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Photofragmentation of a DNA nucleoside thymidine; valence- vs. core ionization

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Synopsis The photofragmentation of free thymidine molecule has been studied using combined electron- and ion spectroscopy. The results show that valence- and core ionization processes produce very different fragmentation patterns and that regardless of the photon energy, the photoionization leads almost always to dissociation of the thymidine molecule.

Although a vast number of different studies concerning the fragmentation of DNA and its components have been carried out during last decades, not so much is known about the fragmentation of free nucleosides. This is partly due to the difficulties to produce intact nucleosides since they tend to crack or polymerize if one for example tries to evaporate them. Thymidine, however, has a small (~ 20K) temperature gap, where it evaporates without any significant thermal cracking. This gives an excellent opportunity to study different fragmentation processes of free thymidine molecules; photofragmentation following valence- and core ionization in this case.

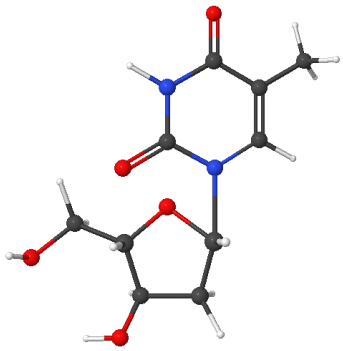

Figure 1. Thymidine molecule ($C_{10}H_{14}N_2O_5$) consists of a nucleobase, thymine (upper ring), and a sugar, deoxyribose (lower ring).

Our experiments were carried out using 50 eV and 330 eV synchrotron radiation combined with electron energy resolved photoelectron-photoion-(photoion) coinciden-ce spectroscopy. This is, to our knowledge, the first study on fragmentation of free thymidine molecules using photons instead of electrons [1, 2].

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The results show several interesting features concerning the valence ionization compared to core ionization of the sample molecule. While the valence ionization causes the molecule to fragment mainly between the sugar-base bond, the core ionization is much more violent producing fragments with relatively small masses. Moreover, comparison of fragmentation between thymidine, thymine and deoxyribose shows that thymine is clearly the more stable component in thymidine molecule than deoxyribose. Especially the small fragments resulting from the core ionization of thymidine seem to originate mostly from the sugar part. This suggests that it is not necessarily the base-sugar or the sugar-phosphate bonds, that are the weak links in DNA.

References

[1] S. Ptasińska *et al.* 2006 *Angew. Chem. Int. Ed.* **45** 1893.
[2] S. Ptasińska *et al.* 2005 *Chem. Phys. Lett.* **409** 270.

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