Photofragmentation dynamics of core-excited water by anion-yield spectroscopy

W. C. Stolte,[1,2] M. M. Sant'Anna,[3] G. Öhrwall,[4] I. Dominguez-Lopez,[5] M. N. Piancastelli,[6] and D. W. Lindle[1]

[1]*Department of Chemistry, University of Nevada, Las Vegas, Nevada 89154-4003, USA*

[2]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

[3]*Department de Física, Pontifícia Universidade Católica do Rio de Janeiro, Caixa Postal 38071, Rio de Janeiro,*
Rio de Janeiro 22452-970, Brazil

[4]*Department of Physics, Uppsala University, Box 530, SE-75121 Uppsala, Sweden*

[5]*Centro National de Metrologia, Caixa Postal 76900 Qrerétaro, Mexico*

[6]*Department of Chemical Sciences and Technologies, University "Tor Vergata," 00133 Rome, Italy*

Partial-anion and- cation yields from H_2O are presented for photon energies near the oxygen K edge. The O^- yield exhibits a feature above threshold attributed to doubly excited states, in contrast to the H^- and cation yields, which are nearly featureless above threshold. Additionally, the lack of the OH^- fragment indicates radiative decay and provides a negligible amount of anion formation.

I. INTRODUCTION

When a core hole is induced in a molecule by photoabsorption, either below or above a core-ionization threshold, dissociation is very likely to occur following or even during electronic relaxation. The main pathway to fragmentation is the decay of the core hole, usually yielding molecular ions either with a single-positive charge (below threshold) or with a double-positive charge (above threshold); the metastable ions subsequently dissociate by breaking one or more chemical bonds. Observation of the molecular or fragment ions produced is informative of the nature of the initially excited or ionized state and of the dynamics of the photofragmentation process. Such experiments are typically performed, with synchrotron radiation as the excitation source, by monitoring the yield of all ion fragments (total-ion-yield mode) or the yields of individual ions (partial-ion-yield mode) as a function of photon energy in the vicinity of a core-ionization threshold.

Due to their low probability for creation following core-hole excitation, anions, thus far, have attracted less attention. Most anion measurements have been performed following valence-shell excitation, although recently several measurements have been performed following core-level excitation [1–6]. The most startling result from the core-level studies is the ability of anion-yield spectroscopy to distinguish shape resonances from other features above the ionization threshold, such as doubly excited states [1]; the complete suppression of shape-resonance features in anion-yield spectra provides an experimental method to verify shape resonances. So far, the only known exception to this new "shape-resonance" rule is SF_6 [2]. Anions have also exhibited 100% site selectivity, where creation of an anion fragment depends, upon which atom in the molecule is initially excited. For instance, methanol yields an OH^- fragment at the carbon $1s$ edge, but not at the oxygen $1s$ edge [3] (carbonyl sulfide displays a similar behavior [4]).

In gas-phase water, high-resolution partial-cation-yield spectroscopy, including both individual ion yields and coincidence yields between two or three cation fragments, has

recently been reported in the photon-energy region near the O $1s$ ionization threshold [7]. The main experimental findings were (1) different fragmentation patterns below and above threshold; (2) the importance of spectator decay of the core-excited state to the subsequent fragmentation process; (3) abundant emission of neutral H at some energies (e.g., it is the most important decay product of the lowest-lying O $1s \rightarrow 4a_1$ resonance below threshold); and (4) resonant formation of the H_2^+ fragment at the O $1s \rightarrow 2b_1$ resonance, which was attributed to a high degree of excitation of the vibrational bending mode.

In the present work, we have obtained partial positive-ion yields in water for all possible fragments with enhanced instrumental resolution and partial-anion yields for the discernible negative ions (O^- and H^-). This work demonstrates that anion yields can provide additional information on the photofragmentation process. In particular, anions, for the most part, originate from decay pathways distinct from the pathways primarily contributing to cation yields. We also are able to address the negligible importance of radiative decay in core-excited water based on the absence of the OH^- fragment. Anion yields appear to be more selective than cation yields in the possibility to observe ultrafast dissociation, which is known to occur in water for the O $1s \rightarrow 4a_1$ resonance on the same time scale as the electronic decay. Furthermore, we show anion-yield spectroscopy is a sensitive tool to detect doubly excited states embedded in the ionization continuum above the K-shell threshold.

II. EXPERIMENT

The measurements were performed on undulator beam line 8.0.1.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The monochromator resolution at 550 eV was ≈ 150 meV, chosen to achieve a reasonable anion signal. The photon energy was calibrated by running a mixture of O_2 and H_2O and comparing the O_2 O1$s \rightarrow \pi^*$ resonance at 540.6 eV [8] with the water spectra. The experimental apparatus used in the present study has been previously described [9]. Basically, it consists of a 180° magnetic
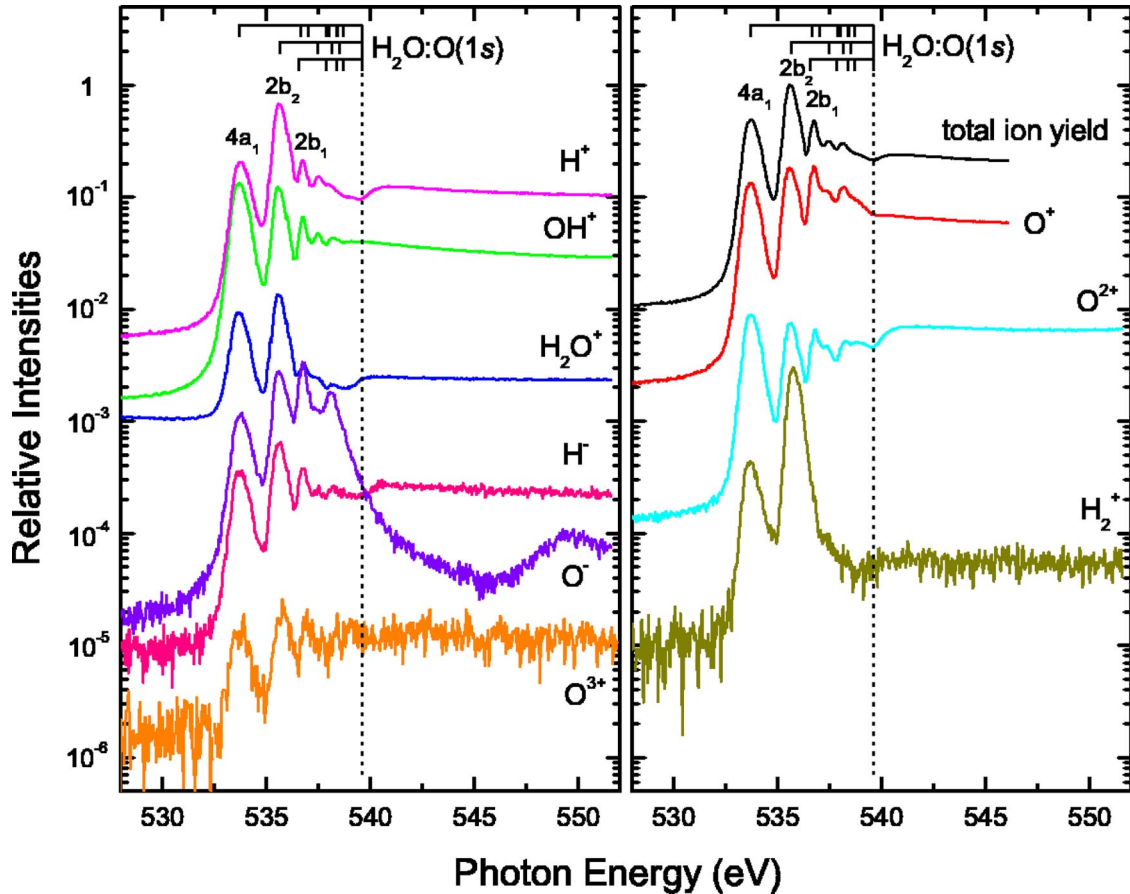
FIG. 1. Relative partial-ionization yields for all measured fragment ions (anions and cations), following photoexcitation of H_2O near the O $1s$ ionization threshold. An intensity value of 1 was given to the calculated maximum of the O $1s \rightarrow 4a_1$ resonance in the total-ion yield.

mass spectrometer (resolution of one mass in 50), a lens system to focus the ions created in the interaction region onto the entrance slit of the mass spectrometer, and an open gas cell which contains both a push plate and an extraction plate to move the ions created in the interaction region into the lens system. The target gas enters the open cell via a 2-mm effusive jet. A channel-electron multiplier (CEM) is used at the exit slit of the magnetic spectrometer to detect the ions. Finally, a differential-pumping system is used to isolate the target chamber vacuum (2×10^{-5} Torr) from the beam line vacuum (1×10^{-9} Torr). The polarity of the lens system, the magnetic field, and the CEM voltages may be switched, allowing measurement of both positive and negative ions produced in the interaction region. An analog output from a MKS pressure manometer was recorded simultaneously with the ion signal to monitor the target-gas pressure. The photon flux was monitored in two ways: with a gold mesh located in the beam line just in front of the apparatus and with a silicon diode located at the rear of the apparatus. The current signals from the mesh and the diode were converted to voltages by a pair of Keithley electrometers, and, along with the voltage output of the manometer, were frequency converted for storage in the data-acquisition computer. Finally, during a period of two-bunch running of the ALS, a time-of-flight mass spectrometer, similar to that described by Masuoka and Samson [10], was used to cali-

brate the relative branching ratios of all cation fragments at the specific photon energies of 545 and 553 eV.

III. CATION OBSERVATIONS

Partial-ion-yield measurements were performed for all detectable anion and cation fragments and are presented on a relative scale in Fig. 1. The anion-yield spectra were placed on this relative scale by assuming the same instrumental efficiency for O^- and O^+ and for H^- and H^+, respectively. A total-ion yield obtained by summing the individual partial-ion yields compares favorably, although with a slightly better resolution, with the previous absorption measurements of Schirmer *et al.* [11] and Piancastelli *et al.* [7]. The two lowest-lying resonant features below threshold at 534.0 and 535.9 eV are assigned as transitions to the $4a_1$ and $2b_2$ unoccupied states, respectively, both with mixed valence-Rydberg character [11], while the sharper features at higher energy correspond to states with pure Rydberg character. The O $1s$ ionization threshold at 539.9 eV also is indicated. Because a comprehensive discussion of partial-cation yields from H_2O exists [7], the discussion presented here highlights only those results that are different with respect to the earlier study.

Although we do not observe vibrational structure in the $1s \rightarrow 2b_2$ resonance, we do observe a 210 meV shift in pho-
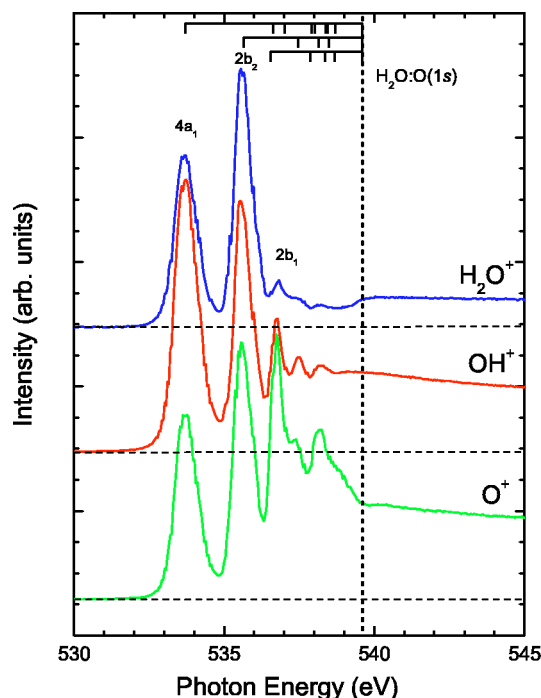
FIG. 2. Comparison of the positive-ion yields for three positive ions: the parent ion H_2O^+ and two of the stronger fragments OH^+ and O^+. For visualization purposes, the intensity scale and the scaling between the shown fragment ions is purely arbitrary.

ton energy towards higher energy for the H_2^+ fragment. Formation of H_2^+ has been attributed to the bending motion mixed with the symmetric-stretching motion [12], the energy offset being due to an increase in bending motion as greater vibrational energy is stored in the core-excited molecular state. This fragment was first observed by Piancastelli *et al.* [7], with a reported shift of 450 meV, and later measured, with vibrational resolution, by Hiraya *et al.* [12], with an observed offset of approximately 200 meV, in excellent agreement with the present observations.

One interesting result is a gradual rise seen in the H_2O^+ fragment leading up to the $1s$ ionization threshold. Unlike the O^{2+} and H^+ ion fragments, this rise occurs before the ionization threshold, and cannot be due to post-collision-interaction effects. A probable explanation for this observation is an increase in the fluorescence yield as the principal quantum number of the Rydberg series leading to the ionization threshold increases, as observed in HCl [13]. Photon-ion coincidence experiments, similar to those recently reported by Meyer *et al.* [13], could verify this hypothesis.

In Fig. 2, we show the partial yields of the parent ion, H_2O^+, and two of the stronger fragments, OH^+ and O^+. An interesting trend is seen in the 537–540 eV spectral region, where the relative intensities of spectral features related to the pure Rydberg states clearly increase along the series $H_2O^+/OH^+/O^+$. Due to the relative delocalization and large spatial extent of the Rydberg orbitals, the core-to-Rydberg-excited states are known to decay primarily through spectator processes to two-hole/one-particle valence final states. In turn, these final states more easily dissociate than single-hole states reached following participator decay. Therefore, more

extensive fragmentation is likely to occur following excitation to a Rydberg state, as we observe along the $H_2O^+/OH^+/O^+$ series, which corresponds to sequential O-H bond ruptures. Similar observations have been made for other polyatomic molecules such as ethylene and acetylene, where the same effect is observed for sequential C-H bond breaking [14].

IV. OVERVIEW OF PROPOSED MECHANISMS

A. Cations

There are several informative differences between the cation and anion yields shown in Figs. 1 and 2. To place the following discussion in context, we begin with an overview of the mechanisms leading to cation and anion production following core excitation.

For fragment cations, the main pathway below the K-shell threshold is dissociation, following spectator decay to final molecular-parent states with either a single- positive charge or a double-positive charge if the initial core-hole decay leads to an intermediate state above the double-ionization threshold. Dissociation leads to a positively charged ion and a neutral fragment, or perhaps two positive ions. Another possible fragmentation pathway for water is ultrafast dissociation [15–17], namely, neutral dissociation of the core-excited state on a time scale competitive to electronic decay, followed by the resonant-Auger decay of one of the fragments. However, this process is hard to identify in cation-yield spectra because it ultimately leads to the same products as fragmentation after electronic decay. Above threshold, the main channel for producing cations is fragmentation of a doubly charged parent molecule formed by the normal Auger decay, and therefore the main pathway is the formation of two cation fragments. In Ref. [7], all possible fragmentation pathways in water, leading to singly and multiply charged cations, are summarized.

B. Anions

In contrast to cations, the main mechanisms for anion production, which represent at most 0.1% of the total fragmentation events in core-excited H_2O, are quite different. The main pathways for anion formation can be distinguished by the charge on the parent H_2O molecule prior to dissociation into an anion and its partner fragment(s), i.e., the parent may be (1) in a neutral excited state; (2) a singly charged cation; (3) a doubly charged cation; or (4) a triply charged cation. To achieve charge balance, the total positive charge on the partner fragment(s) must sum to one, two, three, or, four, respectively. A neutral partner is possible, in addition to a cation, only if the parent H_2O molecule yields three (atomic) fragments.
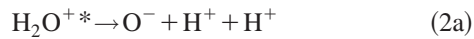
Pathway (1) requires radiative decay of the core-excited state, H_2O^{**}, to a valence-excited state, H_2O^*, which can then yield an anion in several ways:

$$H_2O^* \rightarrow O^- + H^+ + H \tag{1a}$$

$$\rightarrow O^- + H_2^+ \tag{1b}$$

$$\rightarrow H^- + O^+ + H \tag{1c}$$

$$\rightarrow H^- + H^+ + O \tag{1d}$$

$$\rightarrow H^- + OH^+ \tag{1e}$$

$$\rightarrow OH^- + H^+. \tag{1f}$$

The final states in Eqs, (1a) and (1c) may also be reached via an ultrafast dissociation of a neutral H atom from the core-excited neutral parent, followed by a radiative decay of the core-excited OH** fragment and further fragmentation, as indicated.

Pathway (2) involves the emission of one electron, almost exclusively via the resonant-Auger decay to a singly charged, valence-excited parent ion, H_2O^{+*}, prior to fragmentation, which can also yield an anion in several ways:

$$H_2O^{+*} \rightarrow O^- + H^+ + H^+ \tag{2a}$$

$$\rightarrow H^- + O^+ + H^+ \tag{2b}$$

$$\rightarrow H^- + O^{2+} + H \tag{2c}$$

$$\rightarrow H^- + OH^{2+}. \tag{2d}$$

Again, the final state in Eq. (2c) may also be reached via an ultrafast dissociation of a neutral H atom from the core-excited neutral parent, followed by the resonant-Auger decay in the core-excited OH** fragment and further fragmentation, as indicated. While both the O^- and H^- fragments can be produced via pathway (2), there is no possible channel leading to the formation of OH^- following the resonant-Auger decay. In contrast, production of O^-, H^-, as well as OH is possible following radiative decay [pathway (1)]. We therefore can assume that the presence or absence of OH^- indicates the relative importance of radiative decay. The OH^- fragment has been observed in dissociation of methanol [3], so there is no *a priori* reason to expect it to not be observed in H_2O as well. However, the yield of OH^- from H_2O is below our detection limits, indicating that radiative decay of the core-excited parent [pathway (1)] provides a negligible amount of anion formation compared to nonradiative decay modes, at least below the ionization threshold. (Above threshold, radiative decay following core ionization is still possible, of course, but it can never lead to OH^-, which cannot be formed from a positive singly charged parent due to charge conservation.) Evidence for radiative decay also to be negligible above threshold is presented below.

Pathways (3) and (4) involve fragmentation of a multiply charged parent molecule, which can be formed either by the Auger decay above threshold or by the spectator decay below threshold if the energy of the parent ion is above the double- (or triple-) ionization threshold. In both cases, only H^- can be produced, as follows:

$$H_2O^{2+*} \rightarrow H^- + O^{2+} + H^+, \tag{3}$$

$$H_2O^{3+*} \rightarrow H^- + O^{3+} + H^+. \tag{4}$$
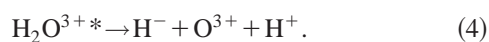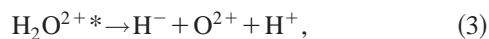
V. ANION OBSERVATIONS

With consideration of pathways (1)–(4) for anion production, we now examine the anion yields in Fig. 1. A common feature of the two anion yields is that the relative intensity of the lowest-lying peak, the O $1s \rightarrow 4a_1$ resonance, is lower than in absorption or total-ion yield [7,11]. This is attributed to the existence of ultrafast dissociation at this resonance, recently reported in water by electron-spectroscopy measurements showing the simultaneous presence of spectral features related to intact water molecules as well as OH** fragments [17]. The neutral core-excited OH** fragment formed by ultrafast dissociation readily undergoes resonant-Auger decay and therefore can be observed in the cation-yield spectra. For it to affect the anion yields, however, OH** would have to decay radiatively, followed by ion-pair formation. Because we have already found radiative decay to be negligible for core-excited water below the O $1s$ ionization threshold, it is reasonable to assume that radiative decay will also be unimportant for OH**. Thus, the relative decrease in intensity of the O $1s \rightarrow 4a_1$ resonance in the anion yields can be related to the fraction of molecules undergoing ultrafast dissociation. In this regard, anion yields may prove more selective than cation yields for observing effects of ultrafast dissociation.

Above threshold, the H^- yield exhibits a peculiar trend compared to previous anion measurements [1–6]: it behaves very similarly to the H^+ and O^{2+} partial-ion yields and the total-ion yield, rather than rapidly dropping back to the background level observed below the K-edge region (e.g., the O^- yield in Fig. 1). Immediately above threshold, the H^- yield shows a gradual rise attributable to PCI effects [6,9] and then becomes essentially flat. The most likely explanation is fragmentation of doubly charged parent molecules via pathway (3). The doubly charged parents can be produced either by the normal Auger decay above threshold or by the spectator resonant-Auger decay below threshold, if the resonant-Auger decay leads to a singly charged state with enough energy to emit a second electron, which should be the case at least for higher-lying Rydberg states just below threshold. Therefore, the unusually large, and relatively flat, H^- yield above about 537 eV can be attributed to fragmentation of doubly charged parent molecules.

A similar pathway, via fragmentation of a doubly charged species, is not possible for O^- production. However, O^- can be produced following photoionization of an O $1s$ electron if, and only if, the resultant core-ionized parent decays radiatively, then follows pathway (2a). Because the O^- yield drops to zero above the K-shell threshold, we take this as further evidence against radiative decay of the core-excited state leading to anion formation, this time in the above-threshold energy region. This decrease to zero above threshold is not abrupt, however, which is explained by the electron recapture of the slow $1s$ photoelectron in the near-threshold region by the parent molecular cation as it undergoes Auger decay, followed by fragmentation via pathway (2a).

At a little higher photon energy, the O^- yield shows a small maximum with no counterpart in any other yield curve.

But, we know O^- is produced neither by pathways (1a) through (1f) nor by pathways (3) or (4), so it must be produced by fragmentation of a singly charged species [pathway (2)]. 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-excited 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 [18].

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