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Excitation of vibrational modes in the ionization of water molecule by XUV/X-ray radiation

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Synopsis We present a theoretical study of the vibrationally resolved core photoionization of the water molecule up to high photon energies. In order to understand the role of the coupled electron-nuclear motion in polyatomic molecules, we thus have implemented a new methodology to describe all vibrational modes of a polyatomic molecule. We show our preliminary results on the O(1s) photoionization, with special focus on the vibrationally resolved cross sections in a large range of photon energies, reaching up to 1500 eV.

Most theoretical studies of coupled electron and nuclear dynamics in photoionization problems have been restricted to diatomic molecules [1] or to a single vibrational mode of polyatomic molecules [2]. In some cases, a reasonable approximation is to reduce the nuclear degrees of freedom to one principal normal mode. This was shown in photoionization problems for highly symmetric targets such that CH_4 or BF_3 [2], whose symmetric stretching mode was the main active mode upon the photon absorption. However, such simplification is not valid in most problems.

The aim of this study is to extend the methodology previously developed in those molecular targets, which used a one-dimensional vibrational wave function, to include an arbitrary number of nuclear degrees of freedom. We thus seek to achieve a complete description of vibrational motion, although, for simplicity our first implementation uses Jacobi coordinates, which are particularly suitable for non-linear triatomic molecules. In the present study, we report results for the O(1s) photoionization of the water molecule induced by synchroton radiation, where all normal modes are simultaneously accounted for : bending, symmetric stretching and asymmetric stretching. Accurate vibrationally resolved cross sections require the computation of dipole matrix elements for the transition from the ground state of the neutral to the core-ionized water molecule. These dipole elements are obtained for the full grid of nuclear coordinates using the static-exchange DFT method developed by P. Decleva and collaborators [3]. The reliability of our approach is tested by comparing our calculated O(1s) vibrationally resolved photoelectron spectrum with available experimental data for a photon energy of 590 eV [4]. We find a good agreement with the vibrational progression at 590 eV, where the dominant contribution is that of the bending mode of the core-ionized water molecule. We further analyze the v-ratios as a function of photon energy, i.e. the ratios between the photoionization cross sections for individual vibrational states. For all normal modes, we observe oscillations around the Franck-Condon factor value, similar to those found in previous works for other diatomic and polyatomic targets (CO, CH_4, BF_3, etc) [1, 2], whose origin comes from diffraction of the ejected electron by the surrounding H atoms.

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