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Charge and energy flows in ionised thymidine

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Synopsis We present a combined experimental and theoretical study of the ionisation and fragmentation of the nucleoside thymidine in the gas phase. Two sources of ionisation/excitation are used, namely UV photons and low-energy multiply charged ions, associated with coincidences measurements, respectively photoelectron/photofragment (PEPICO) and fragment/fragment. Coupling these experiments with quantum chemistry calculations, we obtain a complete picture of the fragmentation dynamics, in particular the charge and energy transfers within the molecular edifice.

The electronic and nuclear dynamics of complex molecular systems following sudden ionisation/excitation is a key of ultrafast chemical reactions. In particular, a charge migration due to hole formation could occur within the molecular structure at the fs timescale [1]. In the case of multiply charged systems, charges can be localised, e.g. due to the presence of "heavy" atoms, and the subsequent Coulomb explosion is associated with high kinetic energy fragments [2]. An intense and fast excitation is associated with intense fs laser electric field but also with collisions of multiply charged ions. Thus, a detailed knowledge of the response of excited complex molecular systems following photoionisation or ion collisions is of fundamental importance.

Moreover, with the development of radiotherapy including hadrontherapy, i.e. based on irradiation with protons or carbon ions, a better understanding of the radiation damage requires a multi-scale and -disciplinary approach. In this context, the molecular scale approach relies on studies, both experimentally and theoretically, of the ionisation/excitation of molecules of biological interest in the gas phase [3, 4, 5, 6]. Recent coupled experiment/theory works give a rather complete picture of the ion-induced fragmentation of amino acids [5, 6]. However a full comparison of experimental and theoretical results may suffer from the indeterminacy of the excitation energy transferred during the ion collision.

Here, we present a study of the ionisation/fragmentation of thymidine in the gas phase. We are coupling photoionisation and ion collisions experiments with quantum chemistry calculations in order to draw a complete picture of the charge and energy transfers.

Particularly, the comparison of the PEPICO mass spectrum with the calculated orbitals shows the strong dependence of the charge localisation with the excited orbitals. Using the PEPICO method, the fragmentation dynamics is followed as a function of the electronic excitation energy and the appearance energies associated with the opening of the main fragmentation channels are determined. The striking similarities between these energies and the calculated ones in the ground state show that the coupling between the electronic excitation and the vibrational one is highly efficient. Thus, we propose a method to evaluate the energy transferred into the system by ion collision using a fitting procedure of the ion-impact mass spectrum with the different PEPICO mass spectra. The obtained excitation energy distribution corresponds to the one expected.

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