Dissociation and recapture dynamics in H$_2$O following O 1s inner-shell excitation

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Abstract. The emission of low–energy and Auger electrons from H$_2$O has been investigated following photo-excitation/ionization at photon excitation energies just below and just above the O 1s ionization threshold. It is found that neutral oxygen atoms in high Rydberg states are formed. Direct evidence of post-collision interaction (PCI) between the Auger electron and the photo-electron is observed. The initially-excited electron is captured into a Rydberg orbital of H$_2$O$^+$, and remains associated with the oxygen fragment even after the cleavage of both O-H bonds. This implies that the Rydberg states are stable, with the electron behaving as a spectator during the dissociation of H$_2$O$^+$.

1. Introduction

Study of the dynamics of atoms and molecules following photo-excitation in the vicinity of inner-shell ionization thresholds reveals many interesting properties [1-6]. When the excitation energy is within a few hundred meV below an ionization threshold energy, an electron can be excited to a high-n Rydberg state. For photon energies just above threshold, an electron can escape from the ion as a slow photoelectron. The core-hole ion, however, immediately undergoes Auger decay, emitting a fast Auger electron. This leads to a drastic increase in the strength of the Coulomb interaction between the slow out-going photoelectron and the residual ion. As a result, the photoelectron loses kinetic energy to the Auger electron. This phenomenon has been termed the “post collision interaction (PCI)” [1]. If the slow electron loses sufficient kinetic energy it is captured into a high-n ionic Rydberg state as a “recaptured” electron [2, 3].

Recently, the production of neutral hydrogen atoms following photo-excitation near the oxygen 1s ionization threshold of H$_2$O has been reported. Excited atomic hydrogen fragments have been found to be efficiently produced following spectator Auger decay [7-10]. This implies that the initially excited Rydberg electron can be trapped by a fragment H ion following ionization and dissociation. The simple view is that the ejected hydrogen ion captures the Rydberg electron, which remains in a highly excited state. Whereas these studies concentrated on capture by the fragment H ion, the question remained as to whether highly excited O or OH neutral fragments may be also generated through similar processes. If the highly excited O or OH fragment subsequently decays by autoionization, emitting the captured electron, the observation of this electron by electron spectroscopy should allow us to obtain information on the intermediate state of the fragment, and
investigate the dynamics of the decay process when H₂O is excited in the vicinity of the ionization threshold.

Studying such processes as a function of excitation photon energy should provide highly detailed information. Of particular interest is the relation between PCI effects and the recapture processes. The photoelectron loses kinetic energy through the PCI effect when it departs from the ion. In the PCI process, there should be also a corresponding energy gain for the Auger electron. Therefore, by investigating the relationship between the energies of the recaptured photoelectrons and the Auger electrons, we should be able to obtain information on how the electrons interacted.

In this paper we first show that, when an inner-shell electron is ejected from the H₂O molecule near threshold, the slow photoelectron can be captured into a high-n Rydberg state and remain attached to the oxygen ion following the cleavage of both of the O-H bonds. Since excited hydrogen atoms are also generated in this energy region [7-10], this means that the fate of the electron depends on the state and position of the nuclei in the molecule. Preferential population of d orbital angular momentum Rydberg states is observed for the oxygen atoms.

2. Apparatus and experimental method

The experiment was performed at the b-branch of the soft X-ray undulator beamline BL17SU at SPring-8. The beamline is equipped with a high-resolution varied-line-spacing-plane-grating monochromator [11], which can provide a highly stable monochromatic soft x-ray beam with a resolving power of over 10,000 [12]. The polarization of the incident photon beam generated by the multi-polarization-mode undulator can be switched by changing the operational mode of the undulator [13-16], between linear, pseudo-vertical and helical modes. In the present study we have chosen the helical mode to achieve the highest possible photon flux. Energy calibration of the incident photon beam was carried out by recording the total ion yield spectrum from H₂O in the vicinity of the O 1s ionization threshold and comparing with the results of [17]. The photon flux was estimated to be of the order of 10¹¹ photons/sec. The absolute accuracy of the incident photon energy is estimated to be about ±0.1eV.

To record electron kinetic energy spectra using circularly polarized light, we have used a hemispherical electron energy analyzer (VG-Scienta2002) equipped with a gas-cell: both were manufactured by Gammadata-Scienta Ab. The lens axis of the analyzer is fixed in the horizontal direction. The electron analyzer was calibrated by recording the low energy electron spectrum corresponding to the recapture process in Ne in the vicinity of the 1s ionization threshold and comparing to the results of [5]. The resolution of electron analyzer was set to be about 20 meV. The typical pressure in the main chamber housing the gas-cell was about 1.0x10⁻³ Pa during the measurements.

3 Results and discussion

Figure 1 shows the electron kinetic energy spectrum for H₂O recorded at a photon energy of 539.6 eV, 200 meV below the O 1s ionization threshold which is at 539.82 eV [17]. A Rydberg series can be seen converging to a kinetic energy of just over 3 eV. These peaks are due to the autoionization decay of neutral excited states in the oxygen atom which lie above the ionization threshold. The peaks can be assigned to an nδ/δ Rydberg series with n = 3, 4, 5, 6... These electrons are ejected when the core ion changes its electronic state from ²D(2s²2p³) to ⁴S(2s²2p⁴). The transition energy between the ²D(2s²2p³) and ⁴S(2s²2p⁴) states is 3.325 eV [18]. A further Rydberg series is also seen for kinetic energies of around 1.6 eV, although the intensity is weak. These peaks can be assigned as a Rydberg series arising from transitions from the core ionized ³P(2s²2p³) state to the ²D(2s²2p⁴) state. The transition energy between the ³P(2s²2p³) and ²D(2s²2p⁴) states is 1.692 eV [18]. No peaks at energies corresponding to the decay of OH fragments are observed. Table 1 summarizes the observed peaks, their assignments, and a comparison of the observed energies to the optical data from [18].

These results suggest that the initially-excited Rydberg electron remains attached to the oxygen fragment even after the cleavage of both O-H bonds. Even though the binding energy of the Rydberg
Figure 1. Electron spectra of H$_2$O when excited at a photon energy of 539.6 eV.

Table 1: Energy levels (eV) of autoionization states of oxygen atoms

| Kinetic energy (eV) | state | optical data (eV) |
|---------------------|-------|-------------------|
| 1.12                | $2s^22p^4(^3P)6s \rightarrow 2s^22p^3(^3D)$ | 1.102 |
| 1.15                | $2s^22p^4(^3P)5d \rightarrow 2s^22p^3(^3D)$ | 1.143 |
| 1.31                | $2s^22p^4(^3P)6d \rightarrow 2s^22p^3(^3D)$ | 1.311 |
| 1.41                | $2s^22p^4(^3P)7d \rightarrow 2s^22p^3(^3D)$ | 1.413 |
| 1.48                | $2s^22p^4(^3P)8d \rightarrow 2s^22p^3(^3D)$ | 1.478 |
| 1.54                | $2s^22p^4(^3P)9d \rightarrow 2s^22p^3(^3D)$ | 1.524 |
|                     | $2s^22p^3(^3P) \rightarrow 2s^22p^3(^3S)$ | 1.692 |
| 1.78                | $2s^22p^4(^3D)3d \rightarrow 2s^22p^3(^3S)$ | 1.778 |
| 2.16                | ? | ? |
| 2.39                | $2s^22p^3(^3D)5s \rightarrow 2s^22p^3(^3S)$ | 2.380 |
| 2.46                | $2s^22p^3(^3D)4d \rightarrow 2s^22p^3(^3S)$ | 2.467 |
| 2.55                | ? | ? |
| 2.77                | $2s^22p^3(^3D)5d \rightarrow 2s^22p^3(^3S)$ | 2.776 |
| 2.93                | $2s^22p^3(^3D)6d \rightarrow 2s^22p^3(^3S)$ | 2.945 |
| 3.04                | $2s^22p^3(^3D)7d \rightarrow 2s^22p^3(^3S)$ | 3.047 |
| 3.11                | $2s^22p^3(^3D)8d \rightarrow 2s^22p^3(^3S)$ | 3.112 |
| 3.16                | $2s^22p^3(^3D)9d \rightarrow 2s^22p^3(^3S)$ | 3.157 |
| 3.20                | $2s^22p^3(^3D)10d \rightarrow 2s^22p^3(^3S)$ | 3.189 |
| 3.23                | $2s^22p^3(^3D)11d \rightarrow 2s^22p^3(^3S)$ | 3.325 |

* The optical data energies have been averaged over the different spin multiplicities, weighted by the degeneracies.
electron is only around 1 eV, this implies that the highly-excited Rydberg states are very stable, behaving like “spectators” throughout the dissociation process. By studying the fluorescence decay of neutral hydrogen atoms formed when it is the H$^+$ fragment which captures the electron, Melero García et al. [9] observed that the orbital character of the initially-excited electron tends to keeps its orbital character (n, l value) when it is captured. Recently we have observed that metastable (with lifetimes longer than a few microseconds) hydrogen fragments can also be efficiently produced in this excitation energy region [10]. These two observations suggest that there are at least two different recapture decay paths: one in which an ejected hydrogen ion captures the Rydberg electron into an equivalent highly excited state, and one in which the electron remains in a Rydberg state and attached to the excited oxygen ion.

To study further the formation mechanisms of the excited oxygen atoms, we have recorded electron spectra for various photon energies between 539.1 eV (0.7 eV below threshold) and 540.4 eV (0.6 eV above threshold). Figure 2 summarizes these spectra. The spectra clearly show peaks appearing at higher kinetic energies as the photon energy is increased, and that increasing the excitation energy by just a few hundred meV changes the distribution drastically. This suggests that the fate of the initially excited electron is very sensitive to the PCI effect. An increase in excitation energy of only 400 meV (from 539.4 to 539.8 eV) change the peak of the Rydberg state distributions drastically, although the peaks are unresolved for n larger than around 8.

![Figure 2](image_url)

**Figure 2.** Electron spectra of H$_2$O for excitation energies between 539.1 and 540.4 eV.
The spectra shown in figure 1 and 2 are surprising in that it shows mainly transitions from \( nd \) Rydberg states. This is in contrast to similar studies in other systems \([4,6]\). For recapture following 1s-\( \epsilon p \) excitation in the Ne atom, de Fanis \textit{et al.} only observed a strong \( np \) Rydberg series \([4]\). No \( nd \) states were observed. Since the Ne 1s electron can only be excited to an \( np \) Rydberg state with a dipole transition, this implies that the photoelectrons are recaptured to Rydberg states with same orbital angular momentum. In molecules, core-excited \( \text{N}_2 \) shows also the formation of nitrogen atom fragments in high-n Rydberg states \([6]\). The assignment shows that both \( np \) and \( nd \) Rydberg states are populated by the recapture of slow photoelectrons. In contrast, we observe mainly \( nd \) Rydberg states, with the \( np \) Rydberg bands showing only low intensity. For example, the peak expected due to the \( 2s^22p^3(^3\text{D})4p \rightarrow 2s^22p^3(^4\text{S}) \) transition at 1.98 eV is not observed in the spectrum of figure 1. One possible explanation for the domination of \( nd \) states is that the highly excited and recaptured photoelectron already has \( d \)-type character before the dissociation takes place, since in H\(_2\)O the two hydrogen atoms have small positive charges and should attract those electrons. Other possibility is that the Rydberg electrons change character from \( np \) to \( nd \) due to the cleavage of the two O-H bonds. Since we do not have enough information to conclude that such processes occur, calculations of the dissociation dynamics will be necessary to understand our results.

Figure 3 shows the Auger electron spectra for several excitation energies between 539.6 and 550.0 eV. At excitation energies around 540 eV, a shift is seen. Since this shift is only observed in the vicinity of the 1s ionization threshold, it can be attributed to the PCI effect; the Auger electron gains kinetic energy due to the change in the Coulomb potential as it “ overtakes” the slow photoelectron. This energy shift has been estimated by the shift at half-maximum, indicated by the black broken line in figure 3. The shift increases as the threshold energy is approached, reaching 0.58 eV at 539.6 eV (0.2 eV below the threshold). This implies that the average energy gain of the Auger electron due to the PCI effect is 0.58 eV at threshold.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Auger electron spectra of H\(_2\)O when excited at photon energies of 539.6, 540.0, 540.3, 545.0 and 550.0 eV. The intensities are normalized at maximum. The black broken line shows where we have estimated the observed energy shifts.}
\end{figure}
Considering only the PCI effect the initially-excited electron should lose the same 0.58 eV kinetic energy. Assuming that the total energy is conserved, this should result in capture into an $n = 7$ Rydberg state. The $\text{H}_2\text{O}^+$ ion core dissociates into two or three fragments which undergo separation mainly due to Coulomb repulsion. This further changes the interaction potential, but the Rydberg electron can be expected to stay in the same electronic state adiabatically. The peak of the Rydberg distribution seen in figure 1 is at $n = 7$, supporting this dynamical picture. A similar calculation for an incident photon energy of 540.0 eV (0.2 eV above the threshold) gives a final Rydberg state $n = 8$, since the average energy gain of the Auger electron due to the PCI effect is 0.43 eV at this energy. Deconvolution fitting analysis suggests that the Rydberg state distribution in the spectrum of figure 2 has a peak at around $n = 8$, again supporting our interpretation.

4. Summary
We have observed photoelectron recapture following O 1s ionization in H$_2$O by detecting autoionization and Auger electrons. In this paper we first investigate the dynamics of the inner-shell excited electron by detecting the slow electrons emitted when neutral excited oxygen fragments decay by autoionization. It is made clear that the dynamics of the electron depends on the initially excited state. An unsolved issue is what determines the final state of the Rydberg electron following cleavage of the two O-H bonds, and what determines whether it attaches to an H$^+$ fragment or to the O$^+$ fragment. This suggests that dynamical changes to the molecule structure upon the excitation of Rydberg states is very important.

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