

September 2020

A Combined Experimental and Theoretical Study of Photodouble Ionization of Water at 32 eV Excess Energy and Unequal Energy Sharing

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Recommended Citation

Penson, Conner; Turri, Giorgio; Avaldi, Lorenzo; Randazzo, Juan; Ancarani, Lorenzo Ugo; and Bolognesi, Paola (2020) "A Combined Experimental and Theoretical Study of Photodouble Ionization of Water at 32 eV Excess Energy and Unequal Energy Sharing," *Beyond: Undergraduate Research Journal*: Vol. 4 , Article 4.

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Abstract

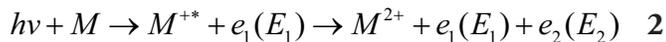
In this paper we present a part of our investigation of the photodouble ionization (PDI) of gaseous water. Synchrotron radiation from ELETTRA storage ring was used to ionize the water molecule, and the two emitted electrons were collected in coincidence after angle and energy selection. We have compared the measured dication states with those known from literature and showed the angular distributions of the two photoelectrons measured for the first time, for different excess energies and under different energy sharing conditions. A detailed comparison with theoretical calculations is given to help understand some details of the PDI mechanism.

Introduction

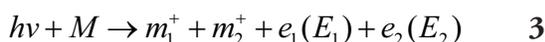
When an atom or a molecule absorbs a Vacuum Ultraviolet (VUV) or X-ray photon, the most likely process is the emission of a photoelectron with an energy and angular distribution that reflect the properties (electronic structure and symmetry of the orbitals) of the target. It is also possible that the absorption of the photon results in the emission of two electrons, i.e. in the PDI.



This process, though less probable, is of some interest because it is completely determined by electron correlations. In atoms heavier than helium, PDI can occur in a single step or through an intermediate singly-ionized state in molecules, there is the further chance of the breaking of the molecule at a step during the PDI process



The first investigations of PDI focused on the showcase case of atomic helium, where only the direct



process can occur. The double ionization potential, IP^{2+} , for He is around 70 eV, and the two emitted photoelectrons share the excess energy continuously. The interaction between the photon and the atom is accurately described by an electric dipole operator, which can only remove one electron; the second electron is emitted by the action of the Coulomb forces from the

nucleus and the first electron in the continuum. For this reason, PDI in He cannot be explained by a central potential model, and thus its investigation provides a very sensitive technique to study the residual atomic forces beyond the central potential approximation, known as electronic correlations. If linearly polarized light is used, then symmetry and energy conservation rules limit the possible emission direction and energy of the two photoelectrons. The process is then fully described by the Triply-Differential Cross Section (TDCS)

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE_2} \quad 4$$

which expresses the probability to emit one electron within the solid angle Ω_1 together with a second electron within the solid angle Ω_e at kinetic energy E_2 . The energy E_1 of the other electron is determined by energy conservation. In the special case of the two photoelectrons having the same kinetic energy (equal

$$h\nu - IP^{2+} = E_1 + E_2 \quad 5$$

energy sharing conditions) the symmetry of the problem also forbids them to be emitted in opposite directions. [1]

The helium model can be extended to the direct PDI process of heavier atoms, but the different symmetries of the final doubly-ionized atom result in different angular distributions of the two photoelectrons, and their emission in opposite directions is possible also in equal-energy sharing conditions. [1] Very few studies are available of PDI in molecules, mainly due

to extreme complexity of the process even in two or three atom molecules. The presence of many decay channels, the high number of degrees of freedom, and the mathematical difficulty to model two free electrons within the Coulomb field generated by many centers, require complex calculations.[2]

The experimental measurement of the TDCS requires the coincidence detection of either both photoelectrons (PEPECO, PhotoElectron PhotoElectron COincidence) or one photoelectron and the doubly charged recoiling ion (PEPICO, PhotoElectron PhotoIon COincidence), both selected in angle and energy. Because these experimental conditions severely reduce the data acquisition rate, high intensity photon sources and specifically designed detection set-ups are required.

In this work, we present some results from our investigation of the direct PDI of water molecule in gas phase. Water is a simple three atom molecule of special interest in biology, chemistry and astronomy, and its spectroscopic properties are well known. The PDI threshold (~ 38 eV), the decay mechanisms near threshold, and the binding energies of the H_2O^{2+} dication states have been previously measured [3,4], but no detailed measurements or theoretical calculations of the photoelectron angular distributions had been reported before our investigation. [2,5,6]

The experimental results were compared with theoretical calculations performed by Randazzo, based on angularly coupled products of Generalized Sturmian functions to describe the correlated two electrons in the continuum and separable products of Moccia orbitals for the initial electronic state. Details can be found in Randazzo et al. [5]

Methods

The measurements have been performed at the Gas Phase Photoemission beamline of the ELETTRA storage ring using the multi-coincidence end station shown in Fig. 1. [1] The incident synchrotron radiation is provided by an undulator source and is 100% linearly polarized. Two independently rotatable turntables are housed in the vacuum chamber. Seven hemispherical electrostatic spectrometers were mounted at 30° angular intervals on a turntable that rotates in the plane perpendicular to the direction of propagation of the incident radiation, three other spectrometers were mounted at $\vartheta_1 = 0^\circ, 30^\circ$ and 60° with respect to the polarization vector of the light.

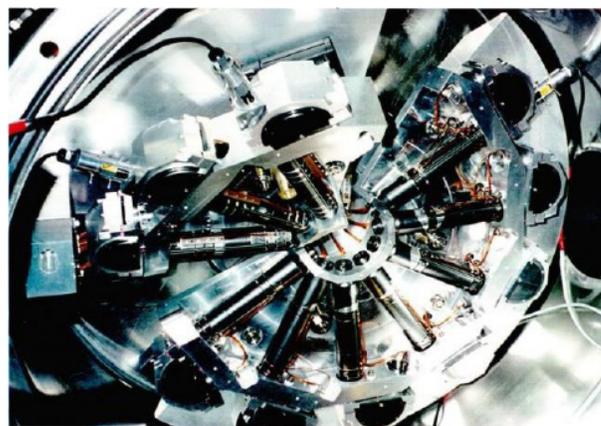


Fig. 1. The multi-coincidence end station at the Gas Phase photoemission beamline of the Elettra storage ring. [1]

To select the photon energy, firstly a measurement where the kinetic energy of each photoelectron is fixed while the photon energy is scanned, has been done. In this way the binding energy spectrum of the water H_2O^{2+} dication has been reconstructed. Two separate sets of dication states were then chosen, and the angular distribution of the photoelectrons produced by direct PDI ending to each of those sets was measured, both under equal and unequal energy sharing conditions. In all measurements, the energy resolution and the angular acceptance in the dispersion plane of the spectrometers were $\Delta E_{1,2} \approx 0.5$ eV, and $\Delta\vartheta_{1,2} \approx \pm 4^\circ$, respectively; the typical rate of acquisition of true coincidences was a few mHz.

Results and Discussion

The H_2O^{2+} binding energy spectrum as measured in this work under equal and unequal energy sharing conditions is shown in Fig. 2, where it is compared with the one measured by Eland. [3] Agreement is observed between the different measurements as far as the threshold and the shape of the spectrum is concerned. The energy positions of several different dication states with their spectroscopic assignment are depicted as vertical bars. The blue arrows in Fig. 2 show the two binding energies chosen for the angular distribution measurements: they correspond to a mixture of the $(1b_1)^{-2} {}^1A_1$, $(3a_1)^{-1} (1b_1)^{-1} {}^1B_1$, $(1b_2)^{-1} (1b_1)^{-1} {}^3A_2$ states at $BE \approx 42$ eV, and a mixture of the $(3a_1)^{-1} (1b_1)^{-1} {}^1B_1$, $(1b_2)^{-1} (1b_1)^{-1} {}^3A_2$, $(3a_1)^{-2} {}^1A_1$, $(1b_2)^{-1} (1b_1)^{-1} {}^1A_2$, $(3a_1)^{-1} (1b_2)^{-1} {}^3B_2$ states at $BE \approx 44$ eV

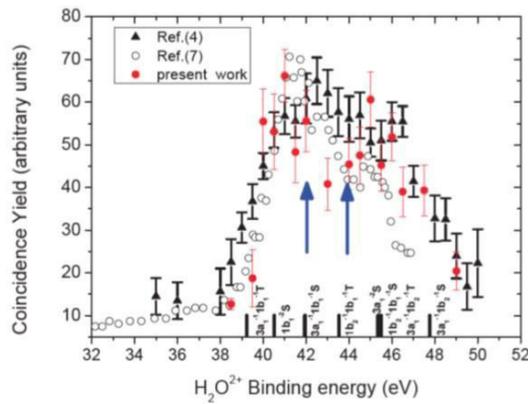


Fig. 2. Water dication binding energy spectrum as measured in this work under equal (red dots) and unequal (black triangles) energy share conditions, compared with the one measured by Eland (open circles). [3] The dication states are also reported. The blue arrows indicate the binding energies chosen for the angular distribution measurements.

The angular distributions of 10 eV kinetic energy electrons, in equal energy sharing conditions at 63 eV photon energy are depicted in Fig. 3, for three directions of one photoelectron (red arrows) respect to the polarization direction of the incident light. [5] When one electron is emitted along the polarization direction (top left panel), the measured distribution shows the expected symmetry along that axis. It is also evident that in that case the emission of the two electrons in opposite directions is not forbidden, as in the case of atoms like He when the final dication state and the electron pair wavefunction have $1S^e$ and $1P^o$ symmetries, respectively. Here the theory predicts that the enhanced back-to-back emission comes from the ionization to the $(1b_2)^{-1}(1b_1)^{-1} 3A_2$ state (see Randazzo et al. for details. [5])

A similar pattern is observed at 74 eV photon energy for unequal energy sharing conditions, as shown in Fig. 4, relative to a 25 eV kinetic energy electron emitted at 0° , 30° and 60° , in coincidence with a 7 eV kinetic energy electron. Still there is a non-vanishing emission for the two photoelectrons along opposite directions along the light polarization axis, but now the picture is less clear. Within the length gauge, the $(1b_1)^{-2} 1A_1$ state peaks at $\vartheta_{12}=180^\circ$, while for the other two dication $(3a_1)^{-1}(1b_1)^{-1} 1B_1$, $(1b_2)^{-1}(1b_1)^{-1} 3A_2$ states the angular distributions display a node, whereas in the velocity gauge, the TDCS of both the $3A_2$ and $1A_1$ are not vanishing. [6]

Finally, we show in Fig. 5 the angular distributions collected in the equal energy sharing condition at 65 eV photon energy. Here both the $(1b_2)^{-1}(1b_1)^{-1} 3A_2$ and

the $(3a_1)^{-2} 1A_1$ states contribute to the $\vartheta_{12}=180^\circ$ peak when one electron is emitted along the light polarization direction. A full discussion of the angular distributions at the chosen photon energies and the two energy-sharing conditions is beyond the purposes of this report. For details we refer the reader to the two papers by Randazzo et al. [5] and by Bolognesi et al. [6].

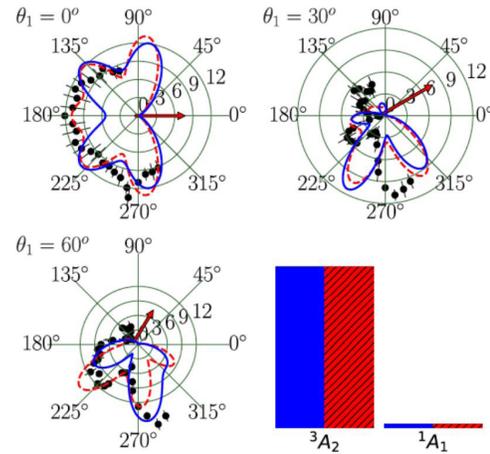


Fig. 3. TDCS of water for 63 eV photon energy under equal energy sharing conditions $E_1 = E_2 = 10$ eV, for three directions $\theta_{1,2,3}$ (red arrows) of one electron respect to the light polarization vector. The full lines are the theoretical calculations performed in the length (red) and velocity (blue) gauges. The histogram represents the contribution of the different dication states to the angular distribution. From Randazzo et al. [5]

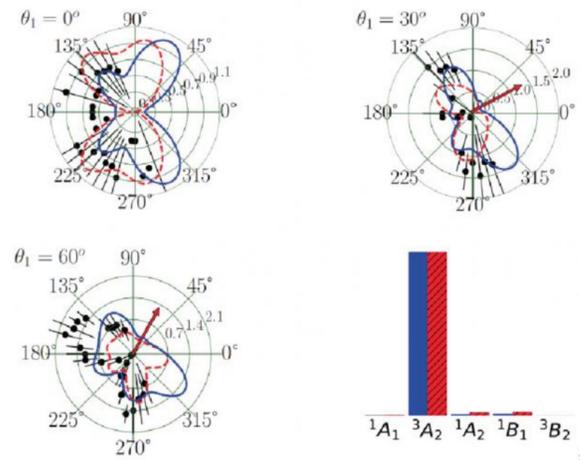


Fig. 4. TDCS of water for 74 eV photon energy under unequal energy sharing conditions $E_1 = 25$ eV, $\theta_1 = 0, 30, 60$ (red arrows) respect to the light polarization axis, and $E_2 = 7$ eV. The red and the blue full lines are the theoretical calculations performed in the length (red) and velocity (blue) gauges. The histogram represents the contribution of the different dication states to the angular distribution. From Bolognesi et al. [6]

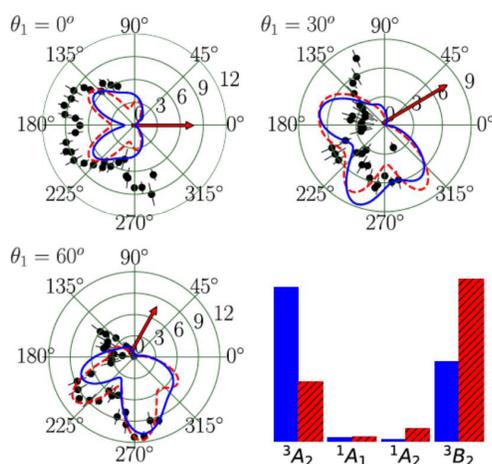


Fig. 5. TDCS of water for 65 eV photon energy under equal energy sharing conditions $E_1 = E_2 = 10$ eV, for three directions $\theta_{1,2,3}$ (red arrows) of one electron respect to the light polarization vector. The red and the blue full lines are the theoretical calculations performed in the length (red) and velocity (blue) gauges. The histogram represents the contribution of the different dication states to the angular distribution. From Randazzo et al. [5]

Conclusion

In this paper we report the angular distributions of PDI of molecular water, for two excess energies and under equal and unequal energy sharing conditions. The experimental results show rich and challenging patterns as expected from a twoelectron emission in a complex Coulomb system such as that of a polyatomic molecule. The comparison with a theoretical calculation based on products of single-electron Moccia orbitals for the initial states, and the generalized Sturmian function approach for the evolution of the two electrons in the continuum shows a reasonable agreement and provide useful insights on the PDI mechanism.

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