

## Ultrafast non-adiabatic fragmentation dynamics of doubly charged uracil in gas and liquid phase.

P. López-Tarifa<sup>1</sup>, M.-A. Hervé du Penhoat<sup>2</sup>, R. Vuilleumier<sup>3</sup>, M.-P. Gaigeot<sup>4,5</sup>, I. Tavernelli<sup>6</sup>, A. Le Padellec<sup>7,8</sup>, J.-P. Champeaux<sup>9,10</sup>, M. Alcamí<sup>1,\*</sup>, P. Moretto-Capelle<sup>9,10</sup>, F. Martín<sup>1,11</sup> and M.-F. Politis<sup>4</sup>

<sup>1</sup>Departamento de Química, Modulo 13, Universidad Autónoma de Madrid.

<sup>2</sup>IMPMC UMR-CNRS 7590, Université Pierre et Marie Curie, Campus Boucicaut, 75015 Paris, France

<sup>3</sup>Département de Chimie, Ecole Normale Supérieure, 75005 Paris, France

<sup>4</sup>LAMBE, UMR-CNRS 8587, Université d'Evry val d'Essonne, 91025 Evry, France

<sup>5</sup>Institut Universitaire de France, 103 Blvd St Michel, 75005 Paris, France

<sup>6</sup>Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

<sup>7</sup>CESR, Université de Toulouse, UPS, 31028 Toulouse Cedex 9, France

<sup>8</sup>CNRS, UMR5187, F-31028 Toulouse, France

<sup>9</sup>Laboratoire Collisions, Agrégats, Réactivité, Université de Toulouse, UPS, 31062 Toulouse, France

<sup>10</sup>CNRS, UMR 5589, F-31062 Toulouse, France

<sup>11</sup>Instituto Madrileño de Estudios Avanzados en Nanociencia(IMDEA-Nanociencia), 28049 Madrid, Spain

**Synopsis:** We have studied the fragmentation of uracil in both gas phase and water environments. We have applied a combination of time-dependent density functional theory and Born-Oppenheimer molecular dynamics methods to investigate fragmentation of doubly-charged uracil. We also present the results of new ion/ion coincidence measurements in which uracil fragments are produced in collisions with 100 keV protons. Breaking of the molecule in more than two fragments mainly arises from inner shell two-electron vacancies. Orbitals of similar energy and/or localized in similar bonds can lead to very different fragmentation patterns, thus showing the importance of the intramolecular chemical environment. Simulations performed in a liquid environment predict the formation of very different fragments.

Collisions with energetic ions are key processes in radiation damage and modern cancer therapies. The early stages of damage, which occur during the first few femtoseconds after irradiation and lead to fragmentation of the biomolecule, are far from being understood. To unravel the mechanisms at this early stage, we present a combined theoretical and experimental study for the fragmentation of uracil[1]. Ab initio molecular dynamics (MD) calculations based on time-dependent density functional theory (TD-DFT) methods [2] have been used. We consider initially two-electron removal from inner molecular orbitals (MO). Non-adiabatic effects in the fragmentation have been considered by first-principle calculations within the so-called Ehrenfest MD approximation where the mean field potential energy surface driving the nuclear dynamics is computed at the TDDFT level. These methods have been already applied to investigate the radiolysis of bulk and water clusters [3,4].

We show not only that theoretical results are compatible with the experimental ones, but also that fragmentation depends critically on the energy, shape and intramolecular chemical environment of the ionized MO. This suggests that, by targeting specific MOs, damage can be induced rather selectively. Calculations show that production of inner-shell vacancies leads to more than two

fragments and almost never proceeds through the energetically most favourable dissociation path. Besides bond breaking, atom migration leading to the formation of new bonds is also observed. Therefore, one can conclude that the experimental observations are mainly due to sophisticated electronic dynamical effects taking place during the first few fs after removal of electrons.

Similar calculations considering the uracil surrounded by water molecules [5] show that when the electrons are extracted from orbitals equivalent to those of the gas phase calculations, the fragmentation patterns observed are very different. We have also considered the effect of the double ionization of the surrounding water molecules.

### References

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\* E-mail: [manuel.alcami@uam.es](mailto:manuel.alcami@uam.es)