



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



Electron impact ionization and attachment studies of biomolecules embedded in He droplets

Stephan Denifl

Radiation Damage in Biomolecular Systems COST Action P9

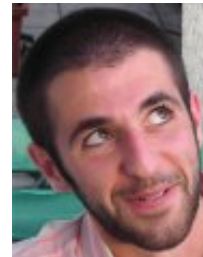


Working Group One: Electron and biomolecular interactions
Lisbon, Portugal

23rd – 25th February 2006

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Michel Farizon
Lyon



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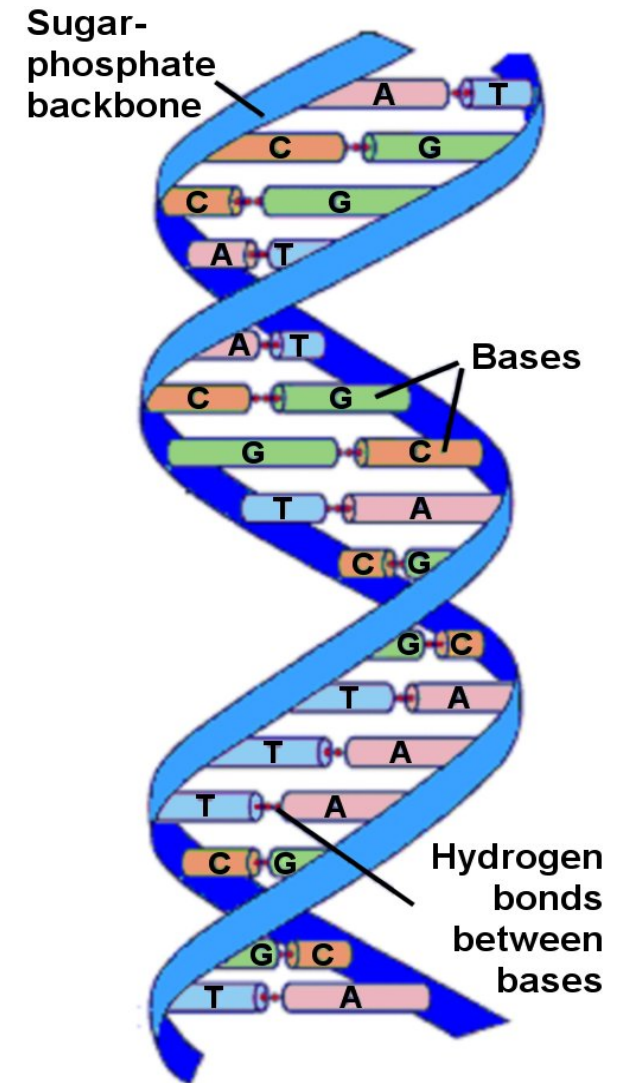
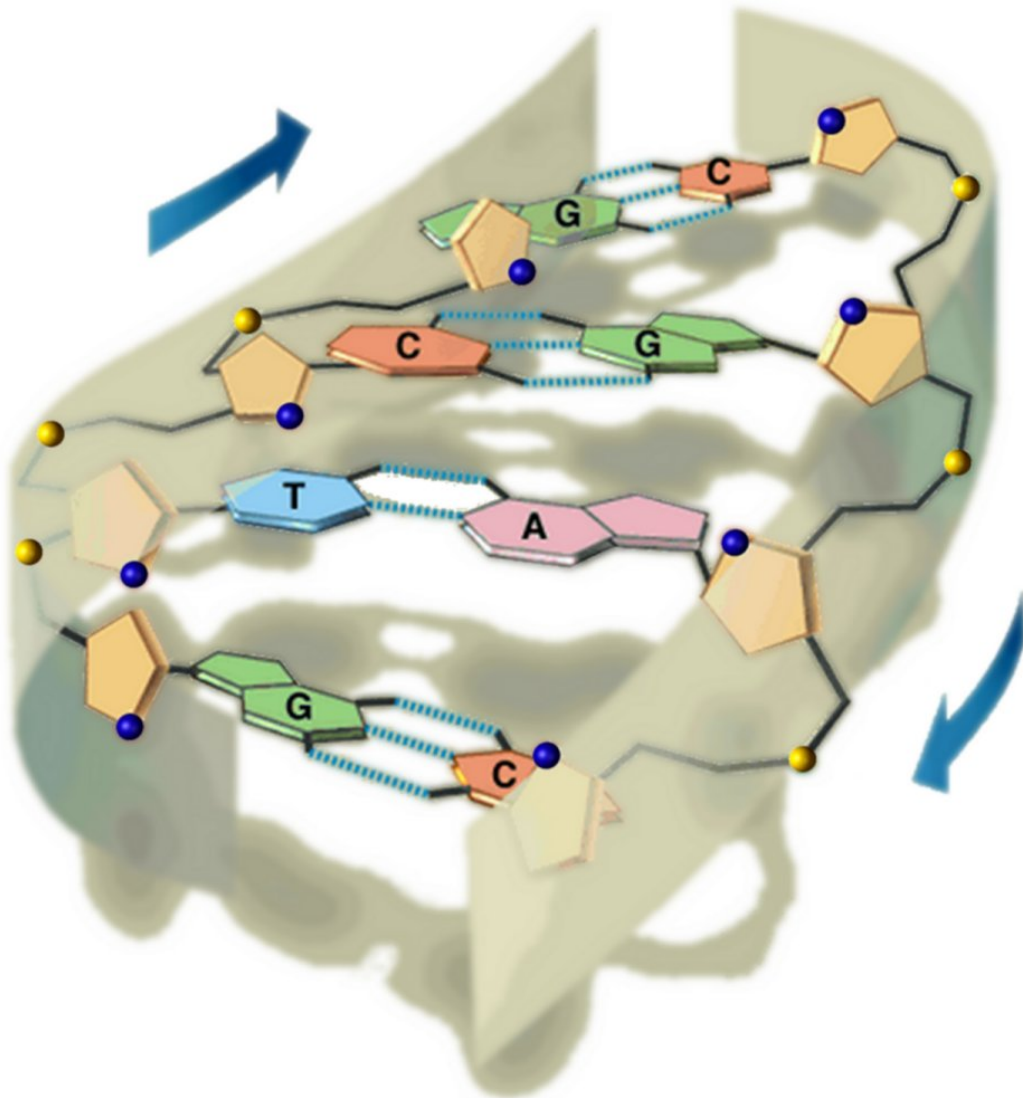
Nigel Mason
Milton Keynes



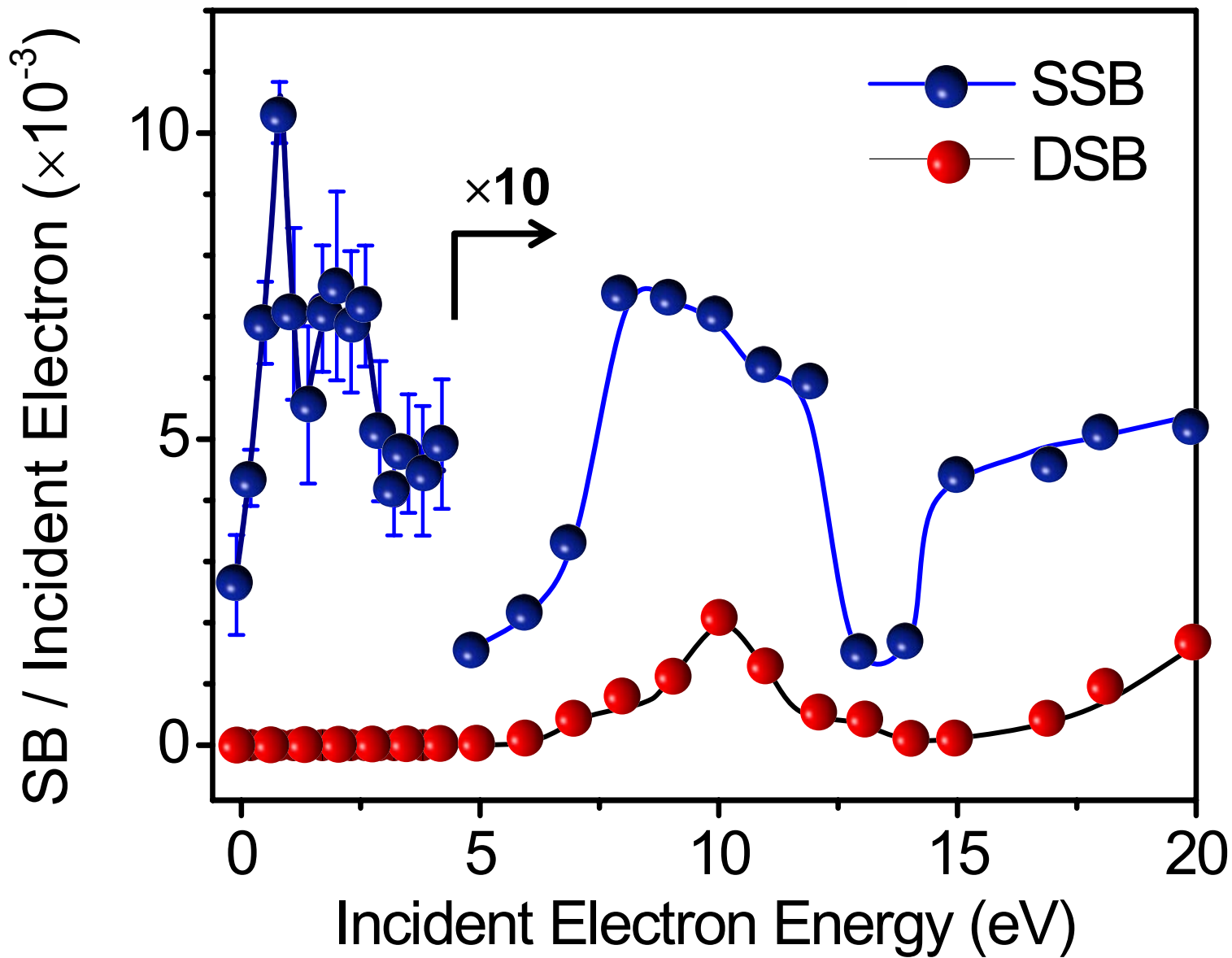
Work partially supported by the FWF and ÖAW, Wien, Austria and the European Commission, Brussels.



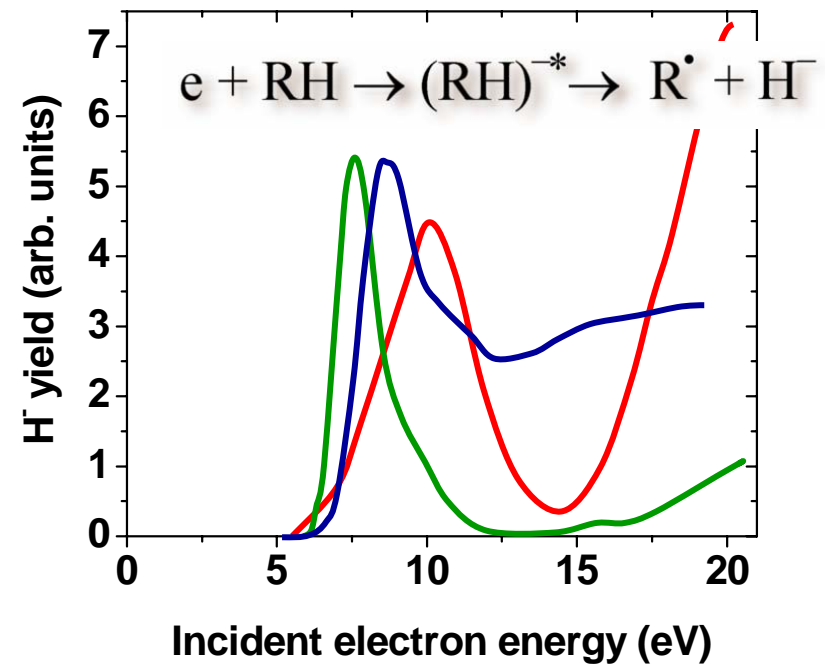
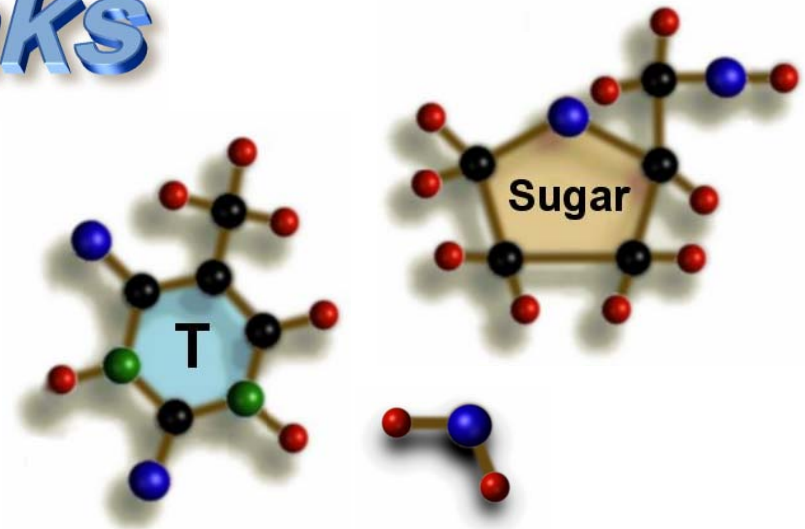
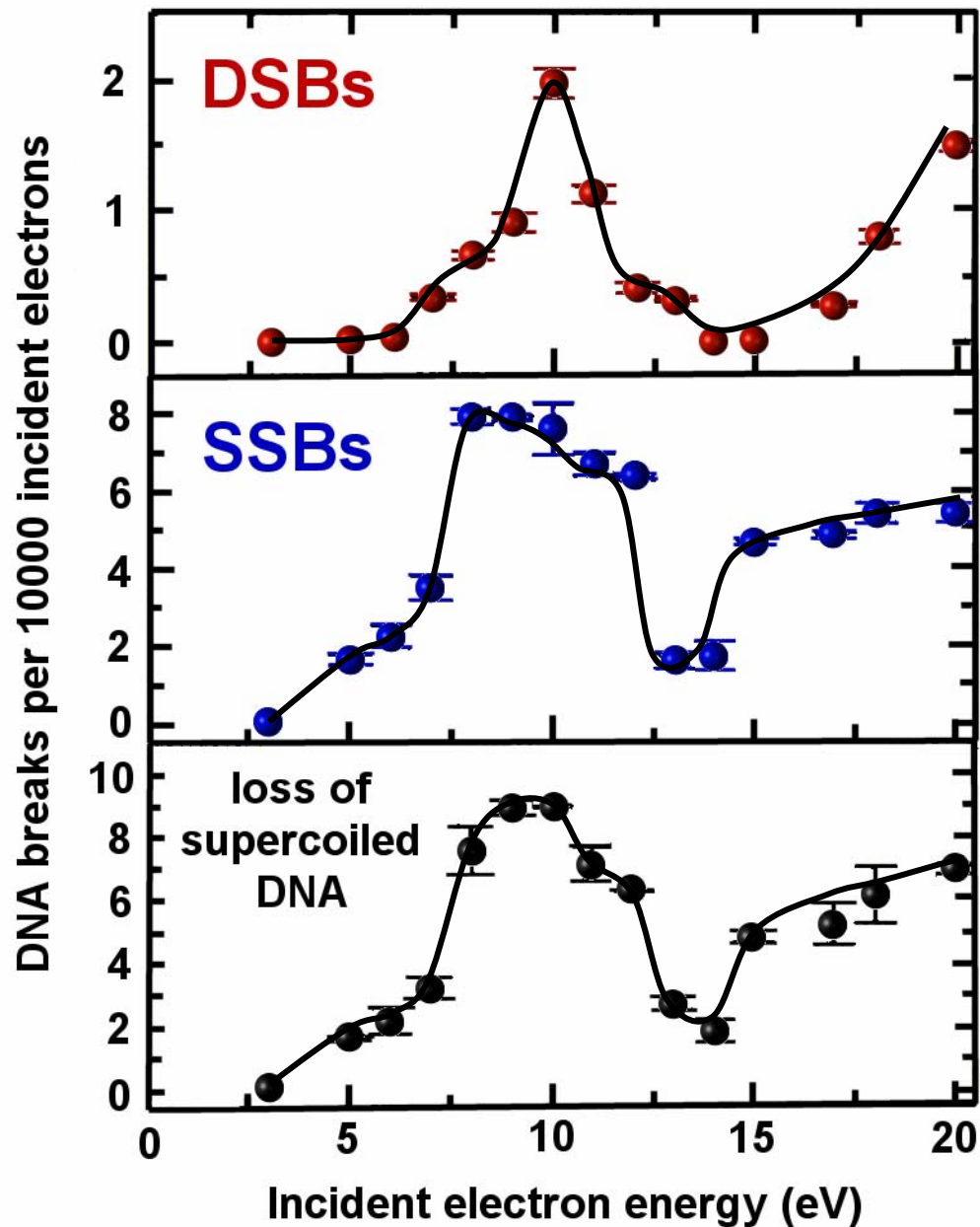
DNA



DNA-strand breaks

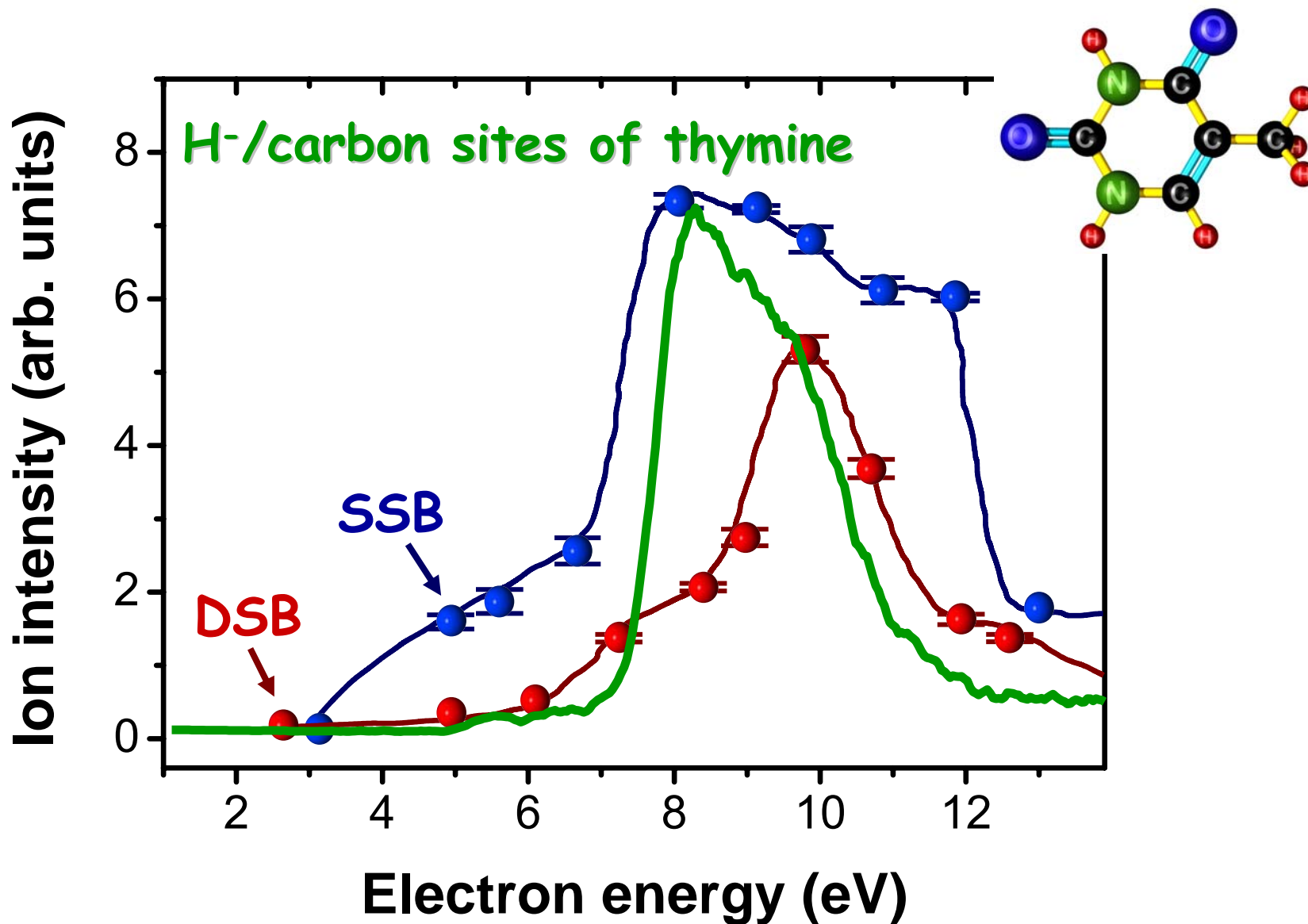


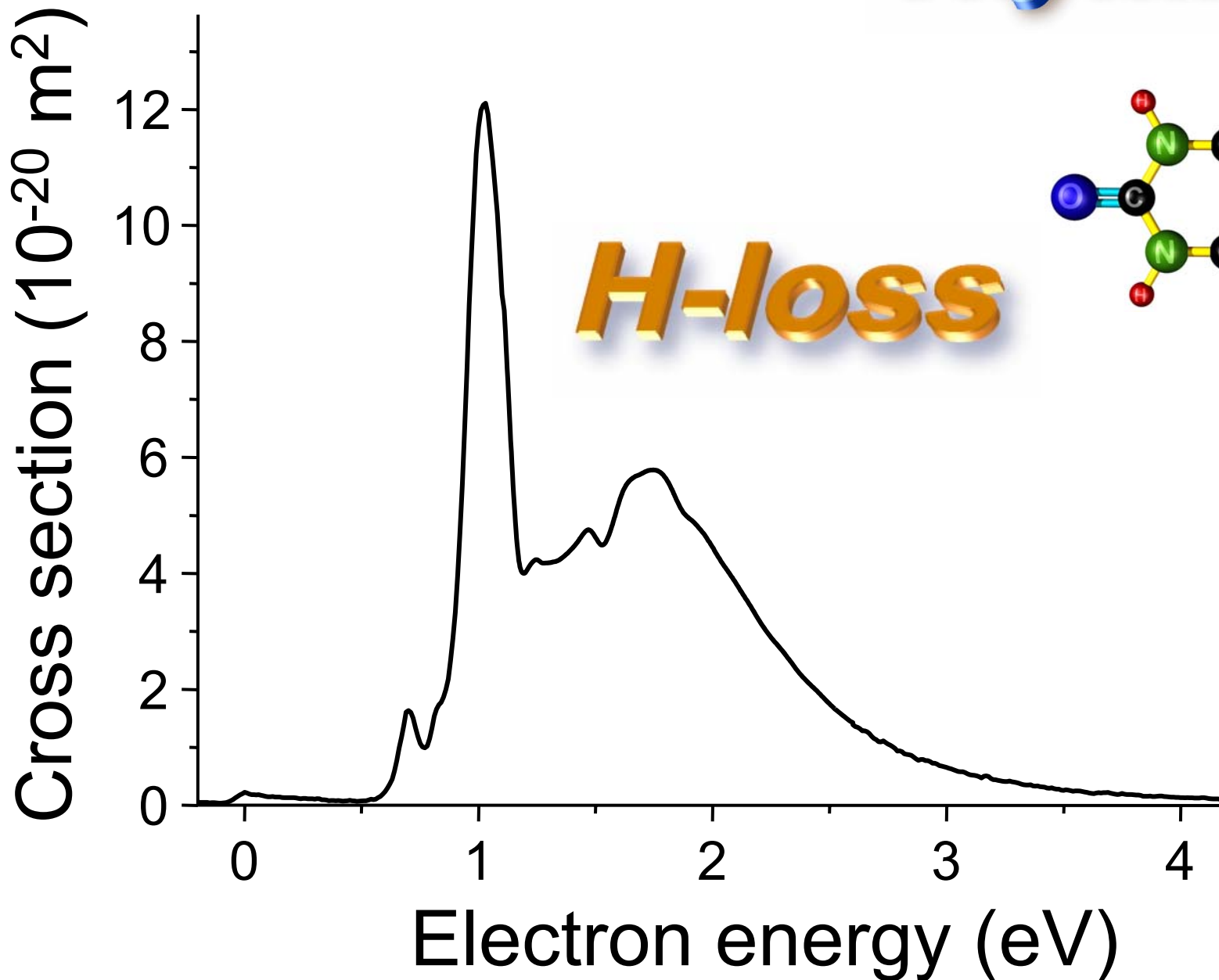
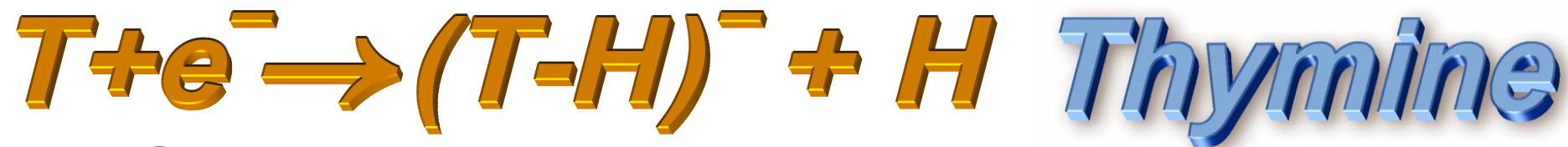
DNA-strand breaks



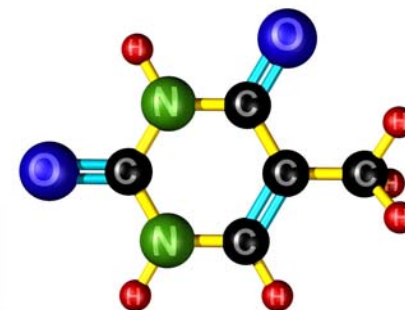
Sanche a.c. Science, 287 (2000) 1658

Comparison to strand breaks

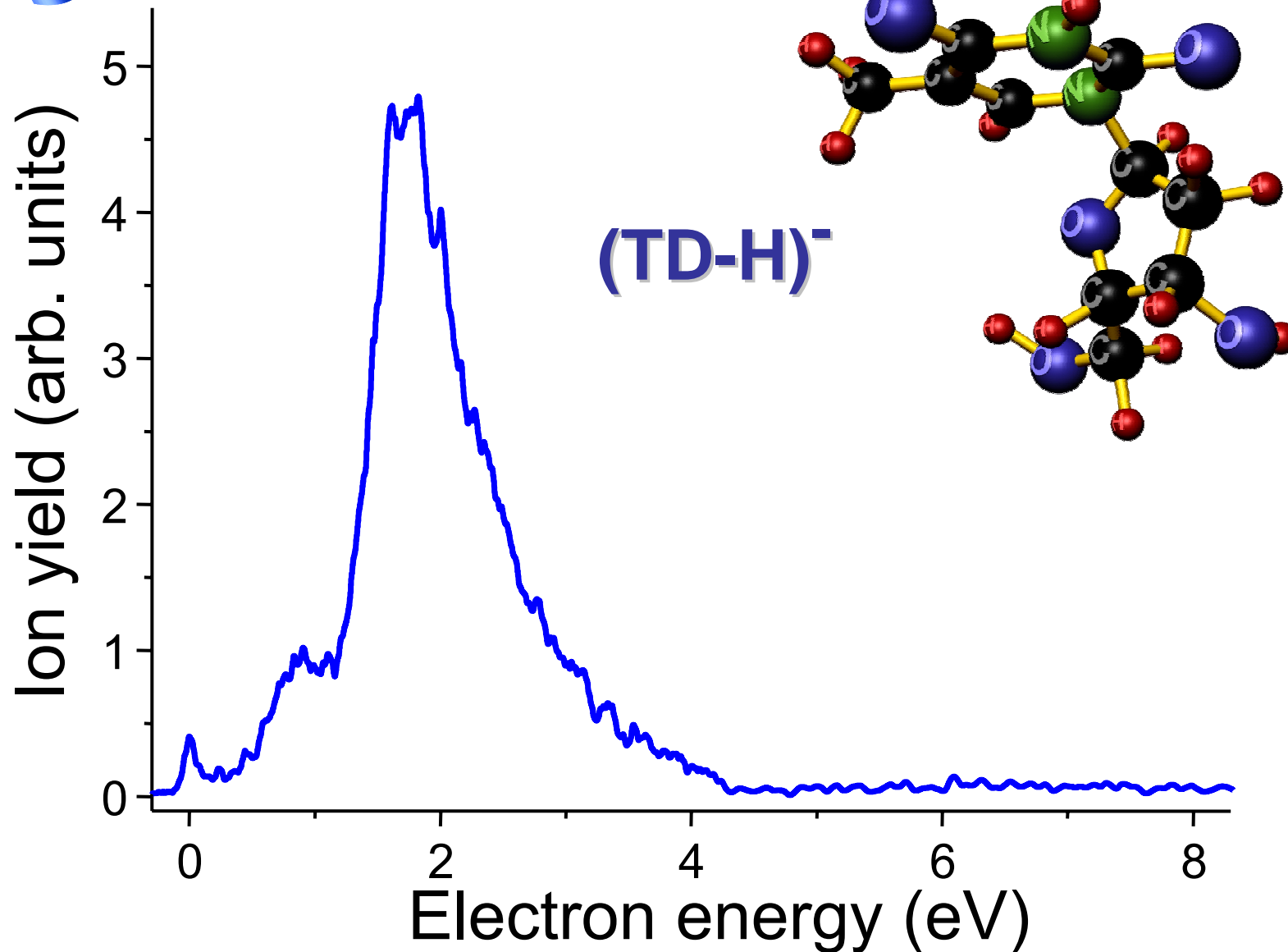




H-loss

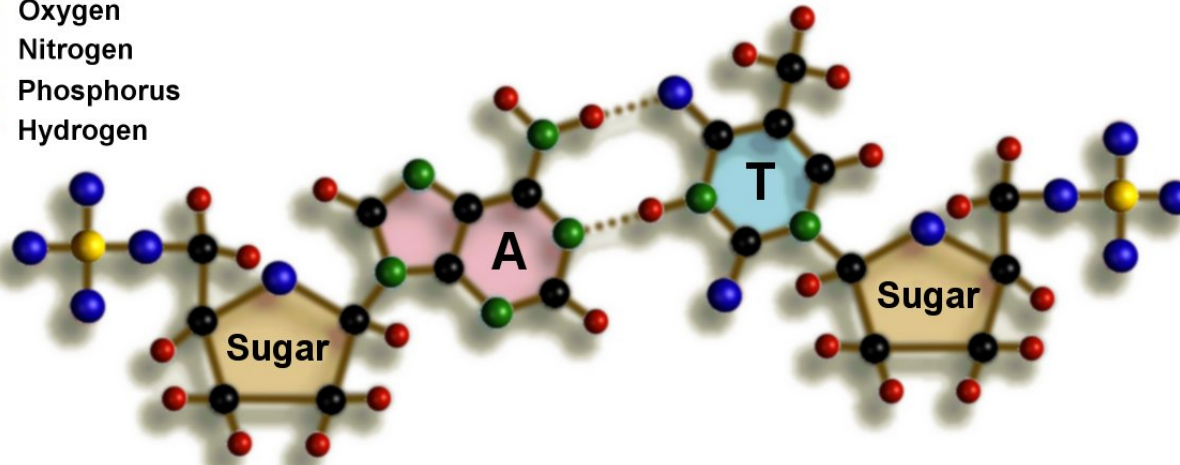


Thymidine

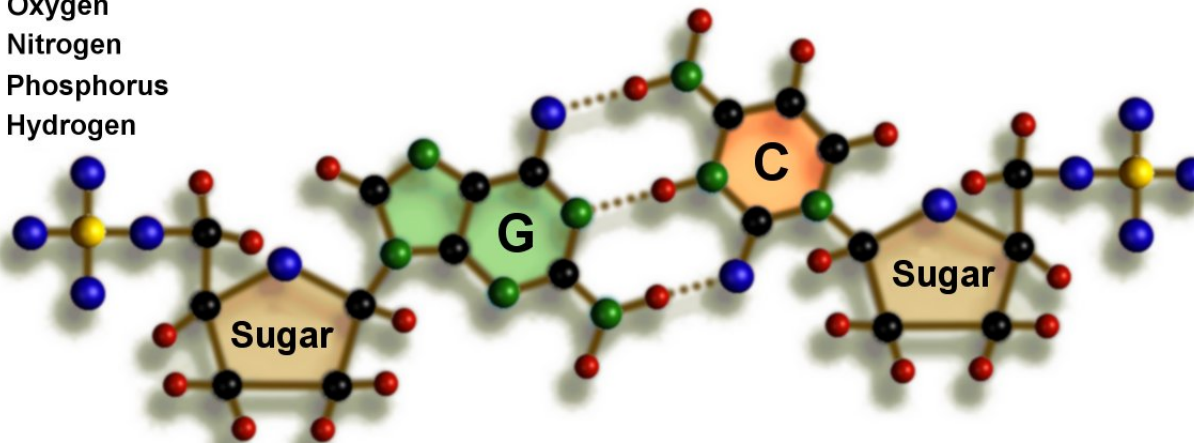


DNA

- Carbon
- Oxygen
- Nitrogen
- Phosphorus
- Hydrogen

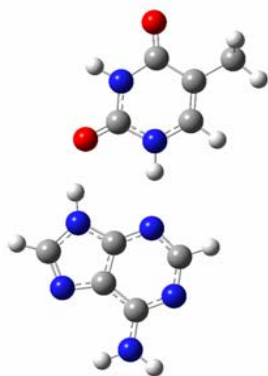


- Carbon
- Oxygen
- Nitrogen
- Phosphorus
- Hydrogen

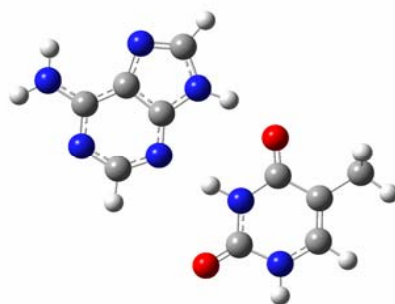


Binding energies for dimers

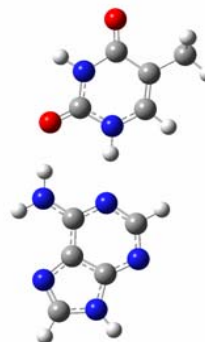
-0.73 eV



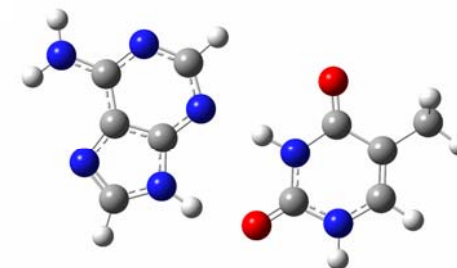
-0.64 eV



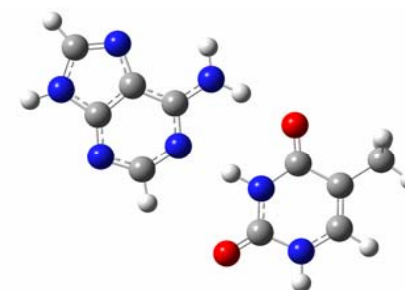
-0.62 eV



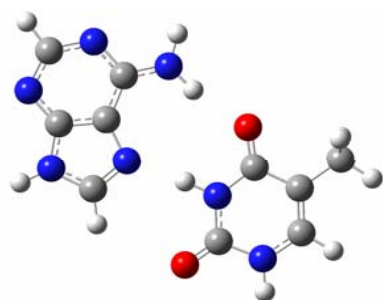
-0.62 eV



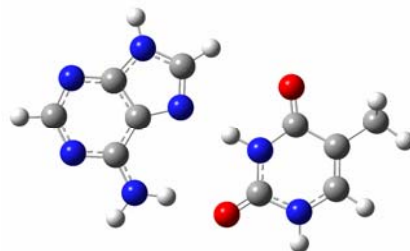
-0.57 eV



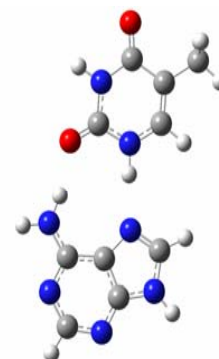
-0.60 eV



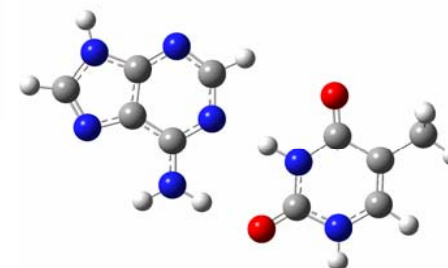
-0.59 eV



-0.57 eV



-0.55 eV



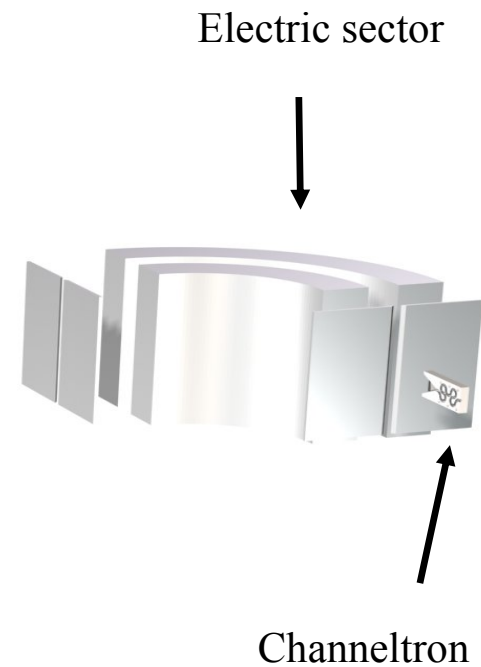
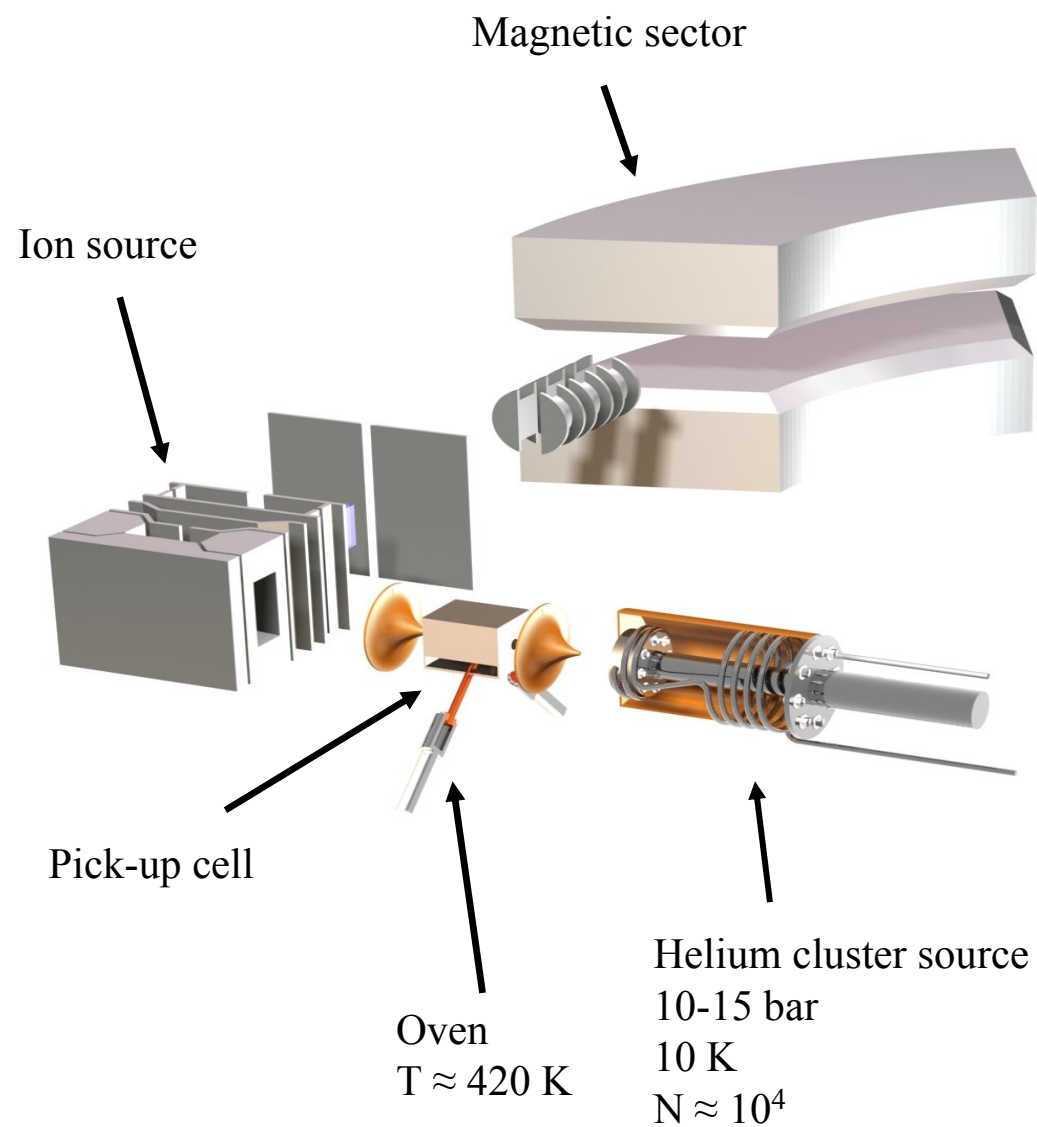
G2MP2, B3LYP/cc-pVTZ and other levels of theory
M. Probst, to be published

He droplets

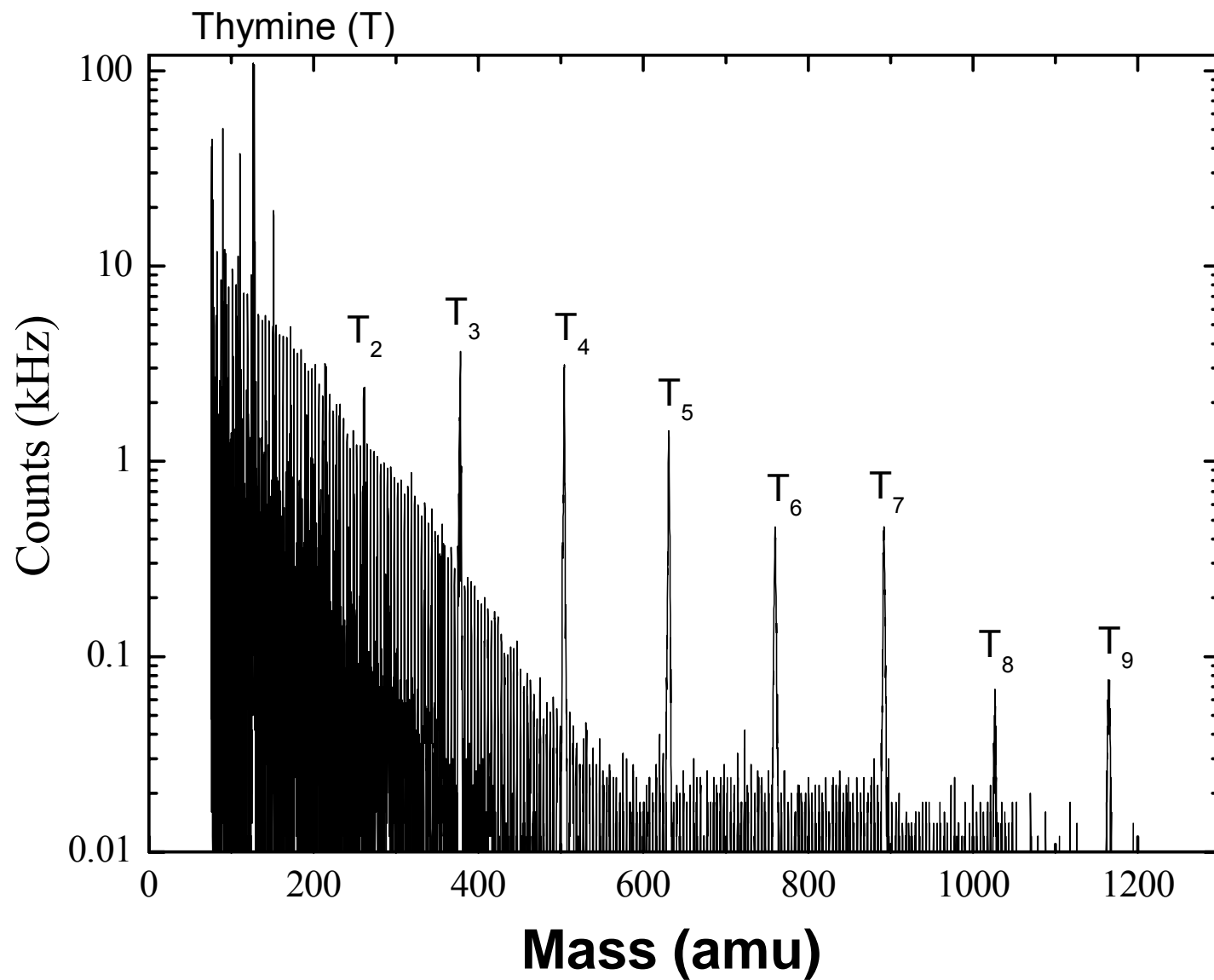
- ▶ Helium droplets provide the ultimate matrix for atoms and molecules.
- ▶ Evaporative cooling produces an isothermal low temperature environment in these droplet at a temperature (0.36 K) that is lower than possible for most solid matrices.
- ▶ They can be doped with atoms or molecules that can then interact to form completely novel molecular complexes either in the interior or at the surface of the droplet

J. P. Toennies, A.F. Vilesov, Superfluid Helium Droplets: A Uniquely Cold Nanomatrix for Molecules and Molecular Complexes. *Angew. Chem. Int. Ed.* **43**, 2622-2648 (2004)

Apparatus

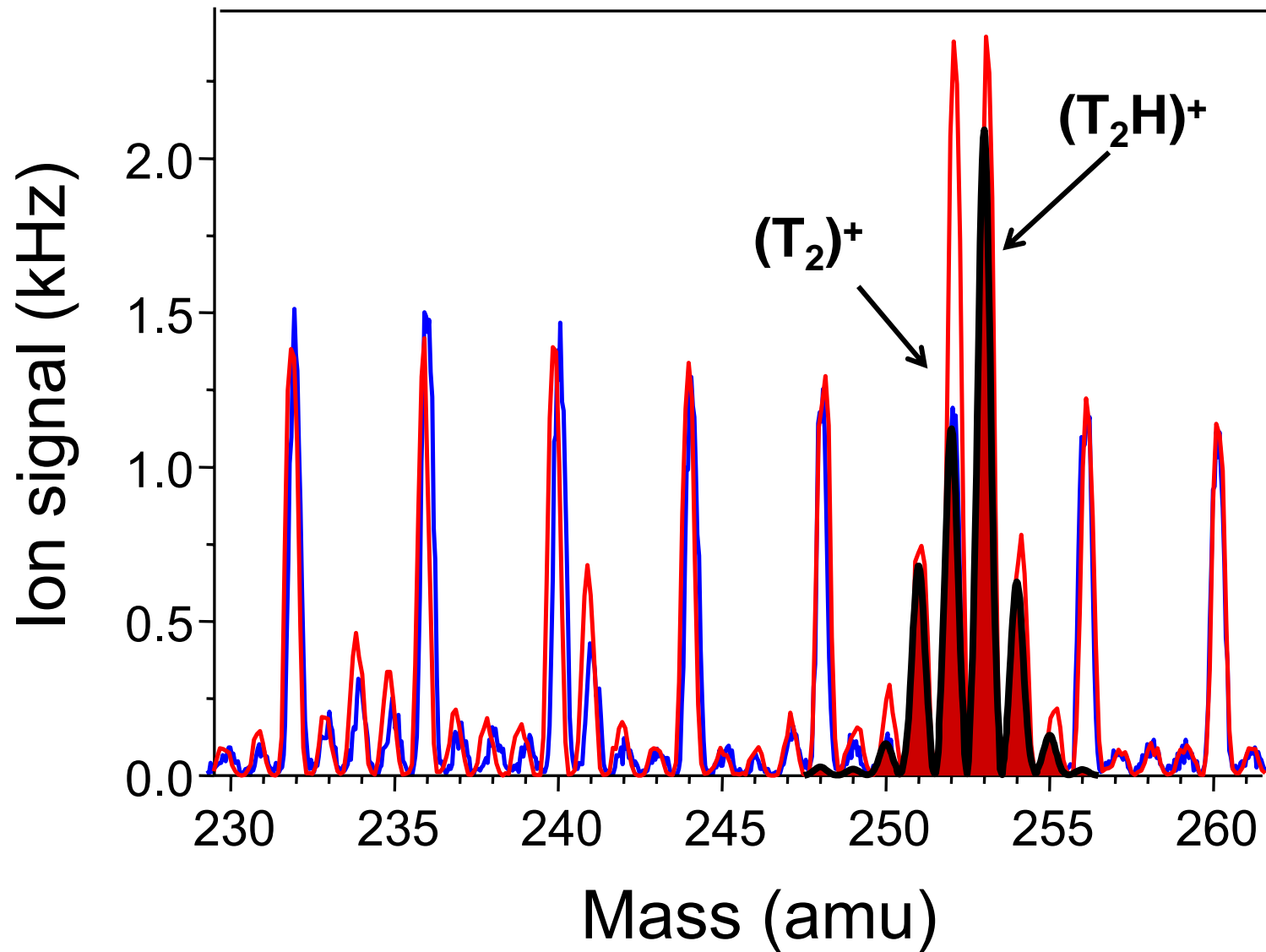


Thymine pickup by He_n

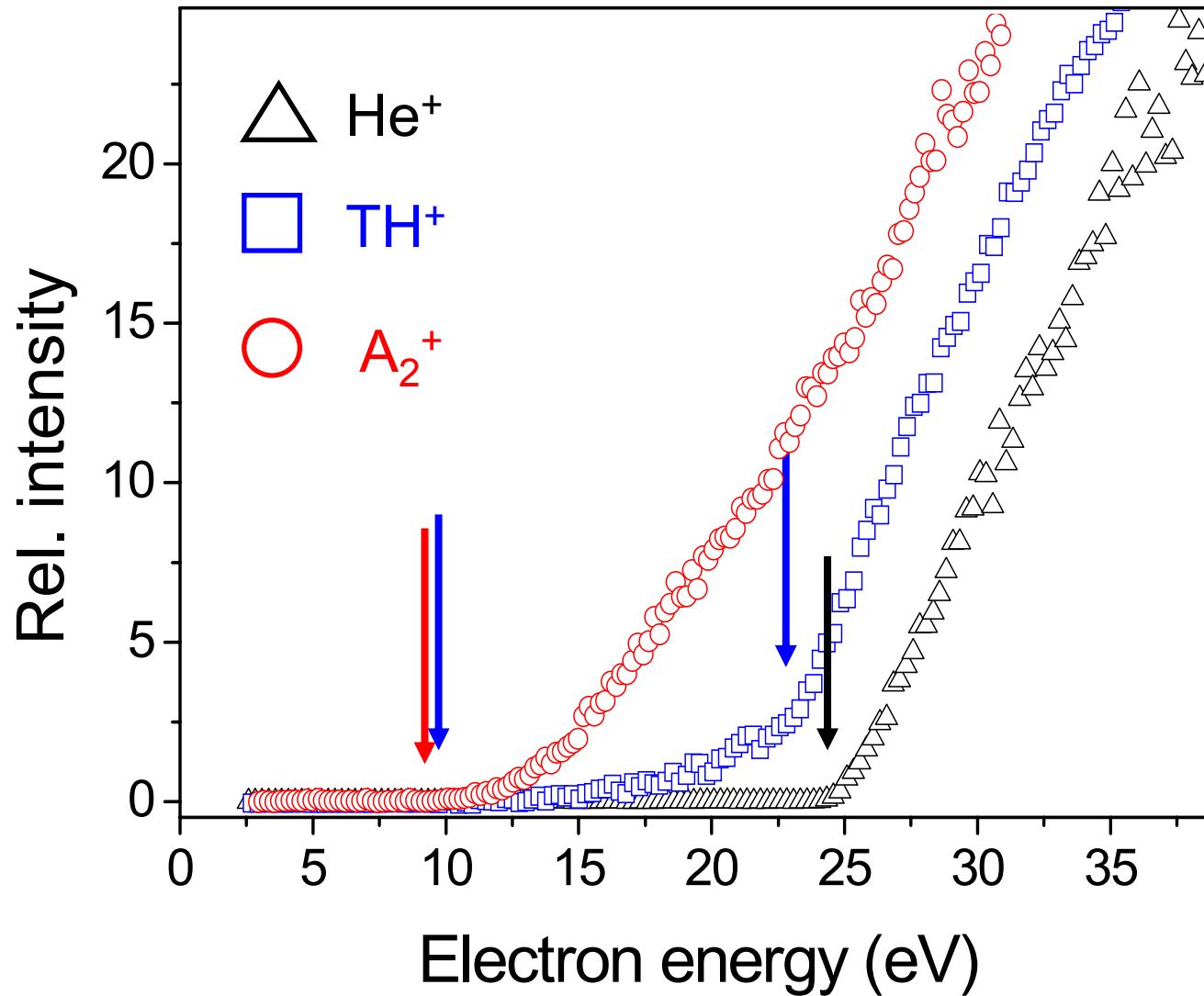


Electron energy: 150 eV

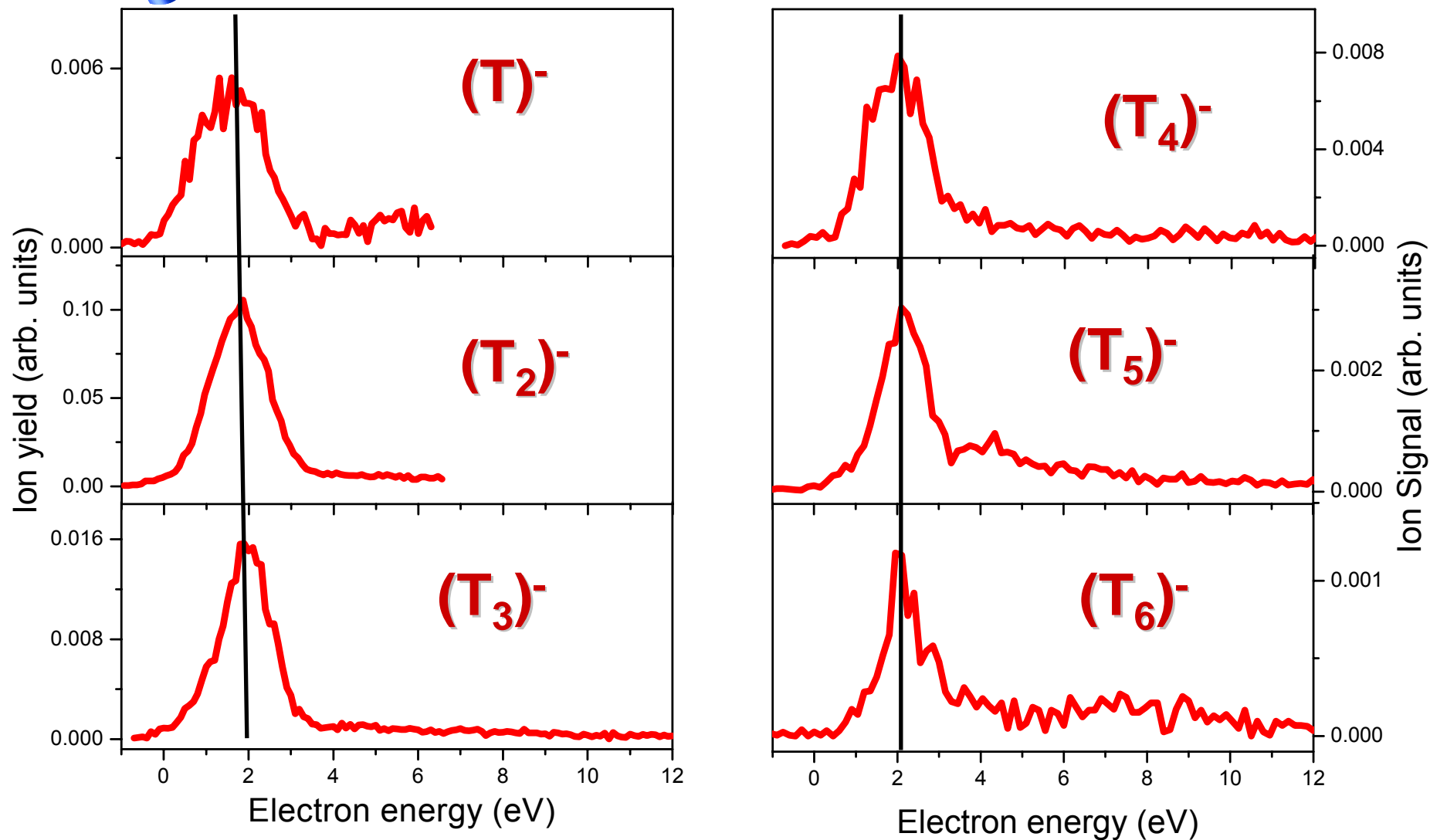
Thymine pickup by He_n



Ionization efficiency curves

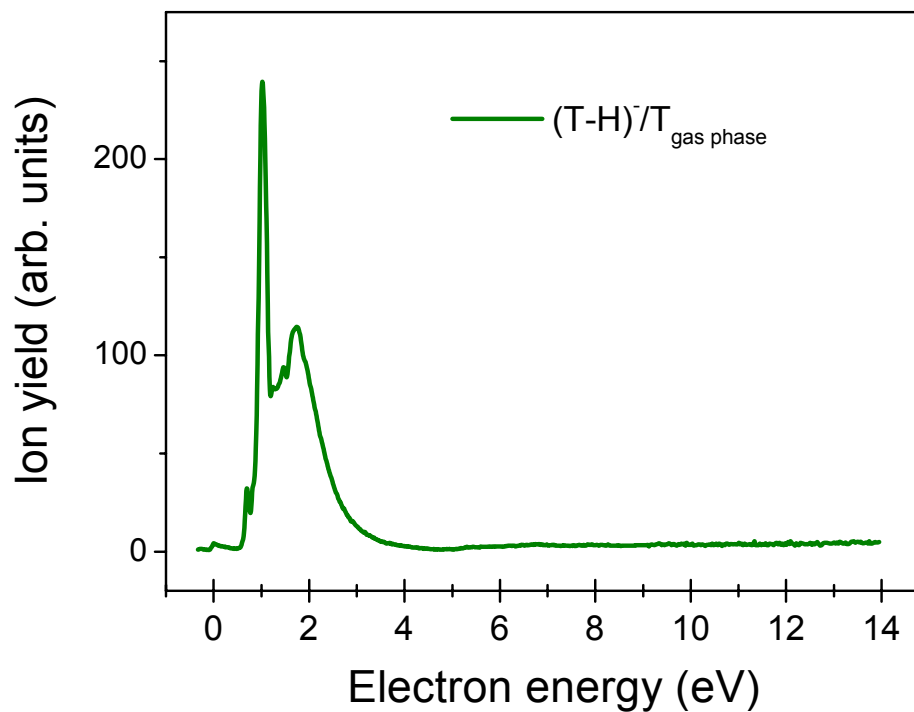
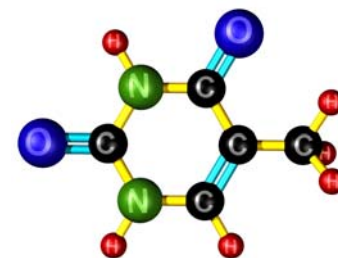
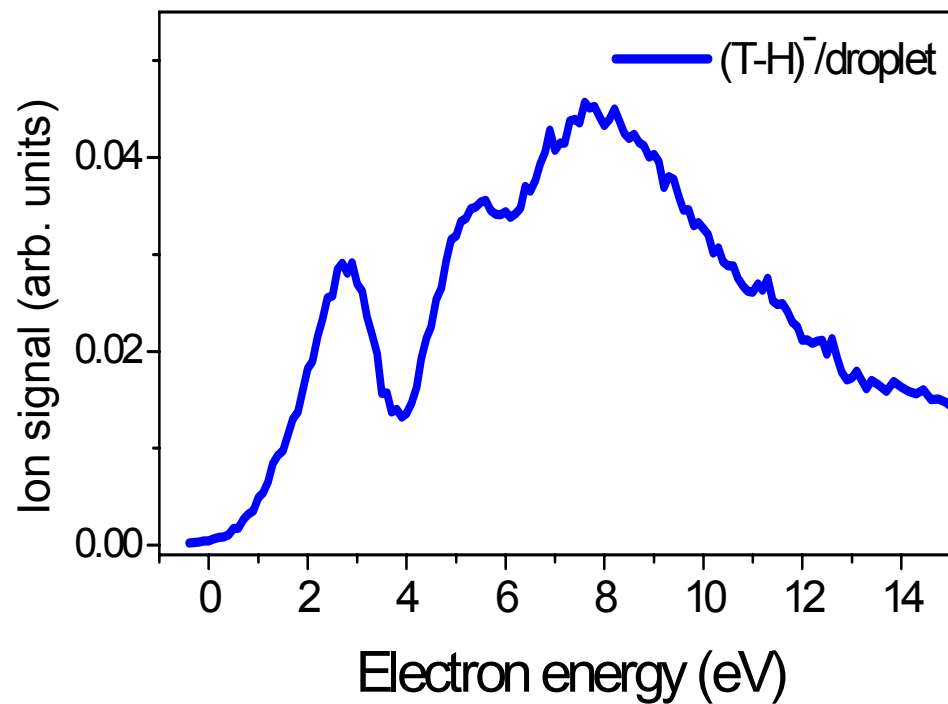


Thymine cluster anions

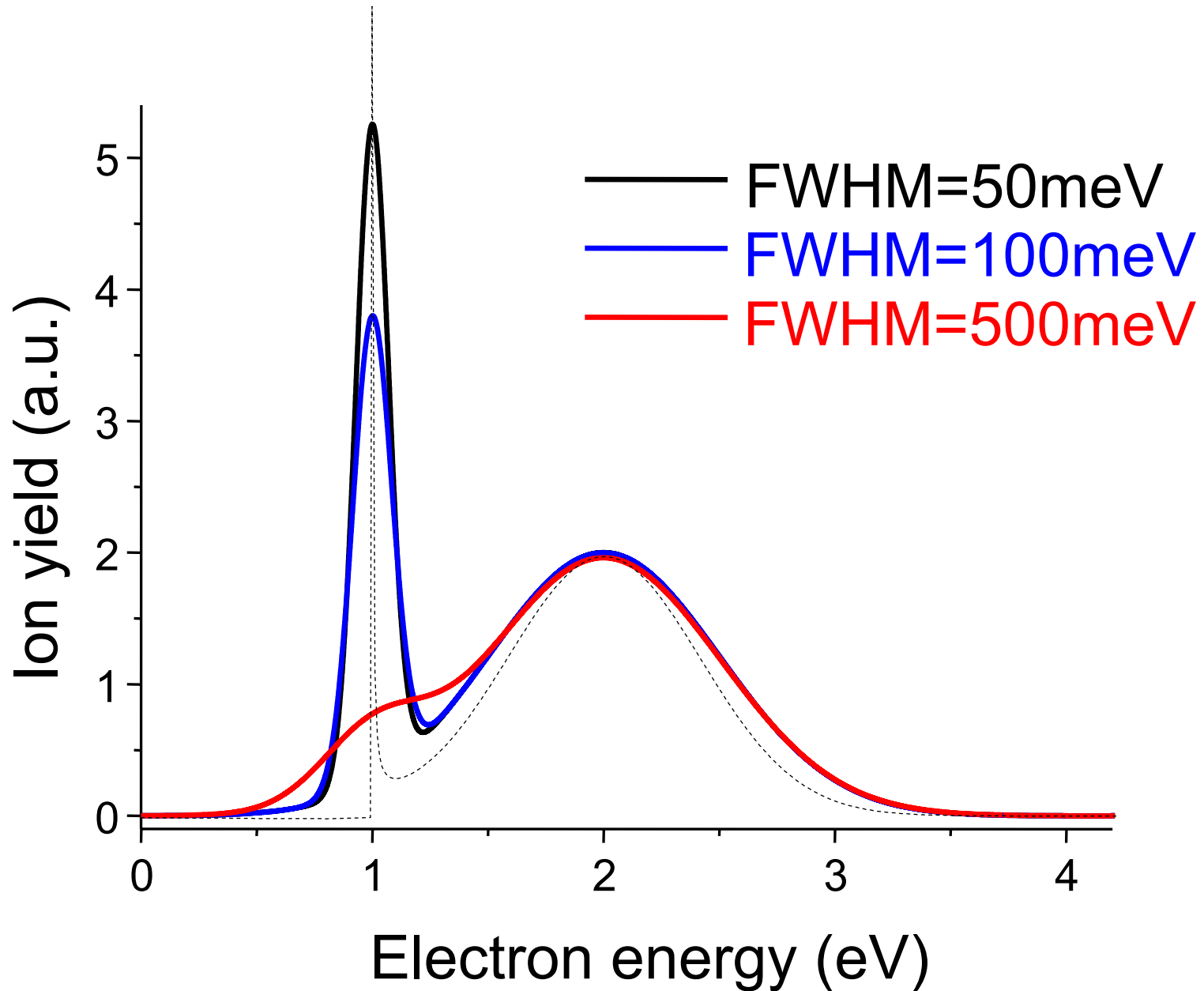


C. Desfrancois, H. Abdoul-Carime, C. P. Schulz, J. P. Schermann, Laser Separation of Geometrical Isomers of Weakly Bound Molecular Complexes, *Science* **269** (1995) 1707-1709

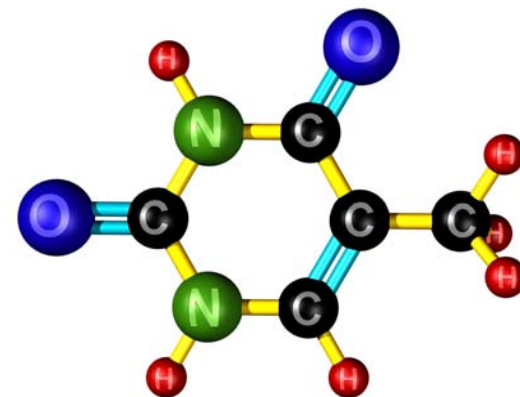
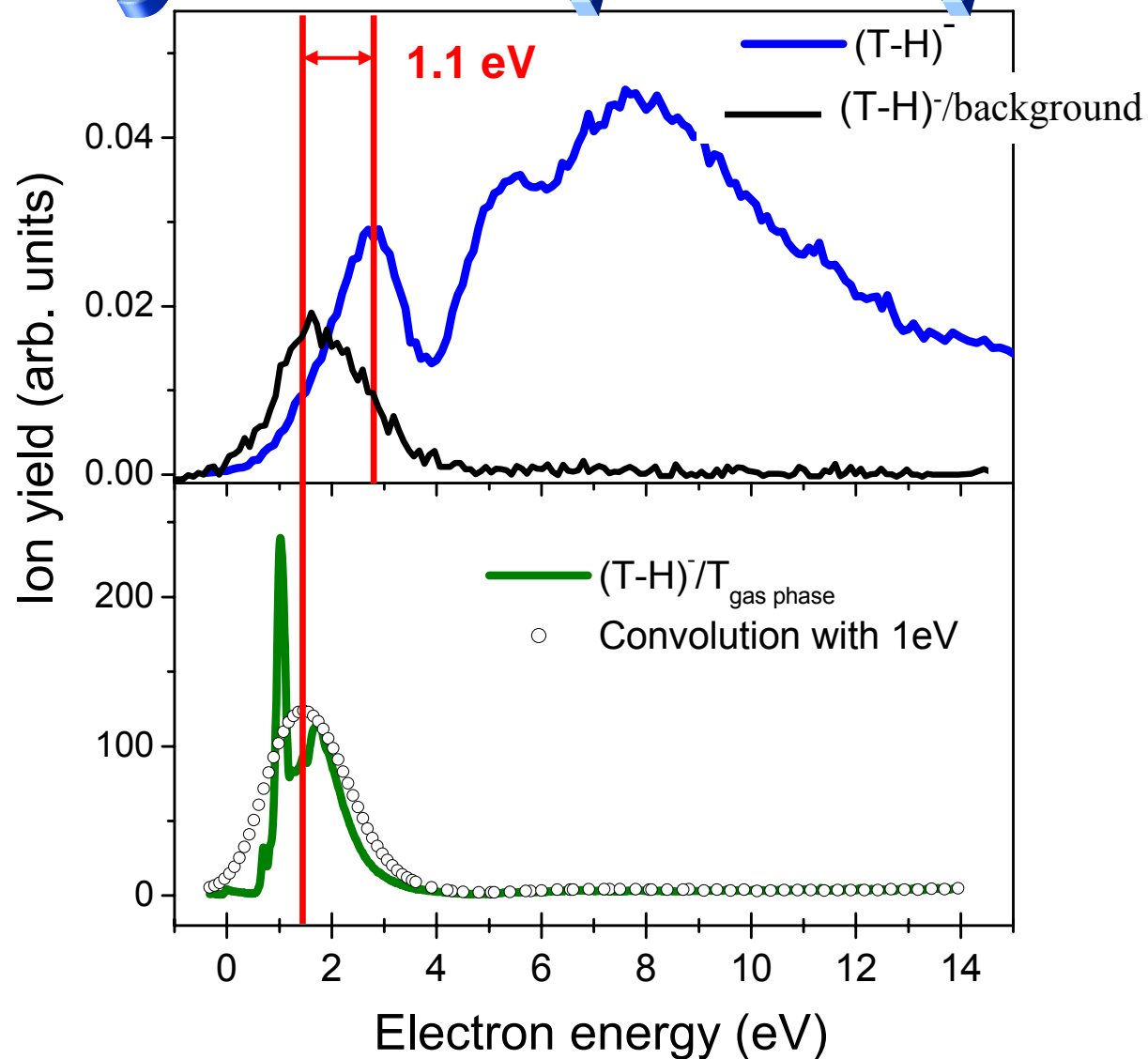
Thymine pickup by He_n



Effects of the resolution

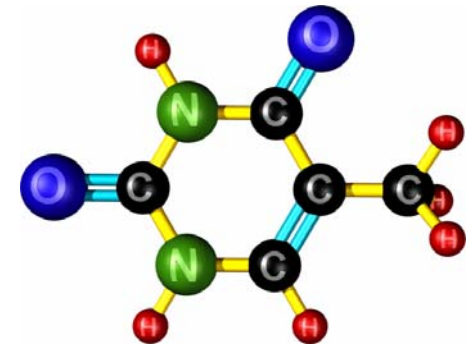
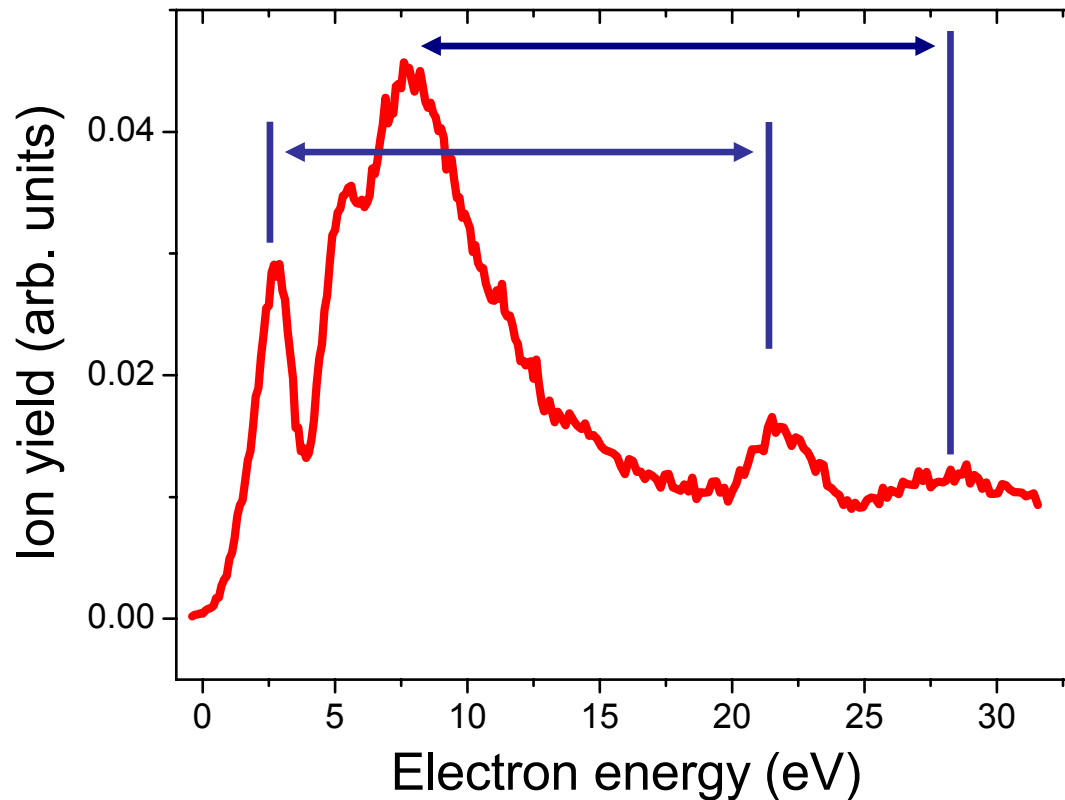


Thymine pickup by He_n



K. Martini, J. P. Toennies, C. Winkler, Electron-scattering from ⁴He and Ne clusters – determination of the cluster density from the electronic surface-barrier potential. *Chem. Phys. Lett.* **178**, 429-434 (1991)

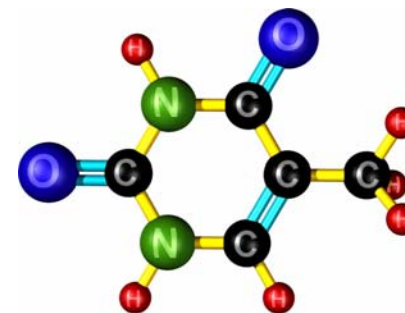
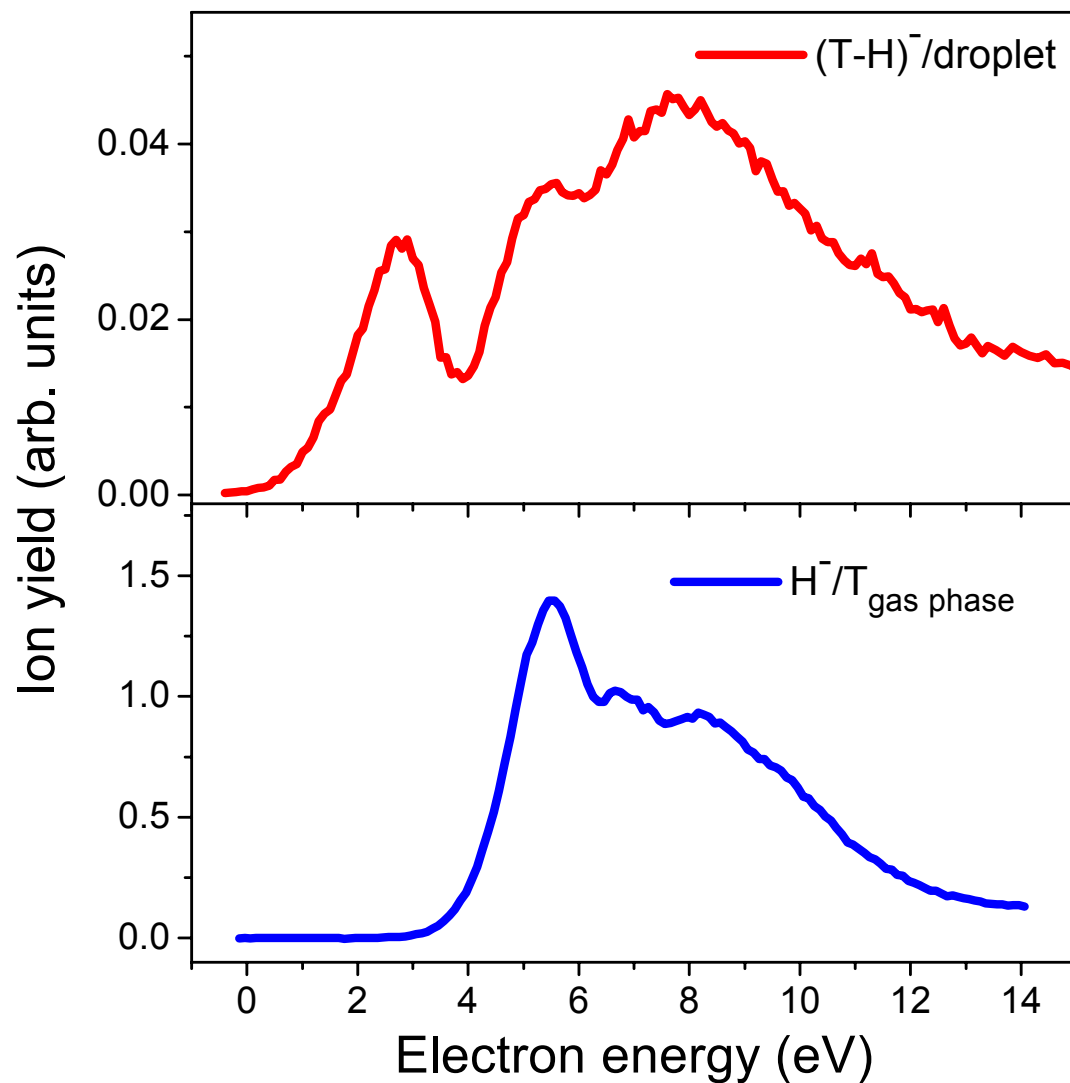
He-scattering



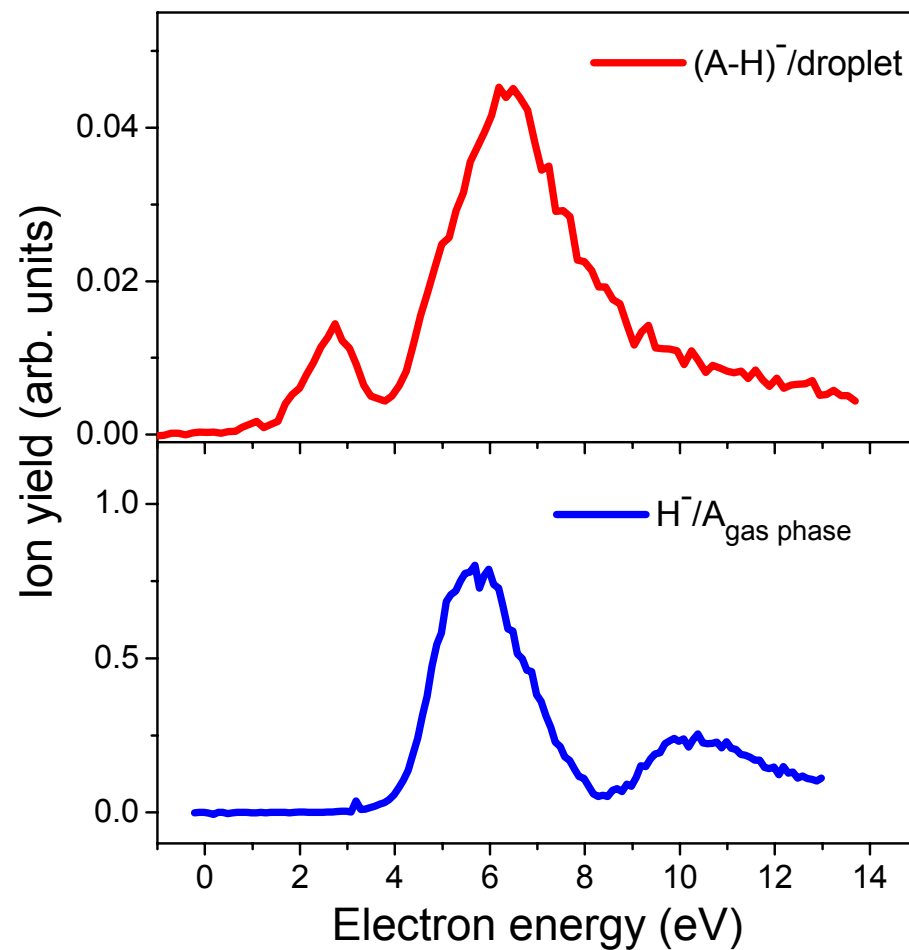
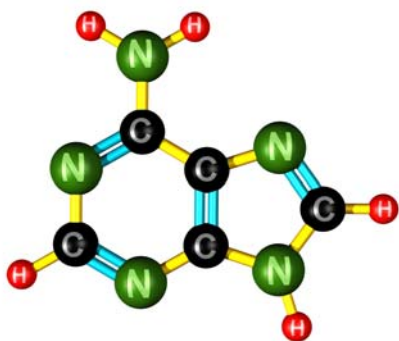
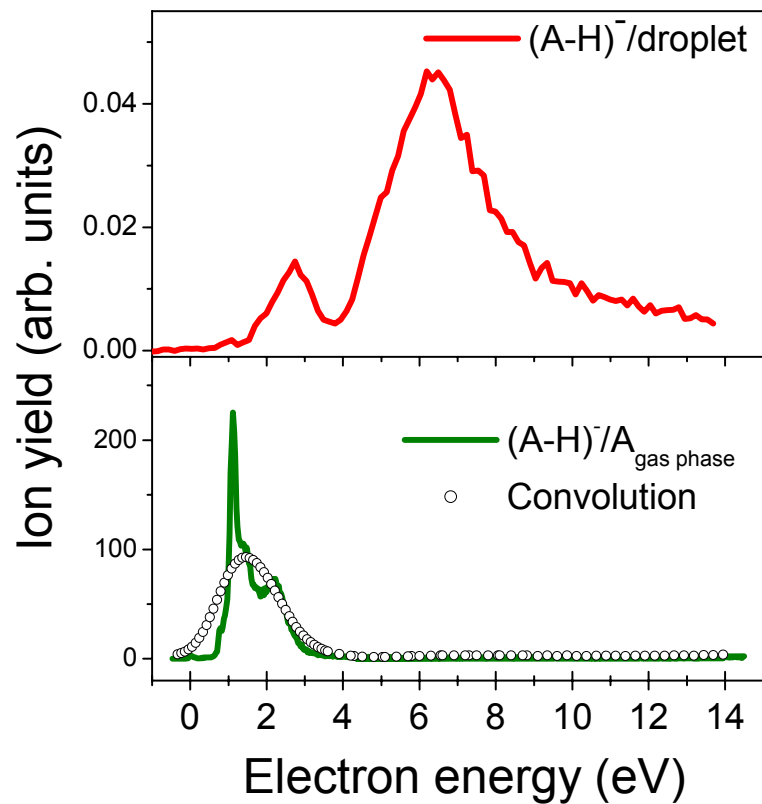
- ▶ lowest excitation energy of helium (2^3S state) is 19.82 eV

U. Henne and J. P. Toennies, Electron capture by large helium droplets. *J. Chem. Phys.* **108**, 9327-9338 (1998)

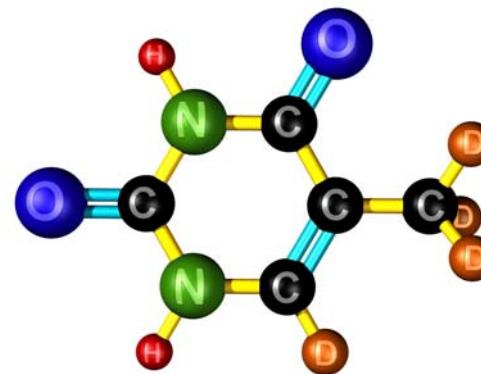
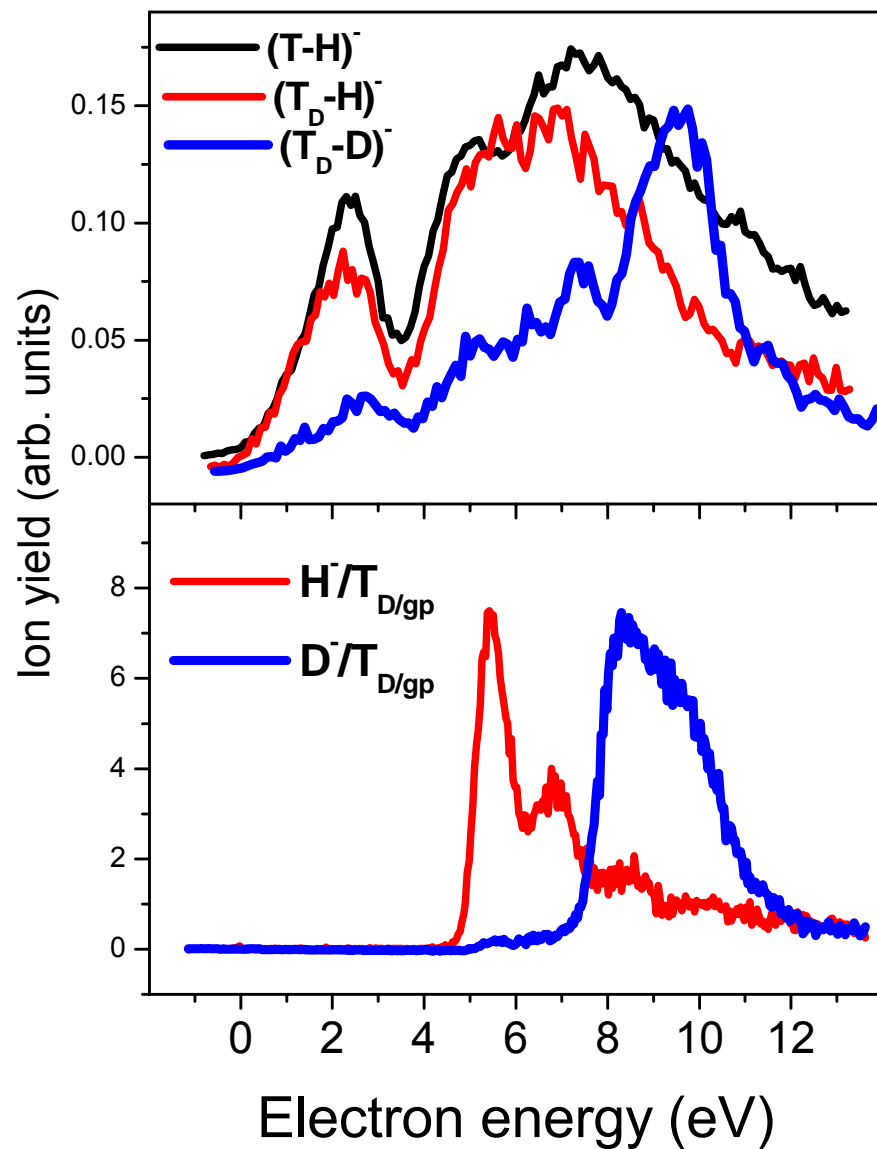
Thymine pickup by He_n



Adenine pickup by He_n



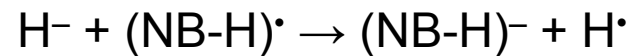
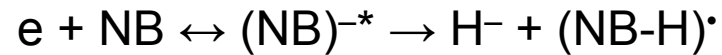
Part. deuterated Thymine pickup by He_n



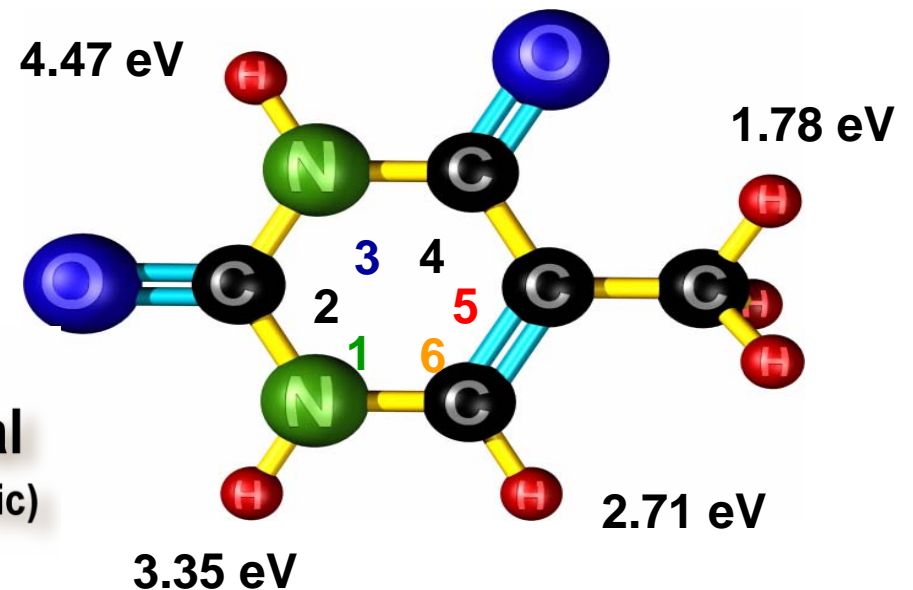
S. Ptasińska et al., Bond-Selective H⁻ Ion Abstraction from Thymine. *Angew. Chem. Int. Ed.* **44** (2005) 1647–1650

Nucleobase pickup by He_n

- ▶ The hydrogen anion transfers very efficiently its excess electron:

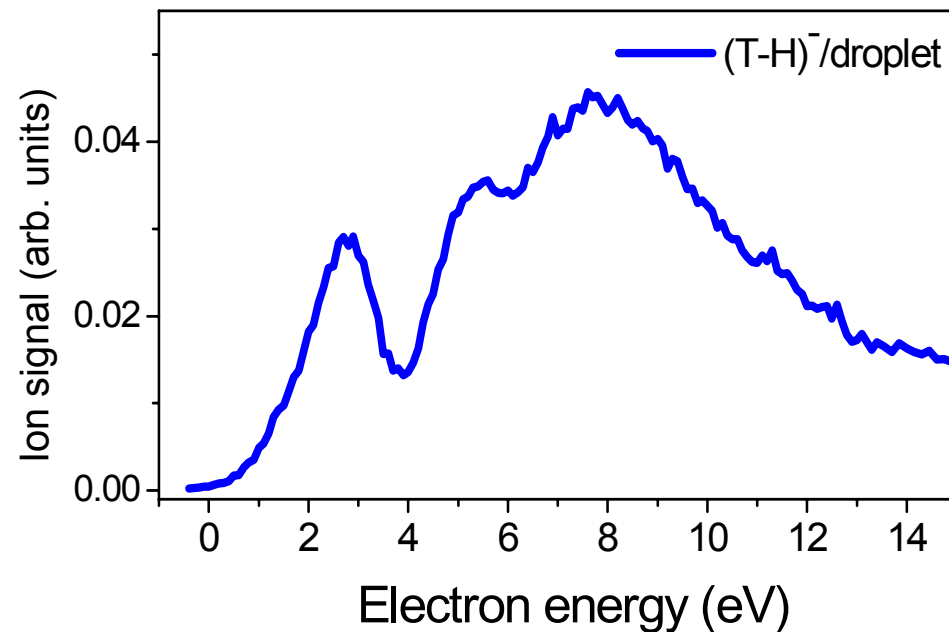


G2MP2 electron affinities of the 4 isomers of the 'Thymine minus' radical (positive values mean: formation of anion is exothermic)



Nucleobase pickup by He_n

- ▶ The resonance of the transient negative ion which leads to H^- in the gas phase is enhanced by about three orders of magnitude in the presence of the solvation environment in the He droplet.



Summary and outlook

- We formed complexes of biomolecules from the gas phase by embedding single biomolecules into cold rare gas clusters.
- First mass spectrometric study of negative ions formed via free electron attachment to molecules embedded in helium clusters.
- Dissociative electron attachment to a DNA base in the cluster initiates formation of the hydrogen anion H^- from which the excess charge is efficiently transferred to the neutral product (NB-H) radical.
- This work will be continued by doping of helium droplets with water and nucleobase molecules