Resonant Auger decay of above-threshold core-excited H$_2$O

M. N. Piancastelli,[1] R. Sankari,[2] S. Sorensen,[3] A. De Fanis,[4] H. Yoshida,[5] M. Kitajima,[6] H. Tanaka,[6] and K. Ueda[7]

[1]*Department of Chemical Sciences and Technologies, University "Tor Vergata," Rome, Italy*
[2]*Department of Physical Sciences, University of Oulu, Finland*
[3]*Department of Synchrotron Radiation Research, University of Lund, Sweden*
[4]*Japan Synchrotron Radiation Research Institute, Sayo-gun, Hyogo, Japan*
[5]*Department of Physical Science, Hiroshima University, Higashi-Hiroshima, Japan*
[6]*Department of Physics, Sophia University, Tokyo, Japan*
[7]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan*
(Received 15 September 2004; published 18 January 2005)

The decay properties of an above-threshold resonance in core-ionized water, which is difficult to identify with usual spectroscopic methods, have been analyzed by resonant Auger spectroscopy. The resonance is shown to correspond to a doubly excited neutral state embedded in the O 1s ionization continuum. The main result of the experiments is the assessment on the dissociative nature of the intermediate state, with a consequent fragmentation in H neutral plus O*H core excited. This dissociation takes place on the same time scale as electron decay, and therefore is categorized as an ultrafast dissociation process.

INTRODUCTION

The study of decay processes of core-excited molecules provides a wealth of information on the nature of the intermediate state with a core hole and an excited electron, 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 occurring on the same time scale of electron decay (the so-called "ultrafast" dissociation).

The H$_2$O molecule has the C_{2v} symmetry structure [$r_{O-H} = 0.958$ Å; $\theta_{H-O-H} = 104.4°$] in the ground state and the electronic configuration is

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2; 4a_1^0 2b_2^0 (^1A_1).$$

Here 1a_1 and 2a_1 are O 1s and O 2s orbitals, respectively. The outermost orbital 1b_1 has mostly the out-of-plane O 2px character, while the in-plane components O 2pz and O 2py combine with H 1s and form the O-H bonding orbitals 3a_1 and 1b_2, respectively. The unoccupied orbitals 4a_1 and 2b_2 are the antibonding counterparts of these two orbitals, with some admixture of Rydberg character.

The photoabsorption and partial and total ion yield spectra of water around the O K edge have been measured several times (see, e.g., [1]), recently with state-of-the-art resolution [2]. In the below-threshold region (photon energy lower than the O 1s ionization energy) there are two broad resonances corresponding to the promotion of the O 1s orbital to the unoccupied molecular orbitals 4a_1 and 2b_2, with some Ryd-

berg character as well, followed by sharper structures corresponding to transitions to states with pure Rydberg character. 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 [3]. This feature has to be related to doubly excited states, since it is well known that there are no shape resonances in water. It was shown that the O$^-$ production goes to zero above the K-shell threshold, but at a photon energy of about 10 eV above threshold, the O$^-$ yield shows a small maximum with no counterpart in any other yield curve. Since there is no way to produce O$^-$ from a positively doubly charged species such as H$_2$O^{2+} produced after normal Auger decay, the only pathways leading to O$^-$ imply the existence of a singly charged species such as H$_2$O$^+$. As a result, the observed maximum is related to the excitation of neutral doubly excited states, where two electrons, one from the core shell and one from the valence shell, are promoted to unoccupied valence orbitals. Such states are known to decay through resonant Auger processes mainly to singly charged valence ionized states, which then produce the peak centered near 550 eV in the O$^-$ yield. This attribution is confirmed by electron-energy-loss-spectroscopy measurements, where a satellite threshold is reported at higher photon energy [4].

The phenomenon of ultrafast dissociation has been well characterized in below-threshold core excitation of water [5]. In particular, core excitations lead frequently to dissociative or predissociative states. In some cases, the nuclear dynamics is so rapid that dissociation takes place on the same time scale as Auger electron emission. Ultrafast dissociation is a term used to describe dissociation taking place on a time scale comparable to that of the Auger decay, placing it in the low femtosecond regime. This time scale indeed corresponds to the shortest molecular dissociation times. Ultrafast dissociation in water has been seen when exciting to the O 1s → 4a_1 resonance [5]. This conclusion is based on the behav-

ior of the spectral structures when the excitation energy is varied. It is seen that there are two different types of behaviors in the spectrum, one set of structures which displays a linear kinetic-energy dispersion when the photon energy is changed, while another set of structures remains at constant kinetic energy. The structures dispersing linearly are identified as participator or spectator decay in the H_2O molecule, while the nondispersing peaks are assigned as originating from the O^*H fragment, on the grounds of qualitative arguments and *ab initio* calculations of the Auger decay of a $1s \rightarrow 1\pi$ excited OH molecule, which is the same state the O^*H fragment reaches in the dissociation process of the H_2O molecule.

On the grounds of the above-mentioned findings in water, we have performed an experiment in the photon energy region including the above-threshold resonance visible in the negative ion yield spectra. We have obtained several electron decay spectra while spanning the resonance region. The main result is the appearance of two groups of sharp lines in the binding-energy region $36-39$ eV, superimposed to some spectral structures belonging to the inner-valence region. Based on the vibrational substructure of these peaks, and on their dispersion law, we are able to conclude that these lines originate from the resonant Auger decay of the O^*H fragment. Ultrafast dissociation is demonstrated for doubly excited states embedded in an ionization continuum.

EXPERIMENTAL

The experiment has been carried out at the light source SPring-8 in Japan on the *C* branch of the soft x-ray photochemistry beamline 27SU [6]. The radiation source is a figure-8 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 [7]. The monochromator installed on this branch is of Hettrick-type and provides monochromatic soft x rays with the bandwidth ≈ 50 meV in the O $1s$ excitation region. The light is monochromatized using a variable line-space plane grating [8].

The electron spectrometer is a high-resolution Gamma-data Scienta SES-2002 instrument employing a hemispherical electron energy analyzer. The lens and entrance slit system of the spectrometer are placed in the horizontal plane: the entrance slit is parallel to the incoming photon beam direction while the lens axis is perpendicular to it. The resulting linewidth in the resonant Auger spectra of H_2O was about 0.14 eV.

RESULTS AND DISCUSSION

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. [3], 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 con-
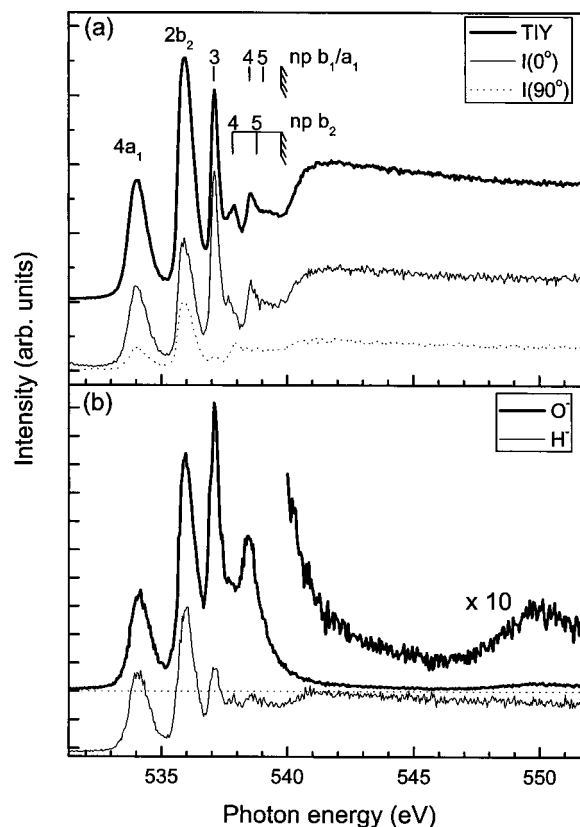

FIG. 1. (a) Total ion yield spectrum of H_2O in the O $1s$ excitation region measured with ~ 50 meV photon bandwidth. (b) Negative ion yields for the H^- and O^- fragments (curves from Ref. [3]).

sider 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 O^*H 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 O^*H fragment was well characterized [5].

In Fig. 2 we report a schematic diagram of the ultrafast dissociation phenomenon in water. If the core excitation leads to a dissociative state, it is possible to distinguish between "early" decay processes taking place in the molecular coordinate region, or "late" Auger decay taking place after the dissociation has occurred, therefore in the O^*H fragment rather than in the intact molecule. This description is simplified, since it has been shown that interference phenomena can occur which make the two pathways to "molecular" or "fragment" decay not really separable [9], but in the water case it is sufficient to account for the experimental findings.

In Fig. 3 we show resonant Auger spectra recorded at 0° and 90°, $I(0)$ and $I(90)$, respectively, with respect to the po-
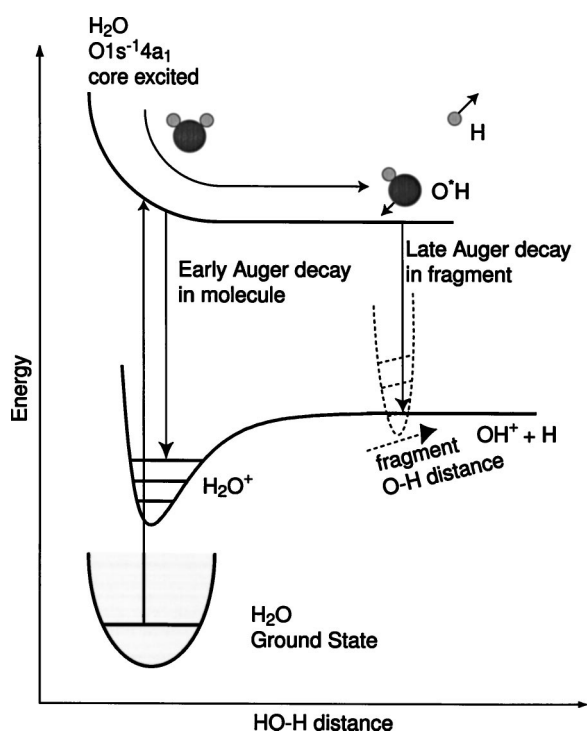
FIG. 2. A schematic and simplified representation of the ultrafast dissociation process in water (from Ref. [4]). Note that this is a cut through the three-dimensional H_2O^+ potential-energy surface along the HO^+-H bond direction. For the OH fragment the potential energy will vary along the O-H coordinate, as indicated by the OH potential-energy curve (broken line).

FIG. 3. Resonant Auger spectrum recorded on top of the resonance at ~550 eV photon energy [see Fig. 1(b)].

larization 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 its high-energy tail, in the binding-energy region 36–39 eV, 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 O*H fragment [5]. 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 O*H radical, 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 behavior is typical of spectral features related to fragments [5]. This behavior can be understood simply on the ground of energy conservation: for decays to molecular final states the only energy dissipation channel is the kinetic energy of the ejected electron, and therefore this energy disperses linearly with the photon energy. In fragment decay there is an additional channel: the nuclear coordinate along which dissociation takes place. Therefore, part of the energy put in the system by the pr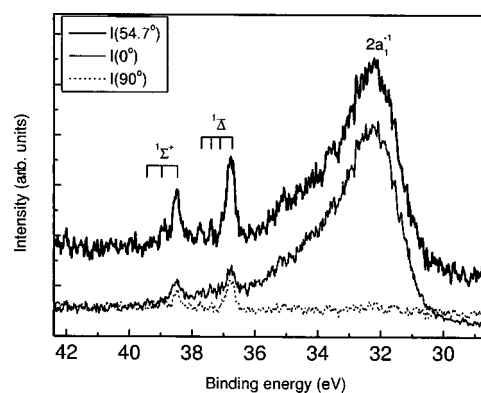imary excitation goes to the motion of the nuclei moving apart and the kinetic energy of the outgoing electron remains constant while the photon energy is changed.

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 next step is the attempt to identify the doubly excited state embedded in the continuum. A way to attack the problem is to examine the O 1s shakeup spectrum of water, and assume that the doubly excited state visible in Fig. 1(b) is below the lowest-lying satellite threshold. The O 1s shakeup spectrum of water has been reported in earlier experimental [10,11] and theoretical works [12–16] and remeasured recently with state-of-the-art resolution at SPring-8 [17]. The first satellite threshold opens at about 17 eV above the O 1s ionization limit, which could be consistent with the position of the above-threshold resonance as a doubly excited state below the satellite ionization limit. The literature assignment for this satellite [13,16] corresponds to a main electronic configuration $1s^{-1}3a_1^{-1}4a_1$, which is consistent with a doubly excited state with two electron vacancies, one in the core orbital and the other one in the $3a_1$ valence orbital. Theoretical calculations outside the scope of this report would be needed for a more precise assignment including the possibility of configuration mixing, as demonstrated in the calculated shakeup electron configurations [16,17].

CONCLUSION

A "hidden" resonance embedded in the O 1s ionization continuum in water has been characterized by resonant Auger spectroscopy. The main result is that the doubly excited core neutral state has a dissociative character, and we are able to detect final states related to molecular decay and final states related to fragment decay. We can single out the spectral structures related to fragments, on the grounds of their dispersion law and their vibrational substructure, as due to the O*H fragment. Therefore, ultrafast dissociation is identified in the decay of a doubly excited state above a core-ionization threshold.

[1] M. N. Piancastelli, F. Heiser, A. Hempelmann, O. Gessner, A. Rüdel, and U. Becker, Phys. Rev. A **59**, 300 (1999).

[2] A. Hiraya *et al.*, Phys. Rev. A **63**, 042705 (2001).

[3] W. C. Stolte *et al.*, Phys. Rev. A **68**, 022701 (2003).

[4] G. R. Wight and C. E. Brion, J. Electron Spectrosc. Relat. Phenom. **4**, 25 (1974).

[5] I. Hjelte *et al.*, Chem. Phys. Lett. **334**, 151 (2001).

[6] H. Ohashi, E. Ishiguro, Y. Tamenori, H. Kishimoto, M. Tanaka, M. Irie, T. Tanaka, and T. Ishikawa, Nucl. Instrum. Methods Phys. Res. A **467–468**, 529 (2001).

[7] T. Tanaka and H. Kitamura, J. Synchrotron Radiat. **3**, 47 (1996).

[8] Y. Tamenori, H. Ohashi, E. Ishiguro, and T. Ishikawa, Rev. Sci. Instrum. **73**, 1588 (2002).

[9] R. Feifel, F. Burmeister, P. Salek, M. N. Piancastelli, M. Bässler, S. L. Sorensen, C. Miron, H. Wang, I. Hjelte, O. Björneholm, A. Naves de Brito, F. Kh. Gel'mukhanov, H. Ågren, and S. Svensson, Phys. Rev. Lett. **85**, 3133 (2000).

[10] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedèn, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[11] K. Siegbahn, J. Electron Spectrosc. Relat. Phenom. **5**, 3 (1974).

[12] S. Svensson, H. Ågren, and U. I. Wahlgren, Chem. Phys. Lett. **38**, 1 (1976).

[13] U. Wahlgren, Mol. Phys. **33**, 1109 (1977).

[14] R. Arneberg, J. Müller, and R. Manne, Chem. Phys. **64**, 249 (1982).

[15] N. Mårtensson, P. Å. Malmquist, S. Svensson, E. Basilier, J. J. Pireaux, U. Gelius, and K. Siegbahn, Nouv. J. Chim. **1**, 191 (1977).

[16] H. Ågren and V. Carravetta, J. Chem. Phys. **87**, 370 (1987).

[17] R. Sankari *et al.* (to be published).