

XUV induced hydrogen migration in 5-halouracil

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Synopsis This work presents a study of the XUV-induced ultrafast molecular dynamics of 5XU conducted with unprecedented temporal resolution. A clear dynamics occurring in 35 fs for both 5FU and 5BrU has been identified and assigned to the hydrogen migration from the C6 site to the C5 site of the molecule. Since 5XU are routinely used as radio sensitizers, the present work provides new important insights in the XUV induced structural changes responsible for the DNA breaking when these molecules are embedded in the DNA chain for radiotherapy.

The interaction of high-energy photons with complex biomolecules is responsible for many chemical changes the molecule undergoes leading to mutations and ultimately damage. The substitution of the H atom at position 5 of the uracil ring with a halogen atom allows to obtain the 5-Halouracils (5XU). When the DNA of a tumor cell is modified by replacing the thymine nucleobase with 5XU, the cell becomes more sensitive to lethal effects of XUV, X-ray and proton radiation [1]. For this reason 5XU molecules such as 5FU are routinely used as radiosensitizers in tumor radiotherapy.

Here we present a time-resolved study of the XUV-induced ultrafast molecular dynamics of 5XU conducted with unprecedented temporal resolution. Charge dynamics in 5XU was initiated by a short train (sub-2fs) of attosecond pulses, with photon energies in the spectral range between 17 eV and 35 eV, obtained by high-order harmonic generation in krypton. The subsequent dynamics was probed by 4-fs, waveform-controlled visible (NIR-VIS) pulses [2,3].

Time-of-Flight (TOF) spectra for the photofragments of 5FU and 5BrU were recorded using a Velocity Map Spectrometer as a function of the delay between the XUV pump pulse and the NIR-VIS probe pulse. The time dependent yield of most of the fragments displayed clear femtosecond dynamics. In the case of 5FU, the XUV pulse ionizes the molecule catalysing the most probable hydrogen migration from C6 to C5 at the first step of the reaction, leading to the fragment $m/z=44$, C6C5FH (Fig. 1a) and $m/z=32$ whose unique assignment is the HC5F⁺ structure. The pump-probe measurement also reveals that at early times, the NIR-VIS pulse inhibits the hydrogen migration process

thus resulting in a sudden reduction of fragments $m/z=44$ and $m/z=32$, and a consequent increase of fragments $m/z=43$ C6C5F (Fig. b) and $m/z=31$ (C5H). As can be observed in Fig. 1, the rising (decaying) dynamics associated to fragment $m/z=44$ ($m/z=43$) occurs with a time constant of about 35 fs which can be related to the time required by the hydrogen atom to migrate from the C6 site to the C5 site of the molecule. Similar behaviours were observed for the equivalent 5BrU fragments.

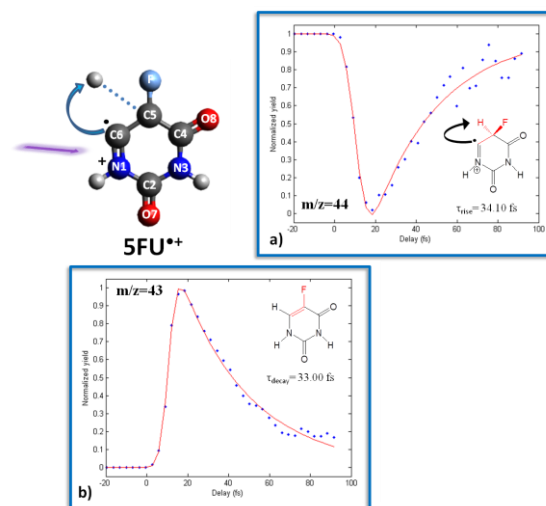


Figure 1. Time dependent yield for fragments a) $m/z=44$ and b) $m/z=43$ of 5FU.

References

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