

## Decay of core excited water

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The users and staff of the Gas Phase beamline frequently apply innovative methods to solve scientific problems. One such method is PIFS, or Photon Induced Fluorescence Spectroscopy. This photon-in, photon-out technique consists of exciting a sample with photons and observing the light emitted in the subsequent de-excitation process. Many processes can give rise to fluorescence: an atom may remain neutral and emit one or more photons or emit an electron, producing an ion in an excited state which then decays towards the ground state by emission of one or more photons. A molecule may undergo these processes or it may fragment and the neutral or charged fragments can fluoresce, as shown schematically in fig. 1. A key problem in understanding photodissociation is the detection and analysis of neutral fragments, which are invisible to electron and ion spectroscopies. This is where fluorescence comes in, with its ability to detect excited neutral products which can give significant contributions to, e.g., the energy deposition in radiolytic processes but which can be very hard to detect.

Recently we have carried out a PIFS study of the water molecule excited just below the oxygen K edge; water is the key compound in all radiolytic processes in biomaterials. The oxygen core electrons of the molecule can be excited to antibonding orbitals or to Rydberg states close to threshold. Rydberg electrons have wave functions that are very diffuse so that the electrons can be thought of as having weak overlap with the molecule and, in particular, with the valence electrons. In this model, the core-to-Rydberg excited  $\text{H}_2\text{O}$  is like a core ionised molecule with a diffuse electron bound to the ion.

It is well known from electron spectroscopy that a core ionised water molecule decays predominantly by Auger decay to give a doubly charged ion. Furthermore, it is known from ion spectroscopy that this doubly charged molecular ion usually fragments due to the “Coulomb explosion”, in which the repulsion between the two nearby positive charges rips the molecule apart. From these considerations it was expected that a core-to-Rydberg excited water molecule would fragment, but it was not clear what role the outer electron would play.

We investigated the process of core excitation and decay of water at the Gas Phase Beamline using a fluorescence set-up developed by Marcello Coreno and collaborators (J. El. Spec. **144-147** (2005) 39) and we observed the fluorescence from the Balmer series of hydrogen. Most readers will recall from undergraduate physics that the Balmer series occurs in and near the visible and is due to transitions from higher excited states to the  $n=2$  shell (2s and 2p orbitals). Thus, in this experiment, the fluorescence signal gives information on excited, neutral hydrogen atoms created after excitation of the molecule by soft x-rays.

The spectra are shown in figs. 2 and 3. The Balmer  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  lines correspond to transitions of H atoms with electrons initially in the  $n=3$ , 4, 5 and 6 orbitals respectively. As the excitation energy increases to higher Rydberg states, the

average energy of the emitted radiation increases. This was described using a model where the electron in the Rydberg state could be considered a spectator to the Auger decay of the molecular ion core. Thus, the electron was excited, a double hole state, i.e. doubly positive ion core, was created through the Auger decay, but where would the excited, spectator Rydberg electron go in the ensuing dissociative process? The measurements detected the fraction of decays where the excited electron attached to the dissociating proton leading to a neutral, but excited, hydrogen atom.

That fluorescence from photofragments should show sensitivity in the core-to-Rydberg excitations is fascinating. It can be explained because the Rydberg electron does not participate in the Auger decay, but only reacts to the changed potential when the molecular charge is increased through the ejection of the Auger electron. If the molecule fragments before this electron dissipates its energy, then the leaving proton can capture the electron while retaining the characteristics of its wave function and finally give rise to a Balmer photon in the subsequent de-excitation process.

This work is described in more detail in two recent publications:

E. Melero García, A. Kivimäki, L. G. M. Pettersson, J. Álvarez Ruiz, M. Coreno, M. de Simone, R. Richter, and K. C. Prince, *Phys. Rev. Lett.* **96**, 063003 (2006).

A. Kivimäki, M. de Simone, M. Coreno, V. Feyer, J. Álvarez Ruiz, E. Melero García, G. Vall-Ilosera, R. Richter and K.C. Prince, *J. Phys. B: At. Mol. Opt. Phys.* **39**, 1101 (2006).

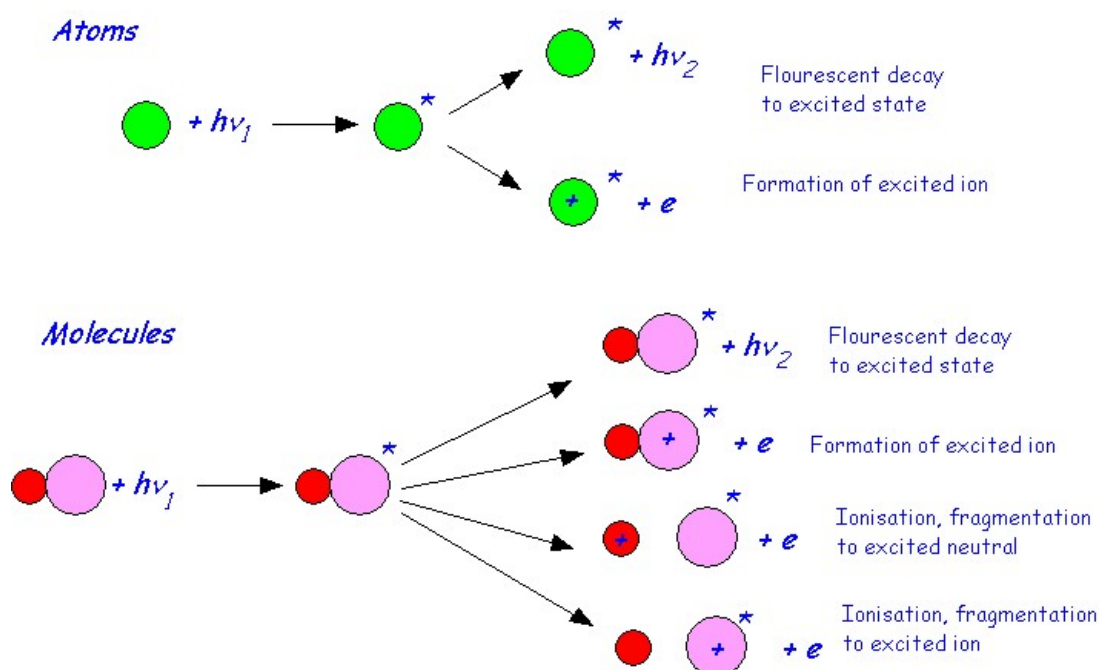


Fig. 1. Schematic view of photoexcitation processes that can lead to species which fluoresce. “+” indicates a positive ion, an asterisk indicates an excited state.

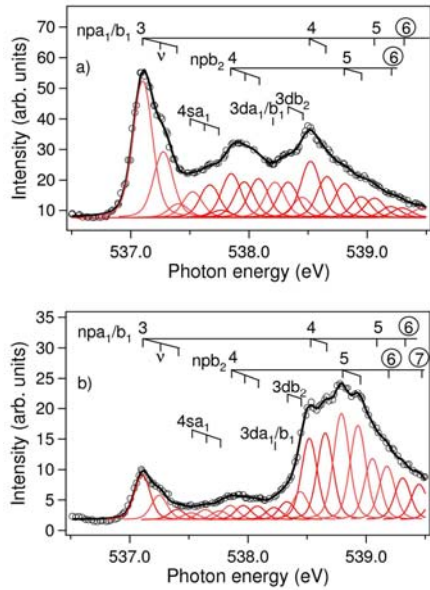


FIG. 2. Upper panel: Balmer- $\alpha$ ; lower panel: Balmer- $\beta$  integrated intensities, measured with a resolution of about 70 meV for the exciting photons. The thick line shows the fit to the experimental points (open circles). The assignments and energy positions (fixed in the fit) are from [10]. Vibrational components are mainly due to excitation of bending motion. Error bars are of the size of the marker.

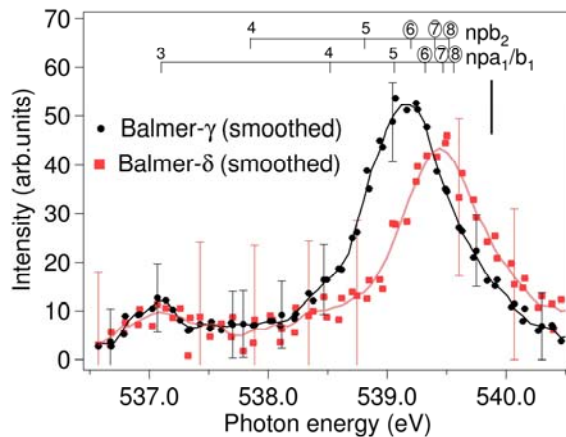


FIG. 3. Balmer- $\gamma$  and Balmer- $\delta$  integrated intensities measured with a resolution of 0.2 eV for the exciting photons. The curves have been arbitrarily scaled for clarity. The vertical line marks the core ionization energy of water.