## Fluorescence Emission of Excited Hydrogen Atoms after Core Excitation of Water Vapor

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(Received 2 November 2005; published 17 February 2006)

The Balmer emission from atomic hydrogen has been recorded across the resonances at the oxygen K edge of the water molecule using synchrotron radiation excitation. The emission is observed to be strongest at excitations to Rydberg resonances. The observations are interpreted using a qualitative model for the dynamics of the core-to-Rydberg excited molecule. The model links the quantum state of the core-excited water molecule via resonant Auger decay and subsequent dissociation to the state of the fluorescing hydrogen atom.

DOI: 10.1103/PhysRevLett.96.063003

The study of the radiolysis of water is an active field with big challenges and many important practical applications [1]. Water is ubiquitous and of fundamental importance in fields as diverse as comet formation, studies of biological reactions (taking place in water), or the improvement of water cooled nuclear reactors, to name a few. In this context the response of water to external excitation sources determines the evolution of the system when exposed to these sources.

Gas phase studies usually provide the simplest approach to study the chemistry of water without the complications occurring in the liquid and solid phases. The significant advances in synchrotron radiation sources in recent years have enabled the study of gas phase excited water with a variety of techniques that characterize all the products produced [2-7]. Specifically, unoccupied orbitals and singly charged excited valence configurations are effectively probed with x rays through excitation of core electrons to those unoccupied orbitals. Neutral fragments, which can play an important role in the transmission of energy to the surrounding medium in many systems, are hard to detect because they are insensitive to manipulation by electric and magnetic fields. However, the optical technique of fluorescence spectroscopy is a powerful method for detecting neutral fragments if they are produced in excited states [8] and also determines their internal energy.

In this Letter we report measurements of the Balmer emission from neutral atomic hydrogen (H) after core excitation of the water molecule. The Balmer emission has previously been observed at the Cl 2p inner-shell excitations of HCl [8]. The Balmer series represents transitions from states of principal quantum number  $n'(\geq 3)$  to n = 2, and this allows us to probe the relative populations of hydrogen atoms in n' states after fragmentation of the water molecule. The comparison is not quantitative, because n's and n'd states decay to 2p states with varying branching ratios, whereas n'p states decay predominantly

## PACS numbers: 33.50.Dq, 33.80.Eh

to the ground state (Lyman series) with a lower transition probability for transitions to 2s (for example, 12% for  $3p \rightarrow 2s$ ) [9]. Nevertheless, for a given Balmer line, it is possible to compare different resonances of water.

The measurements were performed at the Gas Phase beam line at Elettra (Trieste, Italy), using water vapor as the sample. The vapor was prepared from distilled liquid water by purifying it through freeze-pump-thaw cycles. The gaseous water was admitted via a hypodermic needle to a stainless steel chamber pumped to  $10^{-7}$  mbar background pressure. The gas pressure in the chamber was kept constant at  $2 \times 10^{-5}$  mbar and the local pressure in the interaction region is estimated to be 10-50 times higher. The vapor from the needle crossed the synchrotron beam at the focal point of a spherical mirror inside the chamber. This mirror collimated the fluorescence light and directed it out of the chamber through a window to a lens that focused it onto the entrance slit of a commercial ACTON 500*i* spectrometer equipped with a 1200 g/mm grating and a CCD detector (PRINCETON 10:100B). The intensities of Balmer- $\alpha$ , Balmer- $\beta$ , Balmer- $\gamma$ , and Balmer- $\delta$ transitions ( $\lambda = 656, 486, 434, \text{ and } 410 \text{ nm}$ ) were recorded as a function of excitation energy across the oxygen Kedge. Simultaneous measurements of ion current and photon flux were also made for normalization purposes. The photon energy scale was calibrated after the measurements to the energies of [10]. The photon resolution used was from 200 to 70 meV.

Water belongs to the  $C_{2\nu}$  point group and its ground state configuration can be written as  $1a_1^22a_1^21b_2^23a_1^21b_1^2(A_1)$ . The unoccupied orbitals include the two antibonding molecular orbitals  $4a_1$  and  $2b_2$  plus several series of Rydberg orbitals. Within this point group, excitations of  $1a_1$  O (1s) electrons are allowed into orbitals of  $a_1$ ,  $b_1$ , and  $b_2$  symmetries [2,10,11].

For small systems made up of low-Z atoms, such as water, the main decay mechanism of resonantly core-

excited molecules is electronic Auger decay, resulting in short lifetimes (3 fs for the O 1s hole in water [4]). This decay process consists of a radiationless transition of the system from the highly energetic configuration of the coreexcited state into states of the molecular ion in which an ejected electron carries away the excess energy. The system is then generally left in singly charged ionic states with either one hole (participator Auger decay) or two holes (spectator Auger decay) in the valence or inner-valence shell. In the spectator case there is also an electron in the orbital that was filled by the excited core electron. Because of this, spectator states are also named two-holes-oneparticle states. Of these two channels, the spectator Auger decay is usually the strongest (more than 90% of the total intensity), and its probability increases with increasing energy of the orbital to which the electron is excited.

Figure 1 displays the measured ion current and the integrated intensities of the Balmer- $\alpha$  ( $n' = 3 \rightarrow n = 2$ ) and Balmer- $\beta$  ( $n' = 4 \rightarrow n = 2$ ) transitions as a function of photon energy in the core excitation region of water. The ion current clearly shows the above-mentioned molecular and some Rydberg resonances and is almost identical to the absorption spectrum by Schirmer et al. [2]. Variations of the relative intensities among the features of fluorescence and ion signals are clearly seen. The  $2b_2$  resonance is the strongest in absorption, but produces less Balmer- $\alpha$  and Balmer- $\beta$  emission than the Rydberg resonances [curves 1(b) and 1(c)]. The  $4a_1$  is also depressed in intensity compared to the  $3pa_1/b_1$  peak. The variations in the  $4a_1$  and  $2b_2$  resonances can be explained by energy considerations. From [12] and the lowest ionization potential of  $H_2O$  [13] the thermochemical threshold to produce  $H(n = 3) + OH^+$  from  $H_2O^+$  is 17.5 eV, while 18.2 eV are needed to produce  $H(n = 4) + OH^+$ . Only final spectator states with internal energies larger than these values



FIG. 1. (a) Measured ion current and integrated intensities of (b) Balmer- $\alpha$  and (c) Balmer- $\beta$  transitions as a function of incident photon energy at the O 1s edge of water. The assignments of the core excitations are from Refs. [2,10]. The vertical line marks the core-ionization energy of water. Error bars are of the size of the marker.

can dissociate in such a way as to result in Balmer- $\alpha$  and Balmer- $\beta$  emission. The resonant Auger spectrum of water has been measured at the first  $(4a_1)$  and third  $(3pa_1/b_1)$ resonances by Hjelte et al. [4] and by Hergenhahn et al. [3], respectively. At the O  $1s \rightarrow 4a_1$  resonance, the spectator part of the spectrum begins at around 5.4 eV of internal energy, and only a small part of the total spectral intensity is due to states with energies above 17.5 eV. At the O 1s  $\rightarrow$  $3pa_1/b_1$  resonance, in contrast, most of the resonant Auger intensity is found in ionic states above 17.5 eV of internal energy [3]. At the O  $1s \rightarrow 2b_2$  resonance, the minimum energy of the final spectator states should lie at some intermediate level, and the relative population of the states above 17.5 eV should be in between those of the  $4a_1$ and  $3pa_1/b_1$  resonances. Therefore, it is not surprising for the intensity of the first three resonances in the Balmer curves in Fig. 1 to follow the order  $3pa_1/b_1 > 2b_2 > 4a_1$ . Ultrafast dissociation into neutral core-excited OH and H, occurring at the first resonance [4], further reduces the yield of excited H atoms since energy considerations [14] require that the H atom is in the ground state.

The increase of the intensity in the Rydberg region of the Balmer curves is particularly strong when compared with the absorption spectrum in Fig. 1. We studied this region with 70 meV resolution for the synchrotron radiation, but even then the individual excitations cannot be separated. Nevertheless, the fits of the recorded Balmer- $\alpha$  and Balmer- $\beta$  curves (Fig. 2) allow us to identify the excitations corresponding to particular Balmer- $\alpha$  or Balmer- $\beta$ emission enhancement. The Balmer- $\alpha$  emission is found to be strongest for the n = 3 and 4 members of the  $npb_1/a_1$ series and for the n = 4 member of the  $npb_2$  series. The Balmer- $\beta$  emission is strongest for the n = 4 and 5 members of the  $npb_1/a_1$  series and the n = 5 member of the  $npb_2$  series. The intensities of Balmer- $\gamma$  and Balmer- $\delta$ displayed in Fig. 3 have their maxima still closer to the O 1s threshold than Balmer- $\alpha$  and Balmer- $\beta$ , corresponding to the higher members of the Rydberg series. Thus, there is a clear correlation between the core excitation of H<sub>2</sub>O and the state of the hydrogen atom after the dissociation of the water molecule.

We propose the following model of the dynamics of the core-to-Rydberg molecule to interpret the data. The emission of the Auger electron increases the positive charge of the potential to which the spectator electron is bound. This causes a collapse of the orbitals to adjust to the new situation and makes it possible for the spectator electron to be *shaken* up or down to another orbital of the same symmetry during the Auger decay. The probability for this shake process is given, in the sudden approximation, by the overlap between the wave function of the excited Rydberg orbital before the Auger decay and the Rydberg orbitals after the decay as  $|\langle n_i \lambda_i | n_f \lambda_f \rangle|^2$ , where  $|n_i \lambda_i \rangle$  and  $|n_f \lambda_f \rangle$  stand for the wave functions of initial and final states of the Auger decay, respectively. Because of the weak interaction of the spectator electron with the rest of the molecule, we



FIG. 2 (color online). (a) Balmer- $\alpha$  and (b) Balmer- $\beta$  integrated intensities measured with a resolution of ~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. The energies of levels circled were calculated with quantum defect calculations based on [10]. Error bars are of the size of the marker.

consider the molecule to be left essentially in a doubly ionized state after the spectator decay. Theoretical and experimental studies of water dications in the gas phase indicate that all configurations are dissociative, and dissociation into  $OH^+ + H^+$  is the strongest channel [15,16]. Thus, we expect the water molecule to dissociate along one OH-H bond due to Coulomb repulsion. However, the molecule is not really doubly ionized, with the spectator electron still bound to the dissociating system. The electron can be bound to either the  $OH^+$  fragment or to the bare



FIG. 3 (color online). 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 energies of levels circled were calculated with quantum defect calculations based on [10]. The vertical line marks the coreionization energy of water.

proton being ejected. The latter case produces an excited H atom that will radiate. Note that the production of excited hydrogen atoms through the explained process is independent of the Auger final state, in contrast to the molecular resonances in which the molecule cannot be considered doubly ionized due to the stronger interaction of the spectator electron with the rest of the system. This independence causes a qualitative difference between the different types of resonances and explains the increased yield of excited H observed at the Rydberg resonances.

There are several ways to check the validity of our model. If we consider the dissociation of the spectator final state to be adiabatic, we expect to have a smooth transition of the spectator electron to the hydrogen potential conserving the nodal structure, i.e., the principal and the angular quantum numbers, the electron wave function had after the collapse. Then the population of H atoms with the electron in the n' shell, and the intensity of the subsequent emission, should depend on the fraction of the initial population of the Rydberg orbital  $|n_i \lambda_i\rangle$  that is shaken during the decay into the Rydberg orbital  $|n'\lambda_f\rangle$  of the same symmetry. Therefore we computed the orbital overlaps  $|\langle n_i \lambda_i | n_f \lambda_f \rangle|^2$  between the initial neutral core-excited and the singly charged final state for the first seven, variationally determined, orbitals of each  $C_{2\nu}$  symmetry species using the STOBE code [17] and an appropriately extended Rydberg basis set [18]. Because of space considerations only the relevant results for Balmer- $\alpha$  are shown in Table I. In the table the numbers represent the overlaps of the Rydberg orbitals  $|n_i \lambda_i\rangle$  corresponding to core-excited resonances in Fig. 2 (not including the vibrational components) with the  $|3\lambda_f\rangle$  orbital of the singly ionized molecule that has a proper symmetry (i.e.,  $\lambda_f = \lambda_i$ ) and atomic n = 3character. Since the calculation was done in  $C_{2\nu}$  symmetry, the molecular notation is used for the orbitals in Table I. For the orbitals  $|n_i \lambda_i\rangle$  of the core-excited states, the main atomic character found is denoted in the parentheses. The final state orbitals  $|3\lambda_f\rangle$  are  $2b_1(3p)$  for  $b_1$  symmetry,  $2b_2(3p)$  for  $b_2$  symmetry, and the average of  $4a_1$ ,  $5a_1(3s + a_2)$ 3p), and  $6a_1(3p)$  for  $a_1$  symmetry.

The theory predicts a nonzero probability of the spectator electron shaking to a  $|3\lambda_f\rangle$  state from any of the Rydberg orbitals into which we can excite the O 1s elec-

TABLE I. Calculated overlaps  $|\langle n_i \lambda_i | 3\lambda_f \rangle|^2$  of the Rydberg orbitals  $|n_i \lambda_i\rangle$  in core-excited states with those orbitals  $|3\lambda_f\rangle$  of the singly ionized molecule (after the Auger decay) that have proper symmetry and character of atomic n = 3 orbitals. See text for details.

$b_1 n_i\lambda_i\rangle$	$b_1 3\lambda_f\rangle$	$b_2 n_i\lambda_i\rangle$	$b_2 3\lambda_f\rangle$	$a_1 n_i\lambda_i\rangle$	$a_1 3\lambda_f\rangle$
$2b_1(3p)$	0.691	$2b_2(3p)$	•••	$5a_1(3s + 3p)$	0.157
$3b_1(4p)$	0.113	$3b_2(4p)$	0.142	$6a_1(3p)$	0.230
$4b_1(5p)$	0.033	$4b_2(5p)$	0.023	$7a_1(4p)$	0.061
$5b_1(6p)$	•••	$5b_2(6p)$	0.008		•••

tron. We cannot, however, directly relate the calculated overlaps to the measured intensities in Fig. 2 since there are many factors, differing for each particular resonance, that have to be taken into account. Our calculations also show that the  $3pb_1/a_1$  ( $2b_1$  in  $C_{2\nu}$ ) has an average radial distance of ca. 7.5 Å, which is in between the radii of the other Rydberg orbitals (12 Å) and of the molecular resonances (~4 Å). The  $3pb_1/a_1$  resonance is thus an intermediate case, and our model may not work satisfactorily for it, since some coupling between the core and the spectator electron still remains. This intermediate character would account for the intensity at this resonance seen in the rest of the measured Balmer transitions [Figs. 2(b) and 3].

A dissociation process of the singly charged water molecule (after the resonant Auger decay) that produces an excited hydrogen atom should also produce an OH<sup>+</sup> ion. The partial ion yield of OH<sup>+</sup> [6] is most intense at the molecular resonances and does not resemble the fluorescence yield of the Balmer- $\alpha$  line, which represents the strongest Balmer emission. However, the OH<sup>+</sup> ion can dissociate further into  $O + H^+$  or  $O^+ + H$ , the total internal energy needed when these fragments are in their ground states and the emitting hydrogen atom is in the n =3 state being ca. 22.6 eV [12]. Apart from the highest kinetic energy Auger peak, the spectator Auger transitions following the O  $1s \rightarrow 3pb_1/a_1$  excitation [3] populate final states with larger internal energies than this limit, making the above-mentioned dissociation processes energetically possible. An enhancement in the O<sup>+</sup> partial ion vield is observed in the Rydberg region in Ref. [6]; hence the ion data do not disagree with our interpretation.

The data and the model presented here lead to conclusions that are relevant at a more general level. The emission of an excited H fragment seems to be triggered by twoholes-one-particle (Rydberg) excited configurations. We postulate that this process is independent of the specific Auger decay that took place and of the nature of the excitation. Basically, any mechanism that can deposit enough energy in the molecule could create such a twoholes-one-particle excited configuration, without having to resort to the very high core energies that are rarely encountered in normal applications.

In summary, Balmer emission (from  $\alpha$  to  $\delta$ ) due to excited H atoms has been measured at the resonances below the oxygen 1s edge in water vapor. For the molecular resonances,  $4a_1$  and  $2b_2$ , the emission is proposed to be proportional to the population of singly ionized final Auger states with internal energies above the dissociation limits for the reactions  $H_2O^+ \rightarrow H(n \ge 3) + OH^+$ . For the coreto-Rydberg resonances the emission was found to be highly sensitive to the particular orbital to which the core electron was excited. Excited H atoms are postulated to be a major decay channel related to the dynamical evolution of two-holes-one-particle (Rydberg) configurations created after the spectator Auger decay of the core hole. Our data suggest that the emission of excited H atoms is a general process independent of how the excited configuration of the ion was achieved. This result in the gas phase should stimulate the search for similar processes yielding excited neutral H in condensed phases of water that could be relevant for more complex applied models.

We thank L. Avaldi for helpful discussions and V. Feyer for assistance during the measurements. The staff at Elettra are thanked for providing good conditions for measurements. The authors acknowledge support by the European Community–Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science").

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