

The use of isotope and site labeling for the identification of DEA peaks in biomolecules

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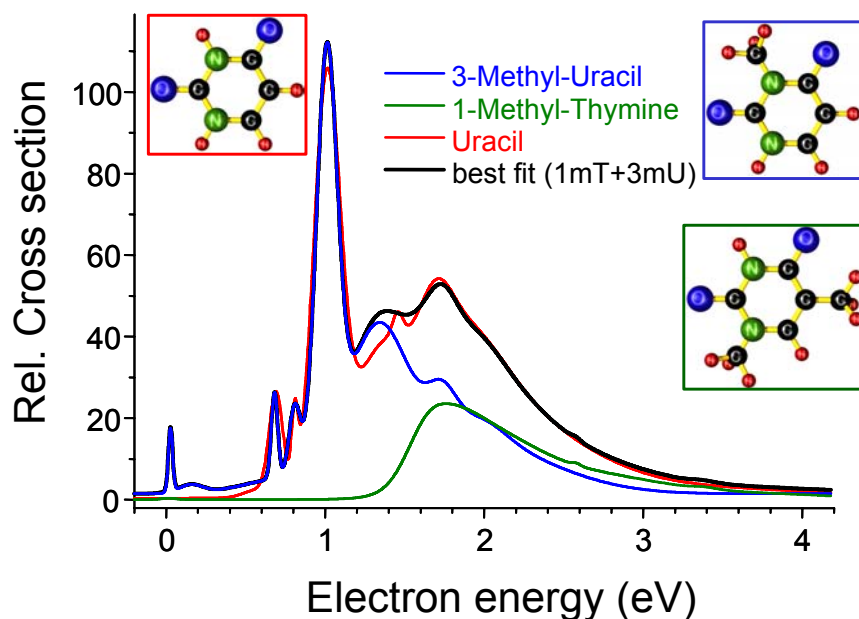
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Free electron attachment to gas phase nucleobases (NB) leads exclusively to the formation of fragment anions. For most of the biomolecules studied so far, the most dominant reaction channel is



For the pyrimidine bases uracil (U) and thymine (T) the attachment cross section in the electron energy range between 1 and 3 eV reveals several narrow resonances [1]. By using partially deuterated T with deuterium connected to all carbon atoms it is possible to show that all these resonances originate from the loss of hydrogen from the two nitrogen sites [2]. However, in DNA T forms a glycosidic bond between the 1N nitrogen and the 1C carbon atom of the deoxyribose and thus the 1N hydrogen atom is missing. Furthermore, the other N-hydrogen is part of a hydrogen bridge to adenine. Attachment cross sections for the H loss from thymidine and 1-methyl-thymine (1mT) show a smooth asymmetric resonance at about 2 eV that can be assigned to the loss of the N3 hydrogen atom. Alternatively, the use of 3-methyl-uracil (3mU) leads to hydrogen abstraction exclusively from the N1 position. The Figure below shows the relative partial cross sections for the dehydrogenated anions of U, 1mT and 3mU. The solid black line is a fit of a superposition of the (1mT-H)⁻ and (3mU-H)⁻ curves to the (U-H)⁻ curve.



The complementary reaction channel of (1) is the formation of H⁻. For the formation of H⁻ from U and T the attachment cross section shows four resonances in the energy range between 5 and 12 eV. Experiments with partly deuterated T and methylated pyrimidine bases show that the different peaks in the H⁻ ion yield can be associated to the loss from the different molecular sites [3]. The

energy dependence for H⁻ abstraction from the carbon sites shows a remarkable resemblance to the energy dependence of strand breaks observed in plasmid DNA [4] suggesting that this reaction may be an important initial step towards strand breaks.

[1] S. Denifl et al., *J. Phys. Chem. A* **108** (2004) 6562

[2] H. Abdoul-Carime et al., *Phys. Rev. Lett.* **92** (2004) 168103

[3] S. Ptasińska et al., *Angew. Chem. Int. Ed.* **44** (2005) 1647

[4] B. Boudaiffa et al., *Science* **278** (2000) 1658