Resonant Auger Decay of Above-threshold Core-excited H_2O

The study of decay processes of core-excited molecules provides a wealth of information on the nature of the intermediate state and on the dynamics of photoexcitation, photoemission and photofragmentation processes. The typical experimental procedure is to identify resonant processes in photoabsorption measurements, and then to tune the photon energy to the position of a particular resonant feature and to investigate the corresponding valence electron emission. The resonant Auger spectrum thus obtained includes features related to final states with one electron vacancy ("participator" decay) or two electron vacancies and one excited electron ("spectator" decay). It is also possible to identify features related to fragments in the case of dissociation events occuring on the same time scale of electron decay (the so-called "ultrafast" dissociation).

In water, the photoabsorption spectrum around the O *K*-edge has been measured several times, recently with state-of-the-art resolution [1]. In the above-threshold region, the photoabsorption curve is rather flat, without pronounced resonant features. However, in one particular experiment, namely negative ion yield spectroscopy, it has been possible to identify a resonant feature approximately 10 eV above the ionization threshold [2]. This feature has to be related to doubly excited states, since it is well known that there are no shape resonances in water.

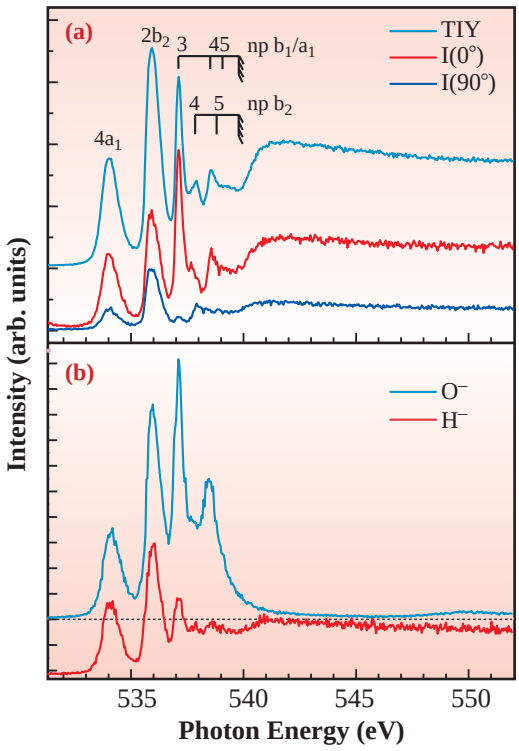

Fig. 1. **(a)** Total ion yield spectrum of H_2O in the O 1*s* excitation region measured with ~ 50 meV photon bandwidth. **(b)** Negative ion yields for the H^- and O^- fragments (curves from Ref. [2]).

In Fig. 1(a), we show the total ion yield spectrum and the angle-resolved ion yield spectra recorded at 0° and 90° with respect to the polarization vector. All spectra appear rather flat in the photon energy region just above the ionization threshold (539.79 eV). At variance with this finding, in Fig. 1(b) from Ref. [2], we show partial ion yield spectra of negative fragments O^- and H^-. It is evident that above threshold the total ion yield spectrum (which we can consider equivalent to photoabsorption) is featureless, while a broad resonance at approximately 10 eV above the threshold is clearly evident in the O^- negative ion yields.

We recorded resonant Auger spectra at several photon energies within the width of the resonance, locating its position with the aid of negative ion yield spectra [3]. The aim was to characterize the possible increase in relative intensity of spectral features related to single-hole final states, and/or to verify the presence of features which could be connected to ultrafast dissociation, i.e. lines derived from resonant Auger decay of the OH fragment rather than from decay of the intact molecule. In a previous work, ultrafast dissociation was investigated in water excited below the O *K*-edge, and the decay spectrum of the OH fragment was well characterized [4].

In Fig. 2 we show resonant Auger spectra recorded at 0° and 90°, I(0) and I(90), respectively, with respect to the polarization vector and the angle-integrated spectrum as given by I(0)+2I(90). The photon energy corresponds to the maximum of the resonance identified in the negative ion yield curves. The decay spectra exhibit a broad feature at a binding energy of 32.2 eV, which is related to an inner-valence molecular state, and superimposed to it some sharp structures with vibrational substructure. The relative position of such features and their vibrational spacing are consistent with the resonant Auger spectrum of the OH fragment [4]. As a further test, we measured the decay spectrum at several different photon energy values within the resonant structure in the absorption. We can confirm the assignment of such peaks as due

to the decay of the OH radical, as indicated in Fig. 2, on the grounds of their dispersion law. Namely, while the molecular structure disperses linearly in kinetic energy as a function of photon energy, thus remaining at constant binding energy, the sharp structures show apparently constant kinetic energy. Such behaviour is typical of spectral features related to fragments [4]. We can conclude that the resonant state evident only in the negative ion yield spectra is dissociative, as proven by the appearance of fragment-related spectral structures. The very high spectral intensity and resolution available at SPring-8 have enabled us to detect such a "hidden" resonant process.

The experiment has been carried out on the c branch of the soft-X-ray photochemistry **BL27SU** [5]. The radiation source is a figure-of-eight undulator that provides linearly polarized light: the polarization vector *E* is horizontal for the first-order harmonic light and vertical for the 0.5-order harmonic light. The monochromator installed on this branch is of Hettrick type and provides monochromatic soft X-rays with the bandwidth ≈ 50 meV in the O 1*s* excitation region.

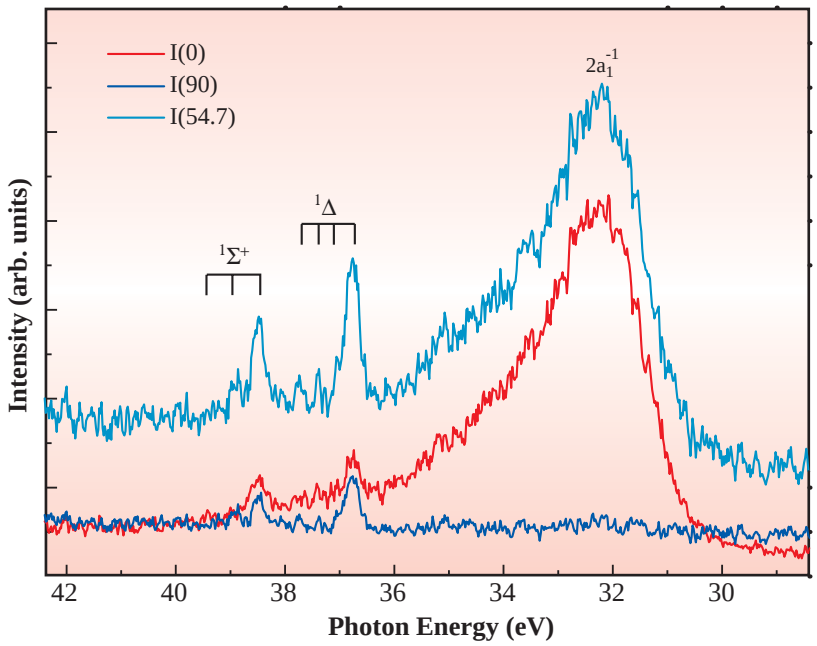

Fig. 2. Resonant Auger spectrum recorded on top of the resonance at ~ 550 eV photon energy [see Fig. 1(b)].

M. N. Piancastelli[a], R. Sankari[b] and K. Ueda[c]

(a) Dept. of Chemical Sciences and Technologies, University "Tor Vergata", Italy
(b) Dept. of Physical Sciences, University of Oulu, Finland
(c) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

E-mail: pianca@roma2.infn.it

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