



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.

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1. 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. [5,4,6] 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 Letter 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 characterise 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 [30,3]. In such impacts the whole energetically accessible range of initial electronic states can be populated, in unknown proportions. In the present Letter 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.

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2. 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 Letter has been described in detail before [33,15] 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 monochromatised 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 Letter 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.

3. 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 optimised at the second-order Møller–Plesset level of theory (MP2) [36] with the correlation-consistent polarised 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 STOBDE-DEMON program [39].

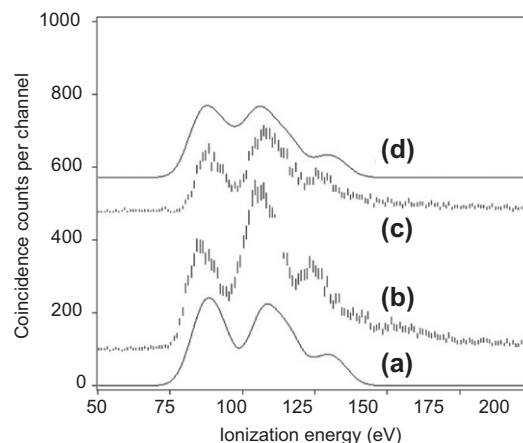


Figure 1. Triple ionisation spectra of water from double Auger decay of the simple 1s-hole state at 539.8 eV. (a) Theoretical spectrum showing doublet final states only. (b) Experimental spectrum taken at 1300 eV photon energy. (c) Experimental spectrum at 650 eV photon energy. (d) Theoretical spectrum 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.

4. Results and discussion

4.1. 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 15 enumerated above. There are so many (cf. Table 1) that to compare them with the experimental spectra in Figure 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

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