DISSOCIATION OF GASEOUS CORE-EXCITED WATER STUDIED BY PHOTON INDUCED FLUORESCENCE SPECTROSCOPY

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INTRODUCTION

Hydrogen oxide, or water, is one of the most interesting "simple" molecular systems that can be found. Present in almost all reactions necessary for life, it has received an enormous amount of attention from the scientific community, which year after year expands fundamental knowledge about all its phases [1,2].

The advances seen in recent years in the field of synchrotron radiation have made possible the study of molecular systems after photo-excitation/ionization of core electrons with high-energy resolution. The resulting core-excited/ionized systems are extremely unstable and decay very rapidly, in the order of femtoseconds, yielding different products through which the properties of the intermediate state and the subsequent dynamics can be studied. These studies have unraveled new and exciting physics like the phenomenon of ultra-fast dissociation [3,4]; or the concept of time duration of x-ray Raman scattering [4,5,6]. A review on the present situation of synchrotron radiation core-excited spectroscopy is unfortunately beyond the scope of this introduction. However, the interested reader is referred to reviews of resonant x-ray scattering [7]and the reviews on photoionization dynamics [8,9].

All the mentioned studies and most of the ones reported in the literature are however concerned with the detection of charged particles, mainly electrons and ions, and X-ray fluorescence. Detection of Auger electrons and X-ray fluorescence give information directly about the core-excited state while detection of ions and other electrons and photons provides indirect information gathered from the fragmentation of the molecule. In this scheme, detection of neutral species and estimation of internal energy of the fragments is achieved through fluorescence measurements in the infra-red and visible range since these photons are due to steps in the radiative relaxation chain of excited atoms/molecules. Meyer and coworkers have reported data on core-excited molecules obtained by fluorescence spectroscopy in the UV-visible range [9,10] but this technique is still seldom used. Here we report our latest results obtained at the Gas Phase beamline of the ELETTRA synchrotron radiation facility on fluorescence emission of core-excited gaseous water. The data

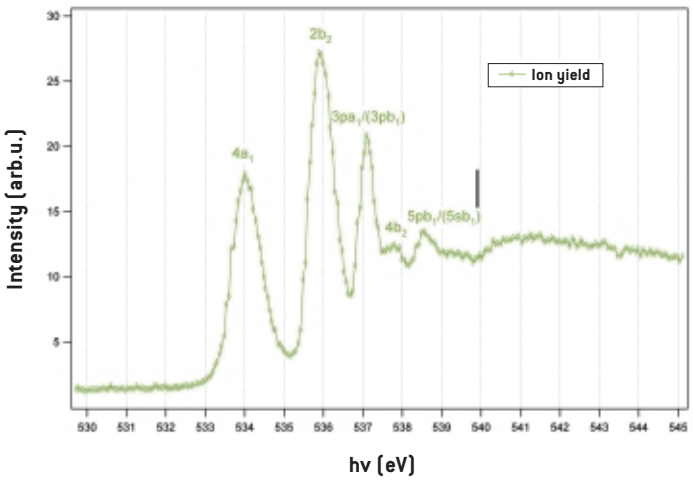

Figure 1. Ion current measured at the region around the 01s edge of water. The assignments and the energy scale calibration are from [14]. The vertical line places the ionization potential of the 0 1s electron (539.9 eV)

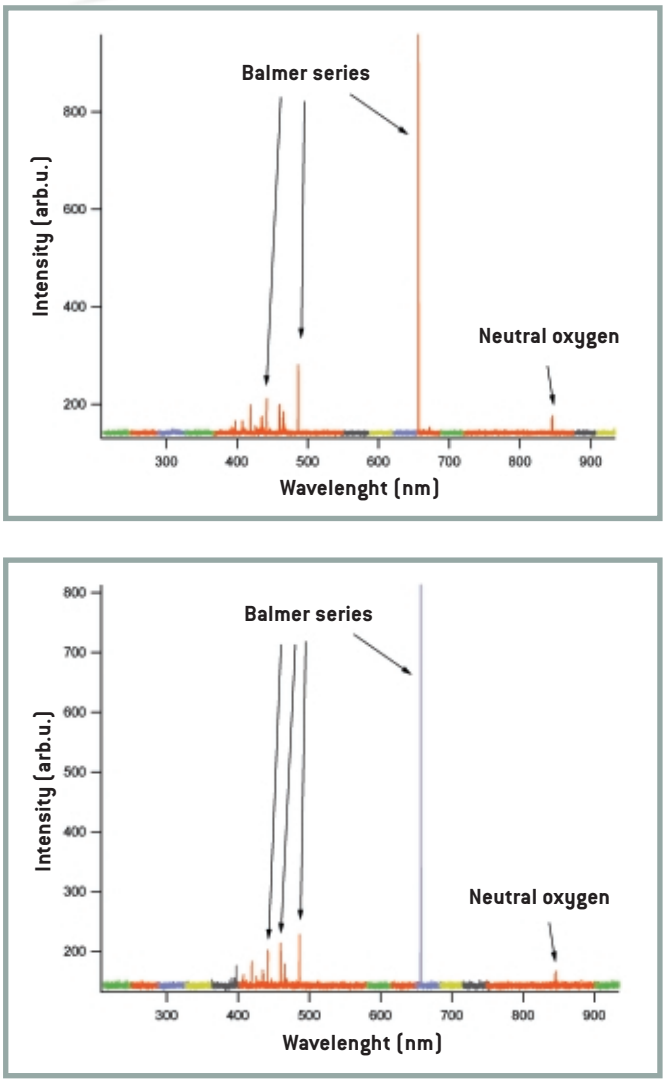

Figure 2. Fluorescence spectra of water taken at the energies of the two first resonances. The most intense line is due to the Balmer α line in the H atom.

shows that fluorescence spectroscopy can yield interesting complementary and also completely new information on the dynamics of core-excited molecules.

EXPERIMENTAL

The experimental set-up was composed of a stainless steel high vacuum chamber pumped by a 1000 l/s turbo molecular pump, with a spherical mirror to collect and collimate the fluorescence. The water introduced from an effusive jet crossed the synchrotron light perpendicularly and the induced fluorescence was collected by the mirror and directed outside of the chamber through a quartz window. A standard optical spectrograph with cooled CCD detector analysed the light. Light flux and the ion signal were measured simultaneously with the fluorescence spectrum.

RESULTS AND DISCUSSION

The absorption of photons in the vicinity of the K-edge of oxygen is dominated by the resonances corresponding to transitions of the O 1s electron to different molecular and Rydberg orbitals (Figure 1). The first resonance $4a_1$, which corresponds to a transition of the core electron to the strongly antibonding $4a_1$ molecular orbital*, is broad and structureless even with very high resolution (~ 55 meV) [11], which is the hallmark of a dissociative state. The second resonance corresponds to the transition to the $2b_2$ molecular orbital and its vibrational structure, with a mixture of stretching and bending motions with a_1 symmetry has been revealed in [12]. The rest of the resonances up to the ionization threshold are Rydberg levels of the molecule (all assignments from [12]).

Figure 2 shows fluorescence spectra measured at the energies corresponding to the two first resonances. In contrast to an earlier fluorescence study [13] with low energy excitation, no molecular bands can be observed in our data and only atomic lines are visible, although the assignment of the dense group of lines between 350 and 500 nm is still undergoing. The spectra are clearly dominated by the Balmer series of neutral hydrogen and specifically by the Balmer α line. The fluorescence was almost zero below the resonances and decreased to zero above the O 1s threshold (539.9 eV) so we conclude that the measured fluorescence comes from the decay of the core-excited states. Since the Balmer series consists of transitions from hydrogen excited to n*l* levels (n>2, *l*=0,1,2), this indicates that many excited hydrogen atoms are emitted by decay of the core excited neutral atom, but much less by decay of the O 1s ionized molecule.

The result of integrating the intensity of the Balmer α line (transitions from the n=3 to n=2 shells of hydrogen) for energies across the resonances below and just above threshold is displayed in Figure 3 together with the ion yield data. Both spectra have been scaled to the same intensity at the $2b_2$ resonance.

* The ground state of H_2O is $(1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^0 2b_2^0)^1A_1$ and it has C_{2v} symmetry

Two main differences can be seen in the spectra. The first difference appears in the intensity of the $4a_1$ resonance and may be related to the ultra-fast dissociation occurring in this resonance which reduces the total amount of atoms that can be emitted in the excited state. However since fluorescence measures the end result of many possible decay cascades, this is only one of many possible explanations, and further experiments are needed. The second difference is the huge change in the relative intensity of the resonances between the ion yield signal and the Balmer α signal at the region of the Rydberg levels. This indicates some preferential decay of the core-excited molecule at the $3pa_1/(3pb_1)$ resonance into fragments containing one excited neutral atom compared to the $4a_1$ and $2b_2$. This preferential process seems to continue for the rest of the Rydberg resonances and is especially dramatic for the Balmer β (transitions from n=4 to n=2 shells) yield as can be clearly seen in Figure 4.

Figure 5 shows the results of plotting the integration of the measured lines of the Balmer series against photon energy. In this case we can see that the different maxima show a clear trend of peaking at a higher energy for higher principal quantum number. A preliminary analysis of the Rydberg series based on quantum defect calculations correlates the maxima measured with the positions of the Rydberg series npa_1 and/or npb_1. This Figure also shows that the intensity of the fluorescence does not go to zero right at the O 1s edge but gradually above it. This behavior can be understood in terms of the post-collision interaction (PCI) in which a fast Auger electron coming from the relaxation of the core-ionized molecule overtakes a slow photoelectron ejected by a photon of energy just above the ionization potential. After the Auger electron overtakes the photoelectron the latter feels a nuclear charge increased by one that can actually recapture the photoelectron.

CONCLUSIONS

The presented data constitutes the first study of fluorescence from core-excited H_2O. The results suggest very interesting new decay dynamics and corroborate already known information on the molecule. They demonstrate the value of photon induced fluorescence spectroscopy in the study of core-excited gaseous molecules.

Upon excitation of one of its O 1s electrons to the Rydberg orbitals the water molecule shows a trend to fragmentation yielding excited neutral hydrogen atoms, which

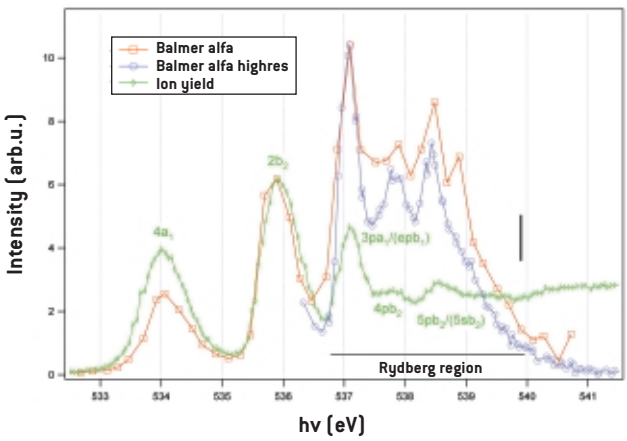

Figure 3. Ion yield and integration of Balmer α plotted against photon energy. Both spectra are scaled to the same intensity at the $2b_2$ resonance

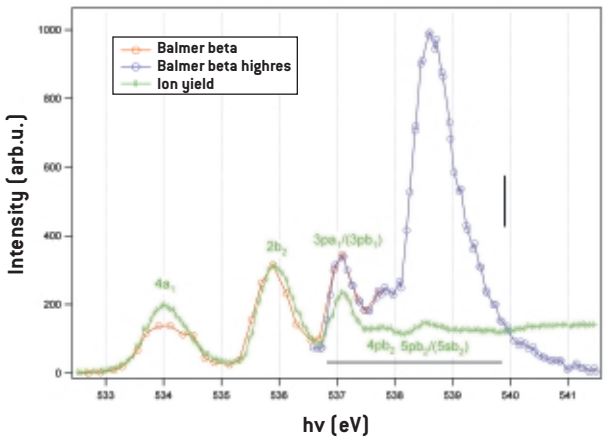

Figure 4. Ion yield and integration of Balmer β plotted against photon energy. Both spectra are scaled to the same intensity at the $2b_2$ resonance.

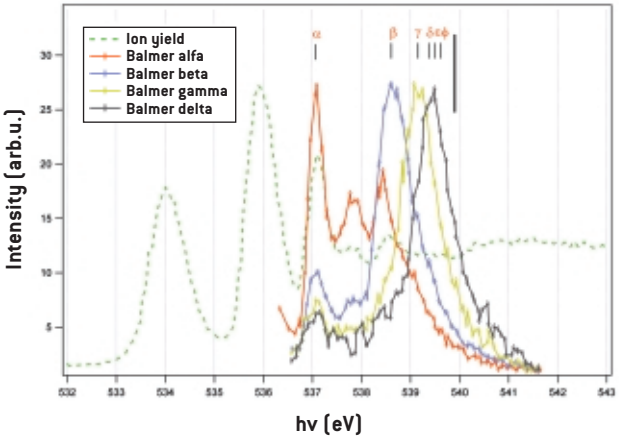

Figure 5. Ion yield and intensities in the region of the Rydbergs excitations of Balmer α to δ (n=3-6) lines plotted against photon energy. The spectra are scaled to display the same maximum intensity and thus no conclusions on relative intensities for the different data should be made. The small vertical lines mark the position of the maximum for the integration of each of the Balmer lines.

have a higher principal quantum number for excitations to higher Rydberg levels. The fluorescence shows signs of the PCI effects and can be tentatively assigned to the Rydberg series (npa_1 and/or npb_1).

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