

Observation of core-hole double excitations in water using fluorescence spectroscopy

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The hydrogen Lyman- α , Balmer- α , and Balmer- β emission has been measured from the H_2O molecule at photon energies exceeding the $1s$ ionization threshold. Fluorescence emission is shown to be a sensitive probe to neutral core-hole doubly excited states and singly ionized $1s$ shake-up states that are embedded in the core ionization continuum. In addition, the photoabsorption spectrum of the water molecule in the energy range of the double excitations has been measured with better statistics than previously.

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I. INTRODUCTION

The absorption of a soft x-ray photon by an atom or a molecule can lead to electronic transitions that directly involve both core and valence shells. Water is a prototypical molecule, and such core electron processes in it have been studied in the appropriate excitation region above the O $1s$ ionization limit (539.79 eV [1]). Wight and Brion [2] measured the electron energy loss spectrum of H_2O up to about 30 eV above the K edge. They found a weak, broad structure in the $1s$ ionization continuum and assigned it to simultaneous transitions of K -shell and valence electrons. These doubly excited states converge to the $1s$ shake-up states, whose energies can be conveniently determined from the photoelectron spectrum [1]. The shake-up processes can occur at all energies above the corresponding threshold. Recent partial ion yield measurements of water [3] showed a resonant structure in the yield of O^- ions around 550 eV photon energy. It was not observed in any other partial ion yields, nor even in the total ion yield. (The energy loss spectrum of [2] has too low statistics to reveal any structure in this position.) This structure was attributed to neutral doubly excited states because of its position between the O $1s$ threshold and the first shake-up threshold about 17 eV higher. Later, the resonance at ~ 550 eV photon energy was studied using resonant Auger spectroscopy [4]. These doubly excited states were deduced to have a dissociative character, since decay lines due to the core-excited OH fragments were found in the electron spectra.

Ultraviolet and visible fluorescence spectroscopy is not commonly used in core level studies because this technique does not directly probe core-hole states. But fluorescence can give very precise information on the internal energies of the dissociation fragments, both neutral and ionic. In studies of the below-threshold core excitations in water [5,6], it was recently observed that the Lyman and Balmer emission are particularly enhanced at core-to-Rydberg orbital excitations.

The appearance of the excited H atoms after core excitations in the water molecule was explained as follows. Core-excited states decay mostly via spectator resonant Auger transitions to two-hole one-particle states. If the excited electron resides on a Rydberg orbital after the decay, it is far away from the molecular core and does not interact efficiently with the other electrons. Such a state therefore resembles doubly charged states, which are all dissociative, dissociation into H^+ and OH^+ being the most probable dissociation channel [7]. However, the molecule is not really doubly ionized and the far-away electron may be bound to an excited orbital in either fragment. If the electron is bound to the proton, an excited hydrogen atom is formed and it will radiate.

In the present investigation, we have recorded the Lyman- α , Balmer- α , and Balmer- β emission in the energy range above the $1s$ threshold of the water molecule. The fluorescence is found to be a sensitive probe of core-hole doubly excited states, yielding signal-to-noise ratios superior to those in photoabsorption or total ion yield spectroscopy.

II. EXPERIMENT

The experiments were performed at the Gas Phase Photoemission beamline [8] at the Elettra synchrotron radiation facility in Trieste, Italy. The incoming undulator radiation is monochromatized by a spherical grating monochromator equipped with a movable planar premirror. Photon energies have been calibrated according to the excitation energies of the preedge resonances, as reported by Okada *et al.* [9].

The fluorescence measurements were carried out with the setup that was used in our previous studies [5,6]. Briefly, the Balmer emission was recorded with a fluorescence spectrograph (Acton Spectra Pro 500) equipped with a 1200 lines/mm grating and a liquid nitrogen-cooled charge coupled device detector (Princeton 10:100B). The Lyman- α emission was measured with a photomultiplier (Hamamatsu

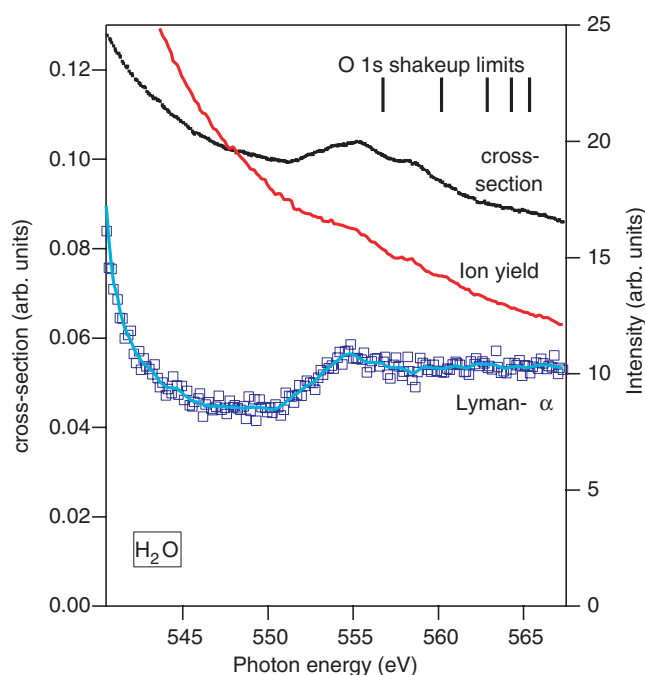


FIG. 1. (Color online) The photoabsorption cross section (dots), total ion yield (solid line), and the Lyman- α emission (open squares) of the water molecule measured with 0.25-eV photon energy resolution in the region above the O $1s$ edge. The thick solid curve across the Lyman data shows the result of smoothing over nine data points. The O $1s$ shakeup limits, taken from [1], are shown with vertical bars.

model R1459) and equipped with a suitable filter (from Acton Research Corporation) with 15 nm bandpass (full width at half maximum) and 10% transmission. The pressure in the chamber was kept in the $(1-2) \times 10^{-5}$ mbar range, but the local pressure in the interaction region is estimated to be 10–50 times higher.

The photoabsorption spectrum of water was measured using a windowless double absorption cell, whose operation has been described by Samson *et al.* [10]. With this setup, the photoabsorption cross section is proportional to the quantity $\ln(I_2/I_1)$, where I_1 and I_2 are the ion currents measured in the two cells that are filled with the studied gas. The gas pressure in this experiment was about 0.5 mbar, as measured by an MKS Baratron capacitance meter. No effort was made to get the result in absolute units, even though that is in principle possible. In order to improve the statistics of the result further, the ion currents were digitally averaged for 10 s at each photon energy.

III. RESULTS

Figure 1 shows the photoabsorption cross section (in arbitrary units) of the water molecule in the energy region above the O $1s$ ionization threshold. For comparison, we also show the ion yield measured simultaneously with the Lyman- α fluorescence using a microsphere detector. The ion yield shows a barely noticeable intensity enhancement around photon energies 555–560 eV, whereas the photoab-

sorption cross section reveals a structure with two local maxima. There is no evident feature in the cross section at 550 eV, where a peak was observed in the O^- ion yield [3]. The vertical bars drawn in Fig. 1 show the O $1s$ shake-up limits, taken from [1]. They represent the energies of the excited core-ionized water molecules with a general electron configuration $1a_1^{-1}(\text{valence})^{-1}(\text{virtual})^1$, where $1a_1$ corresponds to the atomic O $1s$ orbital, “valence” indicates any of the occupied valence orbitals ($2a_1$, $1b_2$, $3a_1$, and $1b_1$) and “virtual” indicates any unoccupied molecular ($4a_1$ and $2b_2$) or Rydberg orbital. The lowest limit of 556.75 eV is attributed to the $1a_1^{-1}3a_1^{-1}4a_1^1$ state [1], achieved by a monopole shake-up transition $3a_1 \rightarrow 4a_1$ taking place simultaneously with the $1s$ ionization.

The first maximum of the photoabsorption structure is located below the lowest O $1s$ shake-up limit. The increase in the photoabsorption cross section must be caused by doubly excited states because there are no other types of new states opening in this excitation energy region and there is no shape resonance above the O $1s$ threshold in water. The second maximum of the structure in the cross section is above the first shake-up limit, but it is still likely to be due to doubly excited states that converge to a higher shake-up limit. Shake-up transitions are energetically possible in this energy range, but they hardly ever create visible features in the photoabsorption spectrum (C_2H_2 may be an exception [11]).

The Lyman- α intensity, also shown in Fig. 1, displays a decreasing intensity above the O $1s$ threshold, but increases again at the excitation energies corresponding to the double excitations. The Lyman- α intensity has a maximum at 554.7 (± 0.3) eV, agreeing well with the first maximum in the photoabsorption cross section. Above the double excitation region, the Lyman- α intensity stays at an elevated level.

In the core excitation region, the Balmer- α line was the most intense visible fluorescence transition from the water molecule [5]. We therefore selected it for an attempt to resolve a possible fine structure in the double excitation region by applying as strict measuring conditions as feasible. The photon energy resolution was set at about 0.12 eV and the average step size was about 70 meV. The measuring time at each photon energy was 5 min, resulting in the total measuring time of around 13 h. The resulting Balmer- α yield is shown in Fig. 2. It has two clear maxima, at ~ 555.4 and ~ 557.6 eV, and a slight shoulder at ~ 553.4 eV. The shoulder may indicate that the first part of the photoabsorption cross-section feature is composed of more than one electronic transition. For intensity reasons, the yield of the Balmer- β emission, also shown in Fig. 2, was recorded with a lower photon energy resolution of 0.5 eV and a larger step size of 0.25 eV. The intensity of the Balmer- α yield just above the O $1s$ threshold is not shown, but from a lower-resolution measurement it was found to have a behavior similar to those of the Lyman- α and Balmer- β yields. The proportional enhancement in intensity around 555 eV is larger for the Balmer lines than for the Lyman- α line. In particular, the Balmer- β line displays a more than twofold intensity at the maximum as compared to the photon energies around 547 eV. The intensity increase below the first O $1s$ shake-up limit can be assigned to double excitations. The maximum of the Balmer- β yield (at about 556.0 eV) is lo-

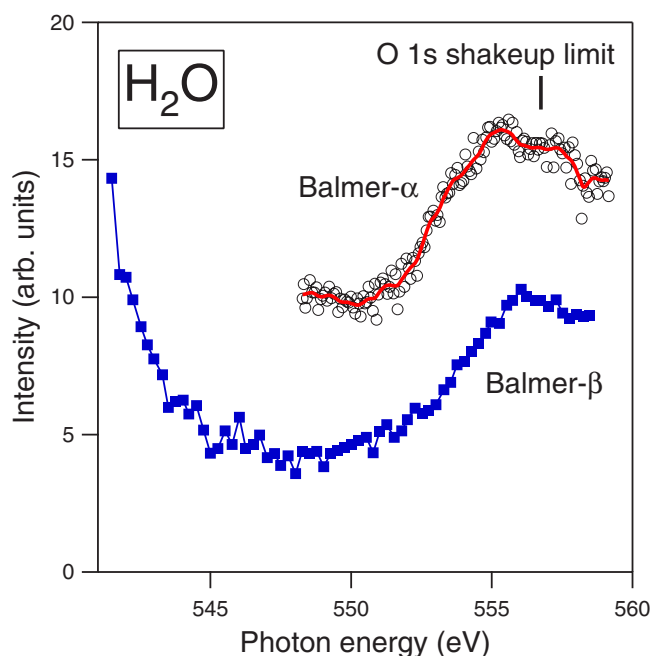


FIG. 2. (Color online) The intensities of the Balmer- α (open circles) and Balmer- β (closed squares) lines in the region above the O $1s$ ionization threshold in H_2O . The thick solid curve indicates the Balmer- α intensity smoothed with nine points adjacent averaging. The lowest O $1s$ shakeup limit occurs in this energy range and is indicated by a vertical bar.

cated at a slightly higher photon energy than the main maximum of the Balmer- α yield (~ 555.4 eV).

IV. DISCUSSION

The most likely explanation of the present observations is that the Lyman and Balmer emission effectively probes the population of the Rydberg orbitals also in the case of doubly excited states. Core-hole doubly excited states can deexcite through Auger transitions so that the possible final states have the following general electron configurations (valence) $^{-1}$, (valence) $^{-2}$ (virtual) 1 or (valence) $^{-3}$ (virtual) 2 . While these Auger transitions have not been studied for the water molecule, there is experimental evidence from methane [12] that the (valence) $^{-2}$ (virtual) 1 states become populated in the decay of the core-hole doubly excited states. These states are identical with the final states reached in spectator Auger decay of the core-excited states below the core level threshold. It was postulated in [5] that the production of excited hydrogen atoms from two-hole one-particle (Rydberg) states does not depend on the way these excited valence states are created initially. Here we have another channel to reach the same states: the decay of doubly excited states in such a way that one of the excited electrons takes part in the Auger transition, while the other one acts as a spectator. One can also expect that the decay of the doubly excited states through double-spectator transitions to the final states (valence) $^{-3}$ (virtual) 2 could lead to the production of excited hydrogen atoms.

We can make some educated guesses of the electron configurations of the doubly excited states. The resonance observed at 550 eV in Ref. [3] is probably due to doubly excited states where both excited electrons are in the antibonding molecular orbitals. The energy of the $1a_1^{-1}3a_1^{-1}4a_1^2$ state, in particular, can be approximated by adding the energies of the O $1s \rightarrow 4a_1$ core excitation (~ 534 eV [13]) and of the $3a_1 \rightarrow 4a_1$ shakeup transition (16.96 eV [1]). The latter transition takes place in the presence of the core hole, so the relaxation of the valence orbitals is taken into account to some extent. An excitation energy of about 551 eV is thus obtained, in good agreement with the position of the resonance. (This method of approximating the energies works within 1 eV for the lowest $1s$ double excitations of isoelectronic Ne, for which all the energies are available [14], if one uses the average energy of the two possible $1s^{-1}2p^{-1}3p^2$ shakeup states.) The population of the antibonding molecular orbitals by two electrons certainly makes the core-excited states repulsive, and would explain the observation of ultrafast dissociation [4].

When one electron is kept in the $4a_1$ orbital and the other one goes to the Rydberg orbitals of increasing principal quantum number, different Rydberg series are formed that converge to the shake-up limit, i.e., the energy position of the $1s^{-1}3a_1^{-1}4a_1$ state [1]. Thus doubly excited states, where higher Rydberg orbitals are involved, are located closer to the shake-up limit. The higher energy position of the Balmer- β yield as compared to that of the Balmer- α yield is probably due to the higher sensitivity of the Balmer- β transitions to the occupation of higher Rydberg orbitals in the molecular ions following resonant Auger decay.

As another example, the energy of the $1a_1^{-1}1b_1^{-1}3pb_1^2$ state can be approximated to be 557.5 eV by adding the O $1s \rightarrow 3pb_1$ core excitation energy of 537.1 eV [9] and the $1b_1 \rightarrow 3p/4pb_1$ shake-up energy of 20.4 eV from the O $1s$ shake-up spectrum [1]. This energy matches very well with the peak position observed above the first shakeup limit in the Balmer- α yield (Fig. 2). The method used for approximating energies may not work well for doubly excited states where the two excited electrons are in different orbitals. This would lead to electron configurations with four open shells and several possible spin couplings between unpaired electrons.

The measurement of the Lyman- α emission was extended above the first five shake-up limits (Fig. 1). The Lyman- α line continues to have an elevated intensity through all of this region. Here doubly excited states converging to different shake-up limits may overlap, leading to a more or less continuous distribution of such states where Rydberg orbitals are occupied. The second O $1s$ shake-up limit at 560.2 eV corresponds to the shake-up states of the type $1a_1^{-1}(\text{valence})^{-1}(\text{Rydberg})^1$ [1]. The spectator-type Auger decay of such states will create (valence) $^{-3}(\text{Rydberg})^1$ states. One can envision that the subsequent dissociation will yield quite likely a proton which with some probability can acquire the Rydberg electron into one of its excited orbitals. It is therefore not unexpected that the decay of shake-up states could also result in Lyman and Balmer emission.

It has once again been shown that the measurement of the cross section is important far above a core ionization thresh-

old, as it is not necessarily proportional to ion yield, and some phenomena may be observed more easily. The cross section shows that the probability of absorption of photons is higher at the core hole double excitations of the water molecule, but the probability of creating ions is not higher (Fig. 1). Therefore the decay paths are changing towards less charged particles. This observation can be explained so that the doubly excited states mostly decay to singly charged ions, whereas core ionization, which is the dominating channel in the photoabsorption cross section at these photon energies, leads to doubly charged ions via normal Auger decay.

V. CONCLUSIONS

We have measured the photon absorption cross section and the intensities of the Lyman- α , Balmer- α , and Balmer- β emission lines at photon energies above the $1s$ ionization limit of the water molecule. They all display enhancements at photon energies below the first shake-up limit, which can only be due to doubly excited states. The production of ex-

cited hydrogen atoms after core-hole double excitations is certainly possible via Auger transitions to two-hole one-particle (Rydberg) states, which were suggested to trigger fluorescence emission after single core excitations in the water molecule [5], but other resonant Auger transitions may contribute to the signal as well. The fluorescence emission is observed to gain intensity also after the Auger decay of the $1s$ shake-up states. Indeed, it appears that whenever a core-hole state is created with an electron excited to a Rydberg orbital, the signature of this can be carried further, via Auger decay and dissociation, to excited hydrogen atoms. The measurement of the Lyman and Balmer fluorescence emission is suggested to be a powerful method to detect weak core excitation processes in the ionization continuum of small molecules containing hydrogen atoms.

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