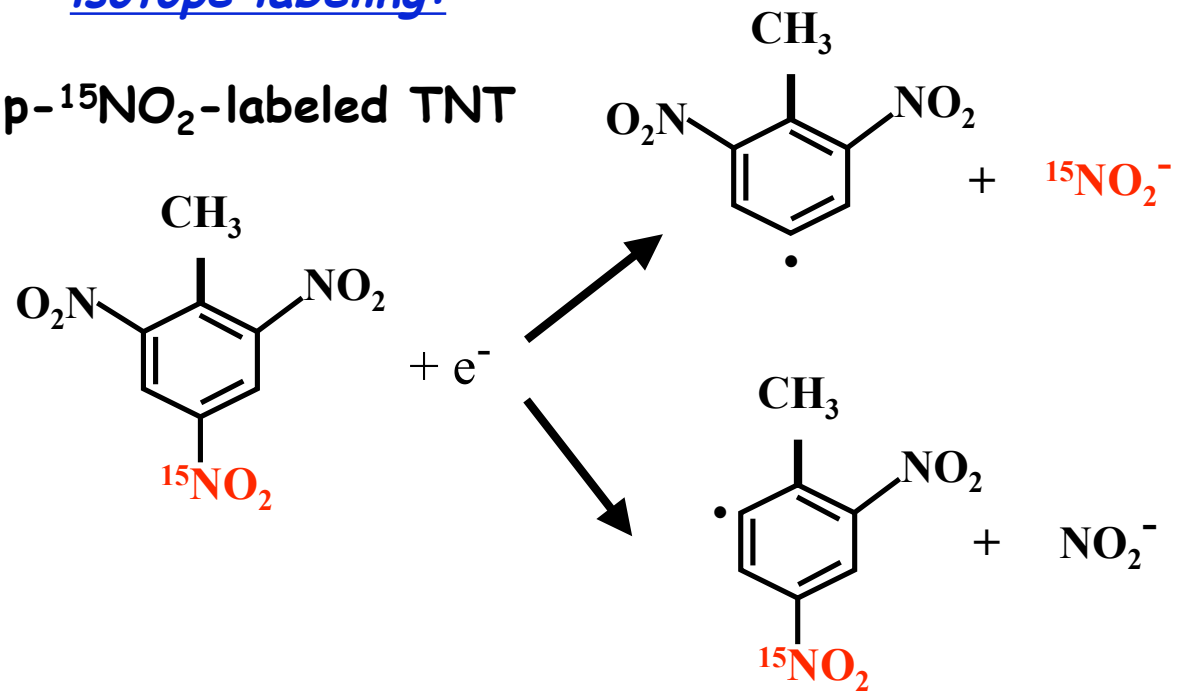
NO_2^- formation

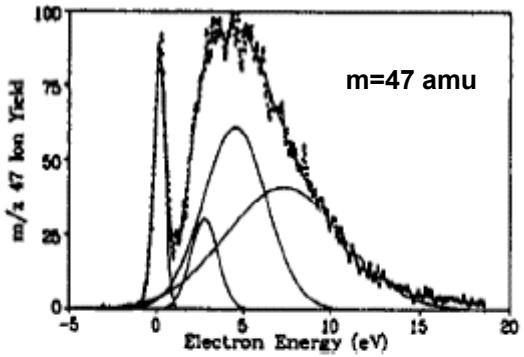
$$TNT + e^- \rightarrow (TNT\text{-}NO_2) + NO_2^-$$

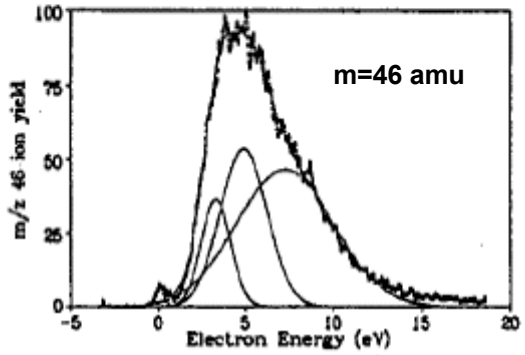


isotope labeling:

p-$^{15}NO_2$-labeled TNT

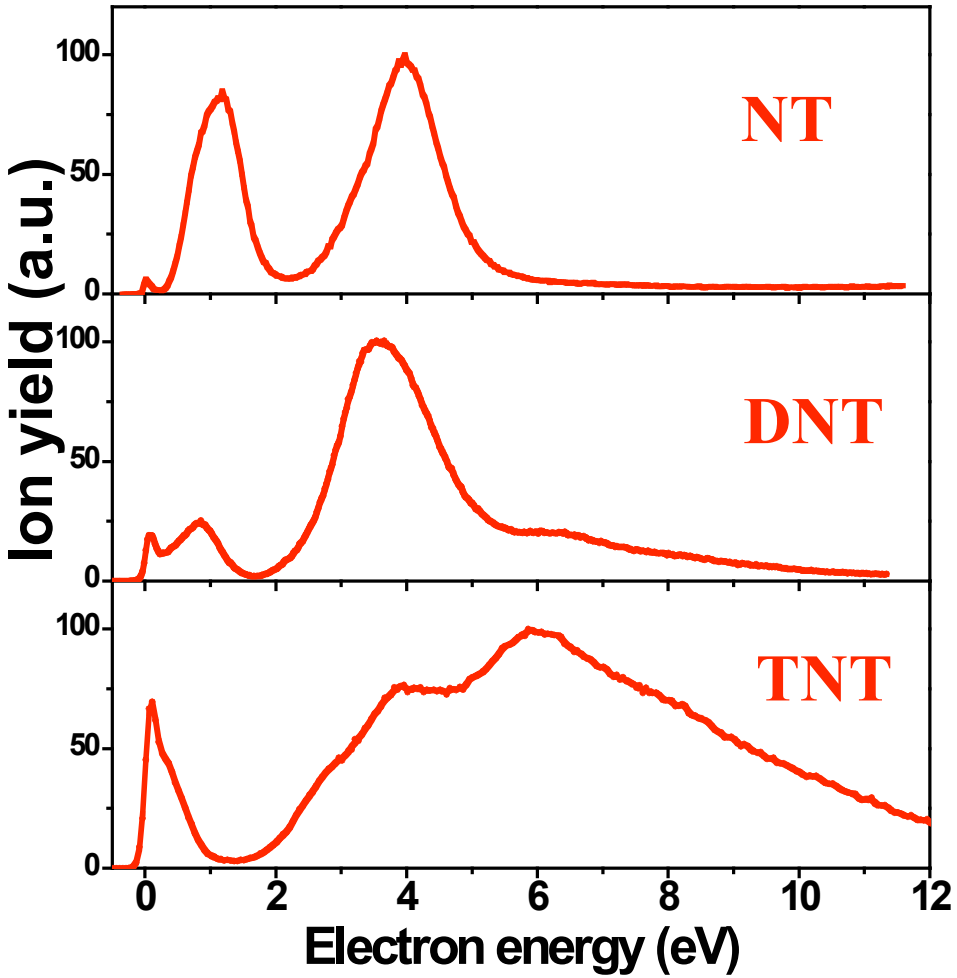






J.A. Laramée and M.L. Deinzer, Anal. Chem. 66, 719 (1994)

NO_2^- formation



Today's challenge is early detection of explosives!

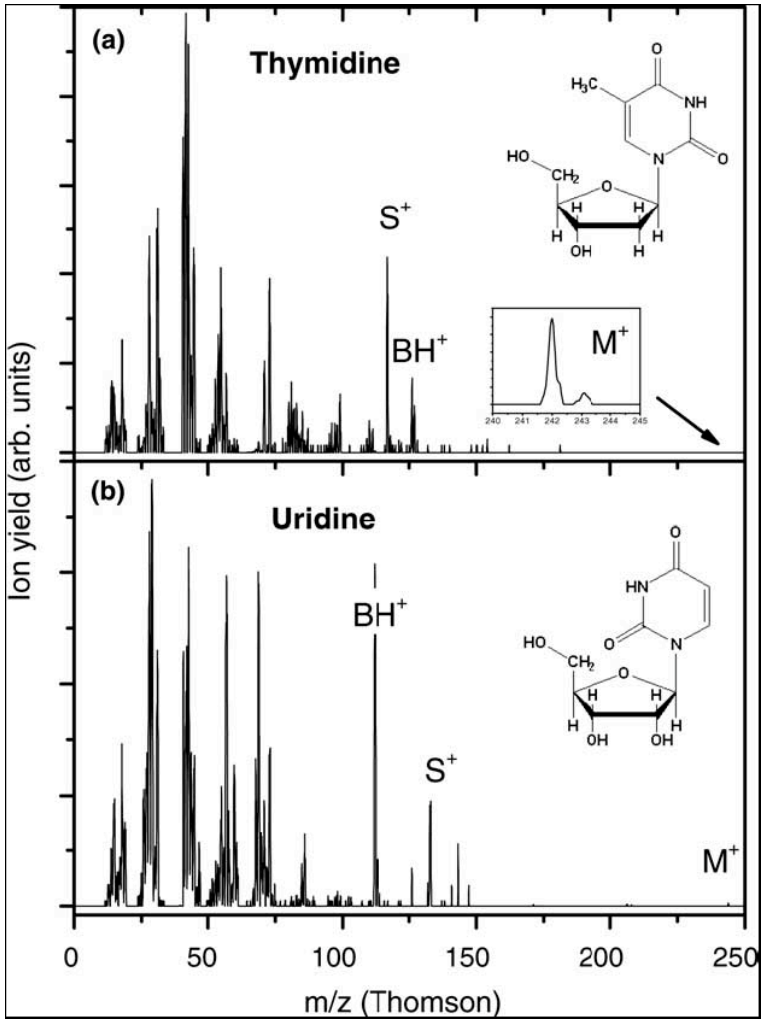
► With the nitro dioxide (m/z 46) anion various nitroaromatic compounds can be identified!

Outline

- Interactions of electrons with molecules of biological relevance:
  - Dissociative Electron Attachment (DEA) to nucleobases: site selectivity for hydrogen ablation (isolated in the gas phase, and –recently- in a cold helium matrix)
  - DEA to nitroaromatic compounds: site selectivity for NO_2^- ablation
  - Dissociative Electron Impact Ionization: appearance energy measurements for nucleobases, comparison of the absolute cross section for positive and negative ion formation.

Dissociative electron impact ionization

Appearance Energy measurements of Thymindine and Uridine



Intensive fragmentation
No simple split into sugar and base fragment
Sugar: most abundant fragment formed by removal of an OH radical
Base: grabs H from the sugar

Chem.Phys. Lett. 409 (2005) 270 - 276

Partial cross sections for positive and negative ion formation following electron impact ionization of uracil

Mass Spectrum at 120 eV electron energy

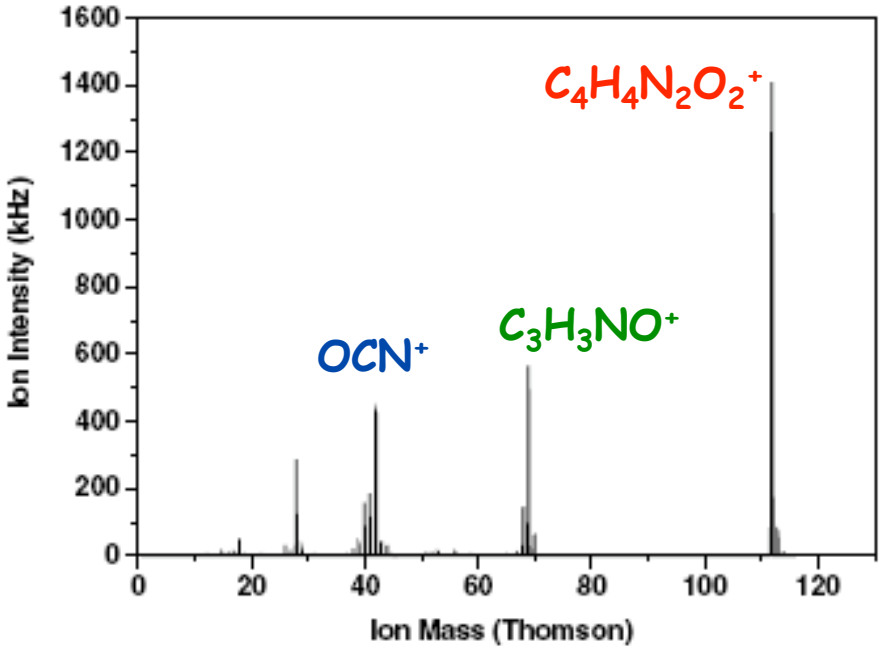


Figure 2. Mass spectrum of positive ions formed by 120 eV electron impact on uracil. The most intense peaks correspond to the parent $C_4H_4N_2O_2^+$ ion and two fragment ions $C_3H_3NO^+$ and OCN^+.

Absolute partial cross section

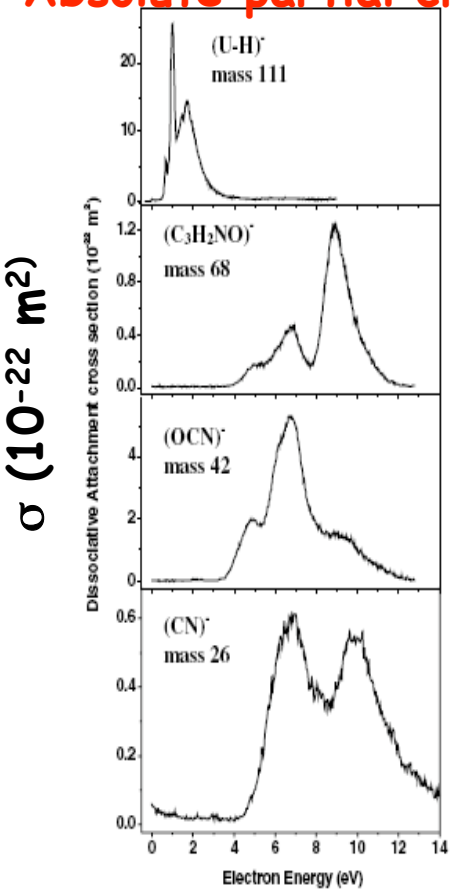
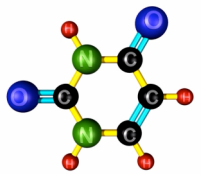


Figure 5. Absolute partial cross sections for dissociative elect of electron energy. $(U-H)^-$ refers to the $C_4H_3N_2O_2^-$ ion.



J. Phys. B: At. Mol. Opt. Phys. 37 (2004) 3013–3020

Absolute partial ionization cross sections for uracil (and some fragments)

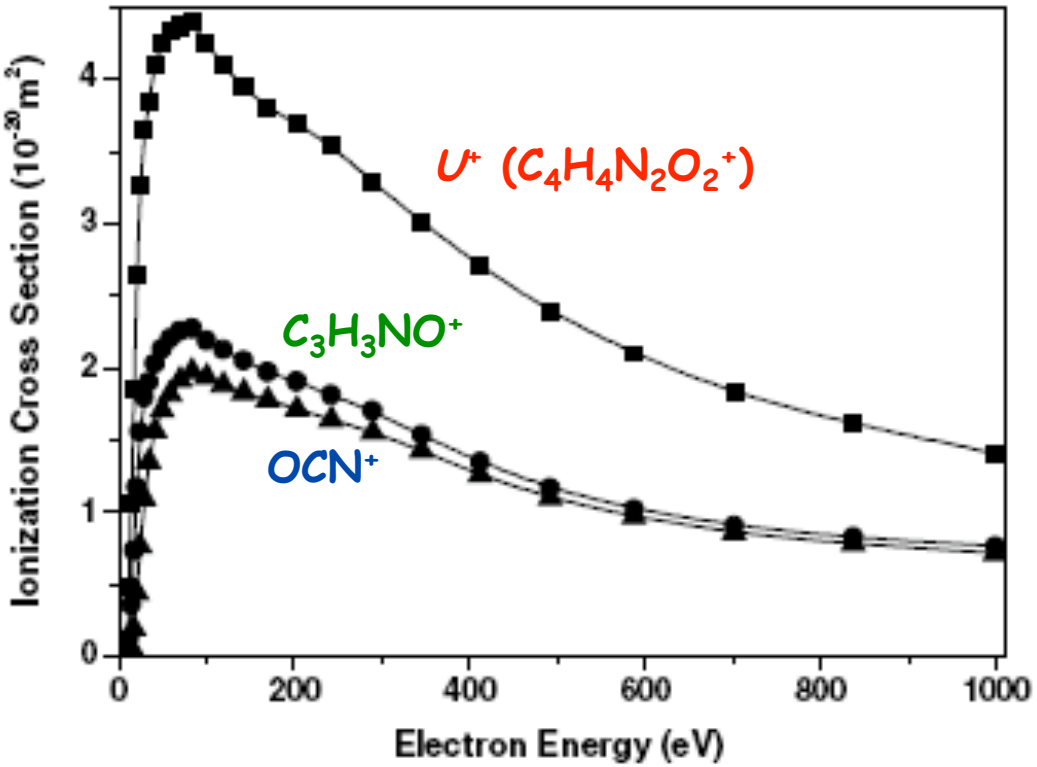
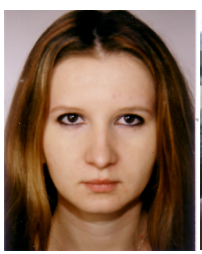


Figure 4. Absolute partial ionization cross sections for the formation of the parent uracil $C_4H_4N_2O_2^+$ ion (squares) and two fragment ions $C_3H_3NO^+$ (circles) and OCN^+ (triangles) as a function of electron energy following electron impact on uracil.

J. Phys. B: At. Mol. Opt. Phys. **37** (2004) 3013–3020

Coworkers

Sylwia Ptasinska
Philipp Sulzer
Fabio Zappa



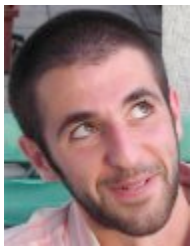
Aleksandar Stamatovic
Beograd

Stefan Matejcik
Bratislava

Eugen Illenberger
Berlin

Paul Burrow
Lincoln

Julien Lecointre
Ingo Mähr
Stephan Denifl



Michael Probst
Paul Scheier
Tilmann Märk



David P.A. Kilgour

Detection Technology
Department Kent

Work partially supported by the FWF and ÖAW, Wien, Austria and the European Commission, Brussels.