State-dependent fragmentation of protonated uracil and uridine

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Synopsis

Protonated uracil (m/z 113) and uridine (m/z 245) were exposed to synchrotron radiation in the photon energy range of 4.5 to 9 eV. The yield of various fragments as a function of photon energy shows maxima that can be attributed to excited electronic states and compared to calculated vertical excitation energies. For the nucleoside uridine, much less fragments were observed, indicating a stabilization of the nucleobase through the attached sugar molecule.

Nucleobases and nucleosides have large absorption cross sections for ultraviolet light. It is still not fully understood how the molecules relax from these photo-excited states and how radiation-induced damage is efficiently prevented. Recording the fragment mass spectra of gas phase molecules after irradiation can give important information to test theoretical models of de-excitation and fragmentation.

Many experiments have been performed on neutral species using synchrotron radiation, which provides high intensity and can be tuned over a wide spectral range [1]. Combining synchrotron radiation with Electrospray Ionization sources (ESI) and a tandem mass spectrometer [2] opens additional possibilities: On the one hand, (de)protonated or hydrated clusters can be investigated as first steps towards solvation. On the other hand, the pre-existing charge allows a mass-spectrometric approach to excited states that are below the ionization threshold of the neutral species.

Our contribution shows recent results for the protonated nucleobase uracil that exhibits a rich fragmentation behavior in the region of 4-9 eV photon energy [3]. Several distinct maxima in the fragment yields as a function of energy are visible (see Fig. 1).

Comparing these peaks with calculated excitation energies of protonated uracil allows investigating how excited states relate to the various fragments.

Photoexcitation of uridine, the nucleoside of uracil, in the same energy range shows almost exclusively protonated uracil as a charged fragment. This indicates that electronic excitation is efficiently driven into the weakest bond, the link between the sugar and the nucleobase and thus the nucleobase itself is stabilized.

Figure 1. Fragment yields of protonated uracil as a function of exciting photon energy. The bars on top of the figure indicate vertical excitation energies calculated using EOM-CCSD for the two most abundant tautomers.

References

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