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Formation and decay of core-orbital vacancies in the water molecule

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Abstract

Primary steps in the interaction of high energy photons with water creating multiply ionised products are examined experimentally and theoretically. Double Auger decay from a 1s-hole state populates triply ionised states between 80 and 140 eV binding energy. Ejection of one 1s electron and one valence electron gives states around 570 eV which decay to triply ionised states between 75 and 110 eV. Nuclear motion in these states competes with Auger decay and substantially modifies the final state spectra. The double core-hole state from ionisation of both 1s electrons is found at 1171 ± 1 eV and calculated at 1170.85 eV.

INTRODUCTION

Water is not only the most important molecule for life on Earth and the arbiter of possible protoplasmic life on newly discovered exoplanets, it is also abundant in the Universe at large, for instance it has recently been detected in the outflow from a carbon star [1]. In many such astrophysical environments, in the Earth's outer atmosphere and in the clinically important processes of radiotherapy [2, 3], molecules of water are subjected to energetic particle bombardment. The highly excited states initially created in such impacts decay, some by Auger effects, releasing low energy electrons of extreme radiotoxicity. Recent experiments suggest that another, related source of such particles is intermolecular coulombic decay of inner valence orbitals, where electronically excited atoms and molecules embedded in a medium decay efficiently by transferring their excess energy to neighbouring species in the environment and ionising them, thus creating low energy electrons and radical cations (see Refs. [4–6] and references therein).

For energy transfers of more than 540 eV to the water molecule, the major initial process is formation of a vacancy in the 1s core-orbital of the O atom. Two of the initial decay processes for such core holes have been thoroughly investigated, namely single Auger decay [7–10] and soft X-ray emission [11, 12]. A third decay process of the simple hole state, double Auger decay leading to triply charged products, has hardly been studied at all. At somewhat higher energy transfers, collisions can create initial states with a core vacancy and simultaneous ejection of a valence electron; these are called core-valence states (see, for instance, Refs. [13–16] and references therein) or shake-off states and their energies and decay processes are hitherto unknown. At even higher energies it becomes possible to create a double vacancy in the core, that is, in the present context, a hollow molecule with no electrons left in the 1s orbital [17–28]. States of this sort are so far unknown in water, but certainly of interest and possibly significant. Recent theoretical predictions [29] indicate, for instance, that the traditional separation between ionisation and dissociation may be particularly inadequate in the case of double core-hole formation.

In this work we use an efficient multi-coincidence electron spectroscopy technique together with photoionisation by synchrotron radiation from a storage ring to examine the double Auger effect and the higher energy effects in ionisation of free water molecules. In this way we characterize the electronic energy levels initially populated in multiply ionised water

molecules which, because of the rapidity of electronic transitions, are still close to the neutral molecule geometry. The molecules afterwards dissociate to a range of ionised fragments in reactions which have been examined previously under high energy particle impact [3, 30]. In such impacts the whole energetically accessible range of initial electronic states can be populated, in unknown proportions. In the present work we specify the initial states and in future work we hope to extend these investigations using a new experimental method [31] to discover the products formed specifically from each initial ionised state.

EXPERIMENT

Experiments were carried out at the synchrotron radiation facility BESSY-II in Berlin using beam line U49/2-PGM-2 [32]. The storage ring was operated in single-bunch mode, delivering light pulses at 800.5 ns spacing. The principle of the multi-electron coincidence technique applied in the present study has been described in detail before [15, 33] and thus only the aspects of it relevant in the present context will be briefly given. Water molecules are introduced into the spectrometer chamber in the form of an effusive gas beam which is crossed by the monochromatized synchrotron radiation beam. The light-matter interaction point is located at one end of the 2 m long magnetic bottle instrument which consists of a strong divergent field of a permanent magnet (~ 0.5 T) confined by a soft iron pole piece and a weak homogeneous magnetic field (~ 10 's of mT) of a long solenoid. Electrons created in an ionisation event are captured by the magnetic field lines and guided towards the MCP detector located at the other end of the flight tube. The electron flight times are referenced to the light pulse signal. The flight time to energy conversion is calibrated using photoelectron lines and Auger lines of Xe [34], recorded before and after each sample run, together with the Auger electron and valence photoelectron signals from water itself within each run. Because of the comparatively long flight tube, arrival times of slower electrons can exceed the light bunch spacing. In order to assign the electrons to the correct ionising light pulse we have relied in this work on detection of high energy Auger electrons from the events of interest. Whenever an inner shell hole on O is created, at least one Auger electron is emitted with sufficient energy (> 22 eV) to arrive within the first 800 ns. The resolving power of the apparatus for single electrons can be expressed as a fixed numerical resolution $E/\Delta E$ of about 50 for electron energies above 1 eV, and a fixed resolution ΔE of about 20

meV at lower energies.

THEORY

Ab initio calculations for the vertical ionisation energies creating the valence triply ionised states (VVV), core-valence doubly ionised states (CV), double core-hole states (CC) and resonant states with double core holes of a water molecule were performed using complete active space self-consistent field (CASSCF) methods [35]. The molecular geometry of the water molecule used in these calculations were optimized at the second-order Møller-Plesset level of theory (MP2) [36] with the correlation-consistent polarized valence triple zeta (cc-pVTZ) basis sets of Dunning [37]. We used the active space comprising all the occupied molecular orbitals (except for the 1s orbital of the oxygen atom) and all valence unoccupied orbitals. Thus, the active space of the CASSCF calculations consists of six orbitals $2a_1$, $1b_2$, $3a_1$, $1b_1$, $4a_1$ and $2b_2$ with core occupancy being fixed. The cc-pCVTZ basis sets were employed in the CASSCF calculations. The CASSCF calculations were performed with the MOLPRO 2010 quantum chemistry package [38].

In order to investigate dynamical effects in the CV states whose two holes are in the 1s core and the $1b_1$ orbitals, an excited state dynamics calculation was performed within the framework of Density Functional Theory (DFT). The initial geometry is the ground state equilibrium structure. The initial velocity for each atom was set to zero. The time step in the simulation was set to 0.1 fs. The Verlet integrator was applied to solve the classical equations of motion and the trajectory calculations were propagated for 10 fs, which is sufficiently long to see the trend of this dissociation. The calculations have been performed using the STOBEDEMON program [39].

RESULTS AND DISCUSSION

Triple ionisation of water by the double Auger effect

Figure 1 shows triple ionisation spectra of water produced by double Auger decay from the O1s hole state, measured in photoionisation at two different photon energies. Because the Auger energies are high the resolution is not better than about 10 eV and the scale calibration has an uncertainty of about ± 5 eV. The spectra have essentially the same shape

at these and other photon energies, showing three broad bands with peaks at about 88, 108 and 125 eV binding energy. By comparison with the photoelectron spectrum of water [40–42], where the valence bands (12.6, 14.7 and 18.4 eV) are centred at roughly 15 eV and the O2s-based inner valence band is at 32 eV, we can attribute the three bands crudely as 1: states with three outer valence vacancies; 2: states with two outer valence and one inner valence vacancy; and 3: states with one outer valence and two inner valence vacancies. This rough assignment is in agreement with the energies of states with leading configurations of these three types in our calculations and in the calculations of Handke *et al.* [43] and also with the relative band intensities. Taking simple hole configurations only, allowing for doublets and quartets and assuming that Auger decay from outer valence (OV) and inner valence (IV) orbitals is equally probable, we count six OV-hole only configurations, six with one IV hole and two OV holes and three with two IV holes and one OV hole. Because of the real differences between the different valence orbitals, the prevalence of configuration mixing and the contributions of 4-hole-1-particle configurations in this energy range, there are in fact many more distinguishable states than the fifteen enumerated above. There are so many (cf. Table I) that to compare them with the experimental spectra in Fig. 1, we have given all simple configuration weights proportional to their squared coefficients in the CI expansion and folded the resulting energies with a Gaussian of 10 eV half-width. Because in normal Auger decay singlets are strongly favoured relative to triplets [45], we compare with separate theoretical spectra including either doublets only or both doublets and quartets. The comparison indicates that in this double Auger process, doublets are preferred. The agreement between theory and experiment is good.

To relate the triple ionisation spectrum to subsequent dissociation processes we note that the thermodynamic onset for ground state products $2\text{H}^+ + \text{O}^+$ is 50.6 eV, for $\text{H}^+ + \text{O}^{2+} + \text{H}$ it is 72.1 eV and for $2\text{H} + \text{O}^{3+}$ it is 113.4 eV. Thus even from the lowest energy triply ionised states initially formed the first two sets of products must be produced with excess energy, either as kinetic energy or as internal energy. The total kinetic energy of 36 eV found for $2\text{H}^+ + \text{O}^+$ by Alvarado *et al.* [3] under particle bombardment is consistent with these products being formed in low energy internal states from the lower energy band of triply ionised water states shown in Fig. 1. At the peak of the first band at about 88 eV the available energy for forming ground state products is $88 - 51 = 37$ eV.

The mechanism of the double Auger effect can be inferred to some extent from the

distribution of energy between the two outgoing Auger electrons. The spectrum shown in Fig. 2 is monotonic, showing no marked features beyond the U-shaped asymmetric distribution favouring one high and one low energy electron. This form of distribution suggests that the double Auger decay is essentially *direct*, that is, it does not involve major participation of intermediate super-excited doubly ionised states. Cascade Auger decay might contribute smooth distributions and so avoid simple detection if all the states involved are unbound. But because the most probable intermediates are doubly charged water states based on three-hole one-particle configurations of relatively low energy, any such cascade Auger decay would manifest itself as an excess of very low and very high energy electrons. To reduce the risk of including such cascade decays in the spectra of Fig. 1, events were selected where all the Auger energies were above 40 eV. This choice also eliminates cascade Auger decays from the doubly-ionised states above the triple ionisation limit, which are populated in the single Auger process and are known from the Auger spectrum [8]. Careful examination of coincidence maps covering the range of the low energy electrons shows that there is, in fact, a very small fraction ($< 1\%$) of cascade decay involving formation of superexcited O^* atoms (presumably with two H^+ ions), which autoionise. Because of severe overlap by background from secondary electrons combined with the much more abundant single Auger decay, we have not been able to characterize this cascade process in detail.

The core-valence states

Figure 3 shows the core-valence doubly ionised states of H_2O^{2+} formed at two photon energies. The probability of forming these states is low, only about 3% at 650 eV relative to overall core-hole formation. The tripartite nature of the spectral band, particularly at 620 eV, is reminiscent of the three valence ionised states of water, well known from the He I photoelectron spectrum [41, 42]. Such correspondence between core-valence and pure valence ionisation spectra is not uncommon [15, 16], and on this basis we attribute the three bands mainly to core plus $1b_1$, $3a_1$ and $1b_2$ orbital ionisations, respectively. Surprisingly, there is no sign of core ionisation together with inner valence ionisation from the orbitals based on O 2s. To compare the experimental spectrum with theory, Fig. 3 shows two spectra calculated from the state energies (given in Table II). In one spectrum all states, including those with an IV hole are given equal weight. In the other, triplet states and singlet states are weighted

statistically 3:1 and IV states are ignored. Comparison with experiment suggests that the statistical weighting is nearer the truth.

The core-valence states decay mainly by emission of a single Auger electron, thereby populating triply ionised final states. Because the emitted electron is of high energy, the apparatus function is again about 10 eV wide in the resulting spectra of $[\text{H}_2\text{O}]^{3+}$, the same as in the double Auger spectra. Two spectra which arise by Auger decay from the two main bands in the CV spectrum (IP range 568-570 and 570-575 eV) are shown in Fig. 4, to be contrasted with a triple ionisation spectrum from direct double Auger decay of the simple core hole. The major difference in shape (essentially one peak, not three) must arise from the different factors governing single and double Auger decays. The substantial shift of the lowest triple ionisation to lower energy is explained by a very rapid change in geometry of the core-valence state towards complete dissociation. This is to be expected for a doubly ionised state of water and is demonstrated by explicit DFT calculations of the rate of dissociation as shown in Fig. 5. The symmetrical dissociation to $\text{O} + 2\text{H}$ species is not exclusive, but even this pathway which we have calculated is so rapid that it competes with the Auger decay. It is unsurprising that different core-valence states decay to different final states as demonstrated by Fig. 3 but to explain such differences in detail will require much more extensive calculations.

The double core holes

Figure 6 shows the spectra of the H_2O^{2+} state containing a double core hole (a), together with the spectrum of the lower energy state in which the double core hole is dressed with one electron in an otherwise unoccupied excited orbital (b) (presumably based on $2p_z$). The energy of the double core-hole state at 1171 ± 1 eV and its associated pre-edge feature at 1156 ± 1 eV is in good agreement with our theoretical values given in Table III. Theory predicts two resonances separated by 1.6 eV that are not readily resolved in the present experiments.

The major decay process of the double core hole state is successive emission of two Auger electrons. The spectrum of the first of these could in principle be extracted, but the statistics are far from satisfactory, despite the comparatively long runtime (7 h) devoted to the measurement. Because the second Auger electron energy is overlapped by the much

more abundant electrons from single Auger decay, we cannot extract its spectrum nor that of quadruply ionised water, which is the final product of double core-hole decay.

Triple ionisation energies of the water molecule were calculated several years ago within the ADC (algebraic diagrammatic construction) scheme [43] at the equilibrium geometry of the neutral molecule and have been recalculated by us using the CASSCF method. Both theoretical approaches give vertical triple ionisation energies of water near 83 eV which is above the apparent experimental onset seen in Fig. 1. The main reason for this discrepancy is the limited experimental resolution, but it should also be borne in mind that in the double Auger process the relevant molecular geometry is that of the single core hole state and not that of the neutral molecule. Another reason could be that the spread of nuclear coordinates from zero-point motion and thermal excitation will always allow a lower ionisation threshold than the true adiabatic one when the final state is entirely dissociative.

The energy distribution of the electrons produced in the double Auger process (cf. Fig. 2) has major peaks between 0 and 40 eV and at around 400 eV, energies at which some of the electrons are highly radiotoxic. Since water is a major constituent of living tissue we believe that these electrons may play a significant part in radiotherapy. Formation of double core holes, although of great interest, probably plays no part in tissue damage.

CONCLUSIONS

In this work we have investigated the formation and decay of high energy ionised states from photoionisation of free water molecules. As the photon energy is increased, above the one-photon double ionisation threshold of 33 eV [44] and one-photon triple ionisation whose threshold we can now estimate as about 80 eV, a major change comes with excitation or ionisation of a 1s core electron. At higher photon energies it becomes possible to ionise both a 1s electron and a valence electron and ultimately to ionise both 1s electrons leaving a hollow molecule. Double Auger decay of the single 1s hole state contributes a significant fraction of the whole, and releases electrons concentrated in the ranges 0-40 eV which are probably active in radiotherapy. Comparison between our experimental final state spectra and the theoretical spectra (cf. Fig. 1) confirms the expectation (cf. Ref. [45]) that doublets should be generally favoured relative to quartet states in the double Auger process. The higher energy core-hole states lead to triple and ultimately quadruple ionisation with

emission of further electrons of energy in the 400 - 500 eV range. The energies of the initial and final states in these processes can now be calculated reliably. A next step in this ongoing investigation will be to characterize the ionic fragmentation products and their energies as they emerge from the different primary electronic processes delineated here.

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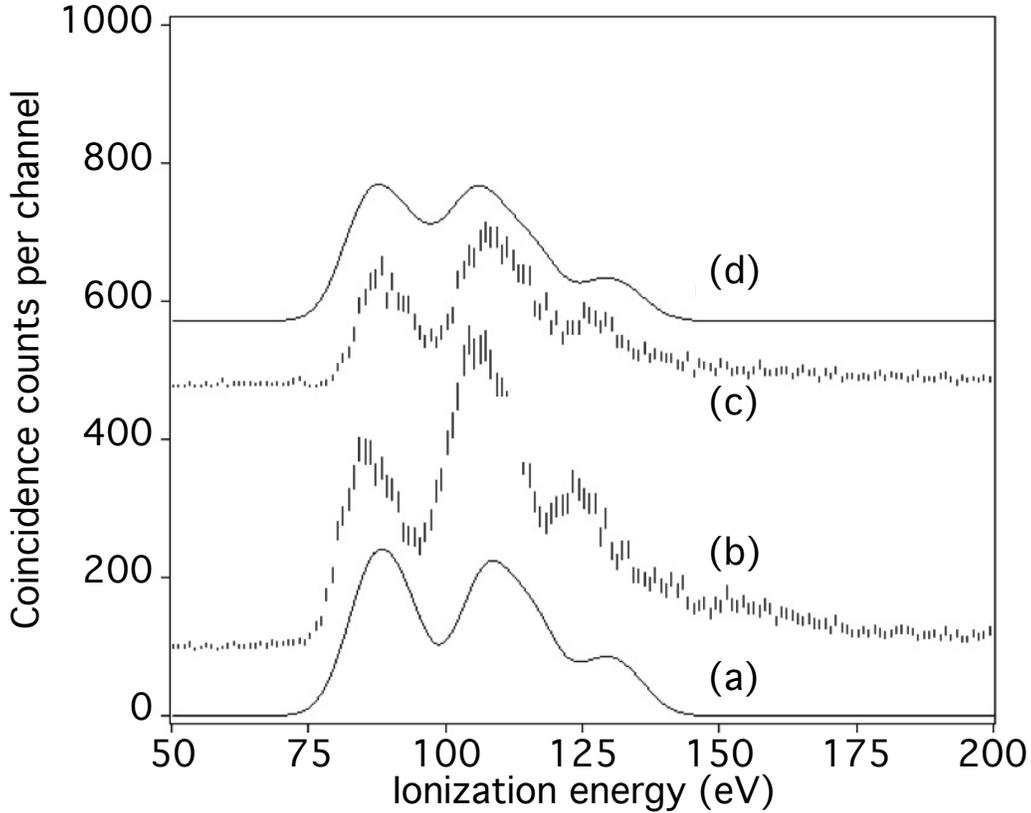


FIG. 1. Triple ionisation spectra of water from double Auger decay of the simple $1s$ -hole state at 539.8 eV. (a) Theoretical spectrum showing doublet final states only. (b) Experimental spectrum taken at 1300 eV photon energy. (c) Experimental spectrum at 650 eV photon energy. (d) Theoretical spectrum including both doublet and quartet states. In the theoretical spectra each state has been weighted by the sum of squared coefficients for simple three-hole configurations in the CI expansion of the final state wavefunction. The instrumental resolution has been simulated as a Gaussian of 10 eV FWHM, but no allowance has been made for any spread of nuclear coordinates. The difference in relative peak intensity between the experimental spectra at the two photon energies may be due to a difference in experimental conditions, particularly the solenoid current, which affects the collection efficiencies for high energy electrons.

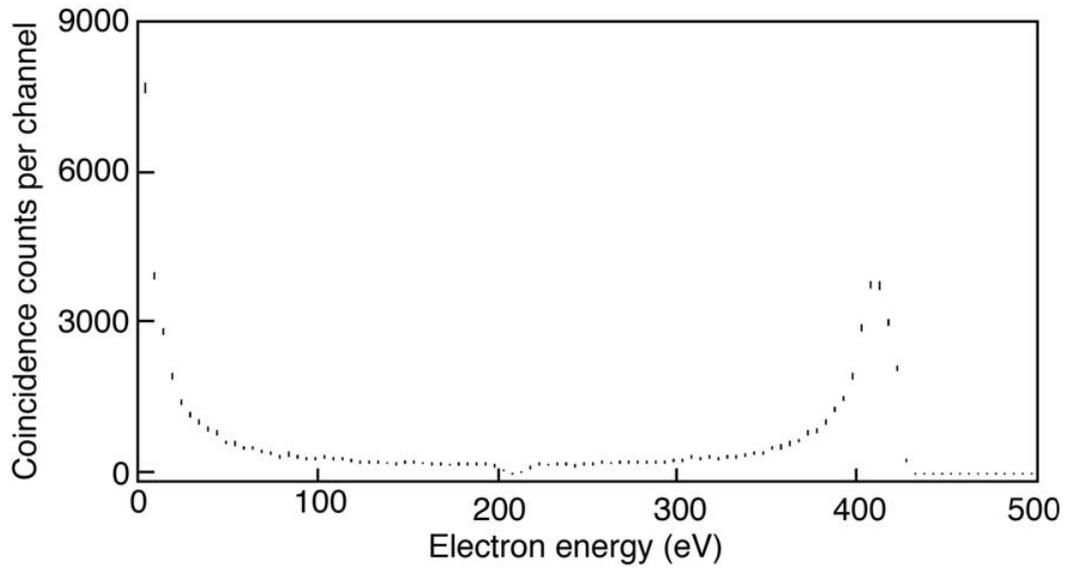


FIG. 2. Distribution of energy between the two electrons emitted in double Auger decay of the $O1s^{-1}$ hole state of water forming $[H_2O]^{3+}$ at around 110 eV. The difference in width and height between the low and high energy horns of the distribution is due entirely to the difference in energy resolution for low and high energy electrons.

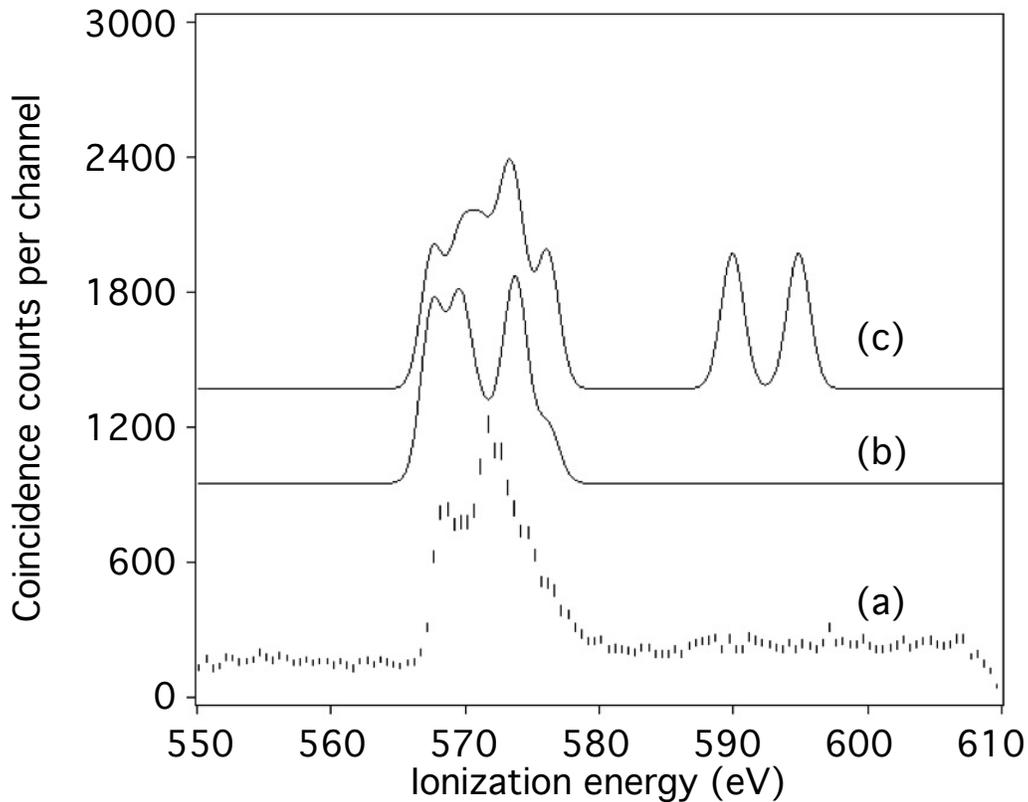


FIG. 3. Spectra of the core-valence states of water, where one electron is missing from the $1s$ shell and one from the outer shells. (a) Experimental spectrum at 620 eV photon energy. (b) Theoretical spectrum with the triplet states given a weight of 3, singlet states weight 1 and states involving loss of an inner valence ($2a_1$) electron given zero weight. (c) Theoretical spectrum where all states, including the inner-valence ionisations, are equally weighted. For the theoretical spectrum the instrumental resolution and spread over the nuclear coordinates have been represented by a Gaussian broadening function of 2 eV FWHM. The pure instrumental broadening should be 1 eV, but as several of these states are thought to be bound, additional broadening due to the spread of the vibrational wavefunction is expected.

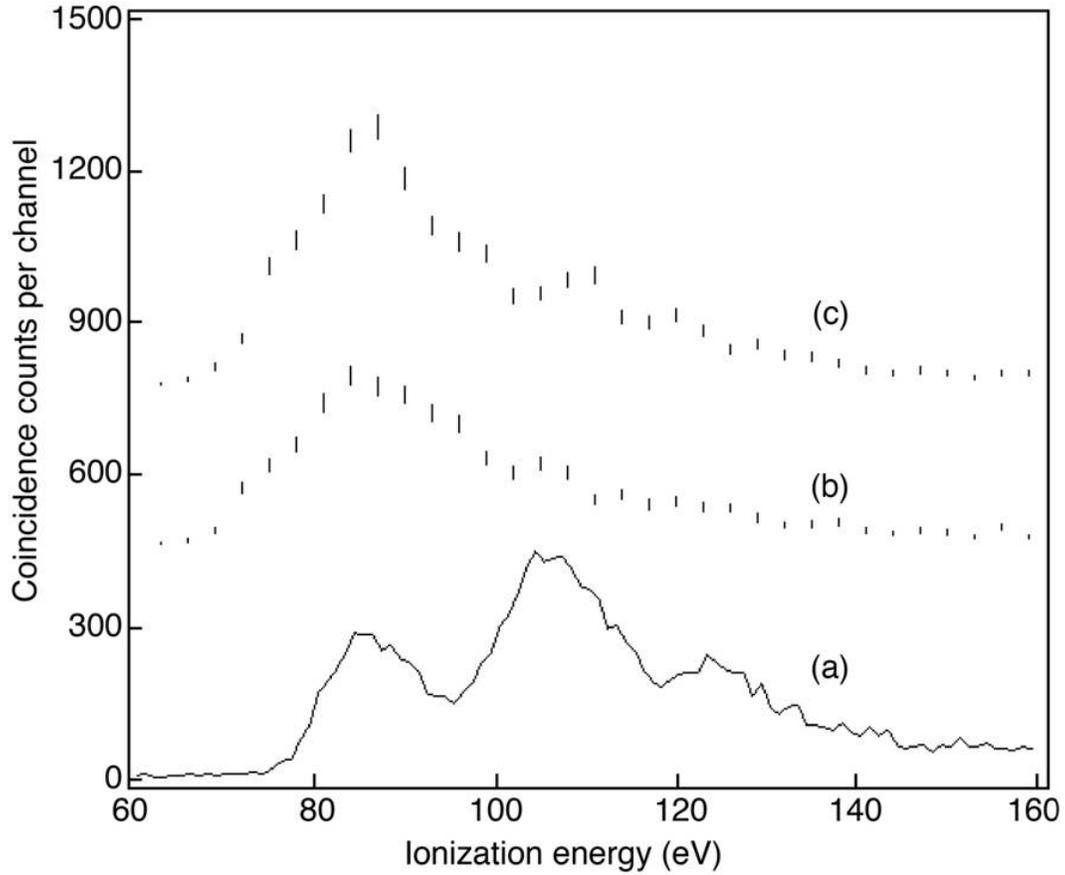


FIG. 4. Triple ionisation of water (a) by double Auger decay of the O1s hole created by 1300 eV photon impact, (b) by single Auger decay from the core valence states in the lowest energy band seen in spectrum (a) of Fig. 3, and (c) by single Auger decay from the peak of the same core-valence spectrum. The data are again displaced, but on a common vertical scale.

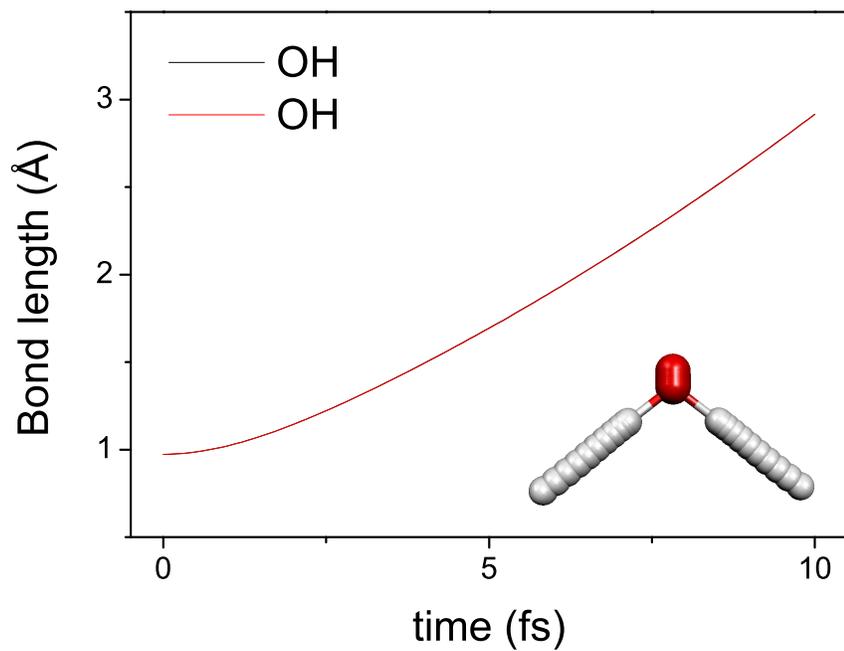


FIG. 5. Propagation of two OH bonds as a function of time in the core-valence states of water. A trajectory of this simulation during 10 fs in steps of 1 fs is shown. The initial geometry is the ground state equilibrium structure.

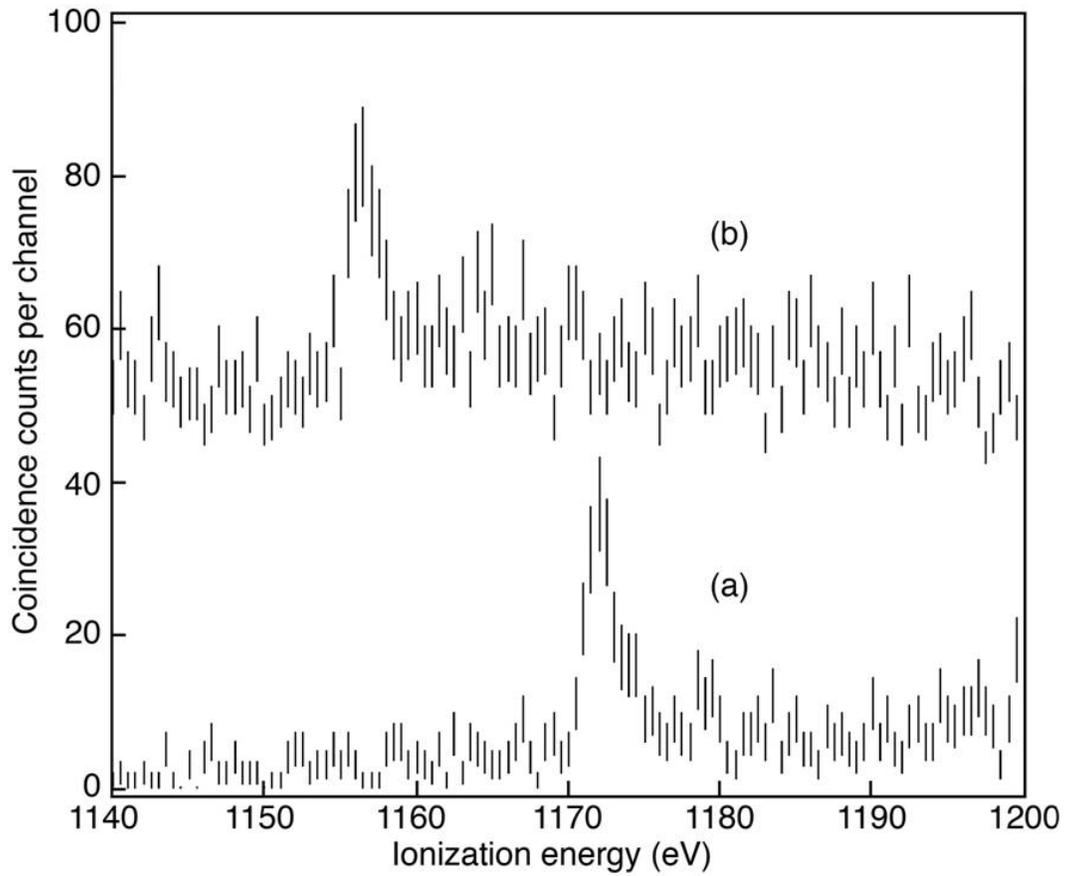


FIG. 6. The double core hole state $O1s^{-2}$ (a) and the associated singly ionised pre-edge resonance (b) from ionisation of water at 1300 eV photon energy. The peak centres are at 1171 ± 1 eV and 1155.6 ± 1 eV respectively. There may be a DCH shake-up satellite at 1178 eV.

TABLE I. Tricationic states of H₂O calculated in the present work on the CASSCF level.

Triple ionisation potential (eV)	State symmetry	Main Electronic Configuration
82.82	2A_1	$(3a_1)^{-1} (1b_1)^{-2}$
83.53	4A_2	$(3a_1)^{-1} (1b_1)^{-1} (1b_2)^{-1}$
84.71	2B_1	$(3a_1)^{-2} (1b_1)^{-1}$
86.95	2B_2	$(1b_1)^{-2} (1b_2)^{-1}$
87.34	2A_2	$(3a_1)^{-1} (1b_1)^{-1} (1b_2)^{-1}$
88.10	2A_2	$(3a_1)^{-1} (1b_1)^{-1} (1b_2)^{-1}$
91.18	2B_2	$(3a_1)^{-2} (1b_2)^{-1}$
92.75	2B_1	$(1b_1)^{-1} (1b_2)^{-2}$
94.08	2A_1	$(3a_1)^{-1} (1b_2)^{-2}$
96.76	4B_1	$(2a_1)^{-1} (3a_1)^{-1} (1b_1)^{-1}$
101.66	4A_2	$(2a_1)^{-1} (1b_1)^{-1} (1b_2)^{-1}$
102.78	4B_2	$(2a_1)^{-1} (3a_1)^{-1} (1b_2)^{-1}$
103.08	2A_1	$(2a_1)^{-1} (1b_1)^{-2}$
104.10	2B_1	$(2a_1)^{-1} (3a_1)^{-1} (1b_1)^{-1}$
107.01	2A_1	$(2a_1)^{-1} (3a_1)^{-2}$
108.28	2A_2	$(2a_1)^{-1} (1b_1)^{-1} (1b_2)^{-1}$
108.95	2B_1	$(2a_1)^{-1} (3a_1)^{-1} (1b_1)^{-1}$
109.10	2B_2	$(2a_1)^{-1} (3a_1)^{-1} (1b_2)^{-1}$
109.74	4B_2	$(3a_1)^{-1} (4a_1)^1 (1b_1)^{-2} (1b_2)^{-1}$
110.97	2B_2	$(3a_1)^{-1} (4a_1)^1 (1b_1)^{-2} (1b_2)^{-1}$
111.46	2A_1	$(3a_1)^{-2} (4a_1)^1 (1b_1)^{-2}$
111.56	4A_2	$(3a_1)^{-2} (4a_1)^1 (1b_1)^{-1} (1b_2)^{-1}$
111.61	4B_1	$(3a_1)^{-2} (1b_1)^{-1} (1b_2)^{-1} (2b_2)^1$
112.49	2B_2	$(3a_1)^{-2} (1b_1)^{-2} (2b_2)^1$
113.55	2A_2	$(3a_1)^{-2} (4a_1)^1 (1b_1)^{-1} (1b_2)^{-1}$
114.03	2A_1	$(3a_1)^{-1} (1b_1)^{-2} (1b_2)^{-1} (2b_2)^1$
114.08	2B_2	$(3a_1)^{-1} (4a_1)^{-1} (1b_1)^{-2} (1b_2)^1$
114.17	2A_2	$(2a_1)^{-1} (1b_1)^{-1} (1b_2)^{-1}$
114.28	2B_1	$(3a_1)^{-2} (1b_1)^{-1} (1b_2)^{-1} (2b_2)^1$
114.88	4A_2	$(3a_1)^{-1} (1b_1)^{-1} (1b_2)^{-2} (2b_2)^1$
115.10	2A_1	$(4a_1)^1 (1b_1)^{-2} (1b_2)^{-2}$

TABLE II. Core-valence doubly ionised states of H₂O calculated in the present work on the CASSCF level.

Excitation energy (eV)	State symmetry	Electronic configuration
539.86	2A_1	$O(1s)^{-1}$
567.46	3B_1	$O(1s)^{-1} (1b_1)^{-1}$
569.49	3A_1	$O(1s)^{-1} (3a_1)^{-1}$
571.06	1B_1	$O(1s)^{-1} (1b_1)^{-1}$
572.77	1A_1	$O(1s)^{-1} (3a_1)^{-1}$
573.81	3B_2	$O(1s)^{-1} (1b_2)^{-1}$
576.05	1B_2	$O(1s)^{-1} (1b_2)^{-1}$
589.84	3A_1	$O(1s)^{-1} (2a_1)^{-1}$
594.77	1A_1	$O(1s)^{-1} (2a_1)^{-1}$

TABLE III. Double core hole state ($O(1s)^{-2}$) and resonant double core hole states ($O(1s)^{-2}(4a_1)^1$ and $O(1s)^{-2}(2b_2)^1$) of H₂O calculated in the present work on the CASSCF level.

Excitation energy (eV)	State symmetry	Electronic configuration
1156.27	2A_1	$O(1s)^{-2} (4a_1)^1$
1157.86	2B_2	$O(1s)^{-2} (2b_2)^1$
1170.85	1A_1	$O(1s)^{-2}$