



## Water molecules in ultrashort intense laser fields

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### ABSTRACT

Ionization and excitation of water molecules in intense laser pulses are studied theoretically by solving the three-dimensional time-dependent electronic Schrödinger equation within the single-active-electron approximation. The possibility to image orbital densities by measurement of the orientation-dependent ionization of H<sub>2</sub>O in few-cycle, 800 nm linear-polarized laser pulses is investigated. While the highest-occupied molecular orbital  $1b_1$  is found to dominate the overall ionization behavior, contributions from the energetically lower lying  $3a_1$  orbital dominate the ionization yield in the nodal plane of the  $1b_1$  orbital. The ratio of the ionization yields of the two orbitals depends on the intensity. Furthermore, even for laser pulses as long as 8 cycles the orientation-dependent ion yield depends on the carrier-envelope phase. In the interpretation of the orientation-dependent ionization as an imaging tool these effects have to be considered.

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### 1. Introduction

Recent efforts to achieve time-resolved imaging of chemical reactions or other structural changes with sub-femtosecond resolution possess a strong interdisciplinary character, since the goal is of interest for physics, chemistry, and biology. Pioneering experiments with near-infrared ultrashort laser pulses like the ones in [1,2] in which structural information about the chemically most relevant valence electrons was extracted from the emitted high-harmonic radiation or electron spectra have been of great interest, since these approaches should intrinsically have the potential for providing also the required time resolution. However, in contrast to the initial assumptions, recent experiments have demonstrated that the molecular strong-field response depends, at least for some molecules, on more than one orbital [3–6]. While such multi-orbital effects clearly complicate simple imaging schemes, they can also be the source for even richer information that can be gained from such experiments. An example is the electron–hole dynamics in the laser-generated ion that may be observed by analyzing the high-harmonic radiation [5]. Though very exciting by itself, this appears to make direct imaging of the valence electrons and their field-free dynamics during, e.g., a chemical reaction more complicated.

The proposed imaging schemes based on linear-polarized ultrashort near-infrared laser pulses may roughly be divided into two categories, rescattering-based schemes and direct imaging. The

first category is based on the celebrated three-step model of strong-field physics in which (1) an electronic wavepacket leaves the molecule around the local maxima of the electric field by tunneling ionization, (2) this wavepacket is accelerated in the laser field and reverses its direction as the field direction changes, and (3) the electronic wavepacket may recollide with its parent ion. As a consequence of this recollision, the electronic wavepacket may partly scatter elastically (diffraction) or inelastically (leading to excitation or further fragmentation), or recombine by the emission of high-harmonic radiation. Clearly, all these processes should depend on the structure of the molecular ion and thus have the potential for revealing structural information. This includes both electronic structure as well as nuclear geometry. Corresponding reviews may be found in [7,8].

### 2. Direct imaging using orientation-dependent ionization

While the rescattering-based imaging schemes are evidently based on the third step of the three-step model and consequently require that this model is at least a good approximation, the direct imaging schemes are based on the first, the ionization step. Measuring the ion yield as a function of the time-delay between two very short pulses has been demonstrated theoretically [9] and experimentally [10] to induce and image vibrational motion in the electronic ground state of neutral molecules. Simplified models like the strong-field approximation of the time-dependent Schrödinger equation suggest also the possibility to image the nuclear

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geometry of a molecule by comparing the energy-resolved electron spectra for different molecular orientations, but were immediately shown to fail using a full-dimensional *ab initio* treatment for H<sub>2</sub> [11]. An alternative, rather straightforward approach to time-resolved direct imaging with intense near-infrared laser pulses is based on recording the dependence of the total ionization probability as a function of the relative orientation of the polarization axis of a linear polarized laser pulse with respect to the molecule. Since this corresponds to the fully integrated electron (or ion) spectrum, it is by far the most intense response signal, many orders of magnitude larger than recollision signals. This makes it experimentally very attractive. Clearly, it is an interesting question whether such an integral observable provides detailed enough information for imaging. In [12] it was demonstrated that the alignment-dependent ionization probability reflects the shape of the highest-occupied molecular orbital (HOMO) for both N<sub>2</sub> and O<sub>2</sub>. However, the therein also considered example of CO<sub>2</sub> turned out to be not as straightforward. A possible reason could be a coherent core trapping of the valence electron [13] which explains that only at lower intensity the imaging appears to work for CO<sub>2</sub>, in agreement with an experiment performed with lower laser intensity [14]. Alternative explanations for the shift of the peak positions have been given invoking either resonances [15] (not confirmed in [13]) or an interplay of coordinate and momentum properties of the HOMO [16].

Finally, it should be reminded that time-resolution is achieved in direct imaging schemes using pump–probe arrangements. Typically, the dynamics has anyhow to be triggered in some way. This may be achieved by two identical, time shifted laser pulses as in [9,10] or by synchronizing another pump laser to the probe pulse. On the other hand, especially the high-harmonic based recollision imaging schemes possess an intrinsic time resolution that is, however, limited in total duration to about half a laser cycle and thus to about 1.6 fs for 800 nm laser light [17]. To follow dynamics on longer time scales, lasers with longer wavelengths have to be used, or a pump–probe scheme has to be applied as in the direct imaging schemes. Furthermore, the intrinsic time resolution can only be used for processes that are induced in the ionizing first step and thus not really adequate for the general purpose of imaging chemical reactions.

In order to image chemical reactions, it is, of course, important that concepts tested so far for linear molecules are also applicable to more general molecules. We have thus decided to investigate the direct imaging proposal based on the recording of the orientation-dependent ionization yield for a simple but very important non-linear molecule: water. Despite its natural importance due to its abundance in nature, there are some additional arguments for choosing this molecule in the present context. The three energetically highest-lying orbitals of H<sub>2</sub>O are known to very roughly correspond to the three p orbitals of the oxygen atom that are, however, differently modified by the OH bonds. All three orbitals are thus structurally relatively simple and a good test candidate for imaging schemes. For example, the energetically highest-lying occupied orbital, the 1b<sub>1</sub> HOMO, is almost identical to an oxygen p orbital. In contrast to true atomic p orbitals, the two hydrogen atoms in water lead, however, to a break of the isotropic symmetry and a deformation, especially of the so called 3a<sub>1</sub> HOMO-1. Furthermore, due to the symmetry reduction the three oxygen p orbitals lose their degeneracy and thus become (also energetically) distinguishable. As a consequence, it is possible to test the sensitivity of an imaging scheme. Note, it has to be mentioned that the field-free alignment of a dipolar molecule like H<sub>2</sub>O is experimentally a challenging task. However, orientation-resolved information for one-photon ionization was obtained in [18], but from a multiple coincidence measurement that allowed to reconstruct the orientation at the incident of ionization. Other approaches that avoid

pre-alignment of the molecule are based on the use of circular polarized laser pulses as was applied to H<sub>2</sub> in [19]. Clearly, in this case the theoretical description should consider circular and not linear polarization. Due to the increased numerical demands, this is, however, so far seldom the case (see, e.g., the theoretical analysis of the just mentioned H<sub>2</sub> experiment in [19,11,20]).

### 3. Previous studies of H<sub>2</sub>O in intense laser fields

Ionization and harmonic generation of water molecules in intense fields have recently stirred some interest and were investigated both theoretically and experimentally. The case of relatively low intensities with supposedly negligible ionization was studied using time-dependent configuration interaction (restricted to single and double excitations) in [21] where polarizabilities and low harmonics were reported. Ionization of the HOMO of H<sub>2</sub>O in electric half-cycle pulses was studied in [22] within a hydrogenic-orbital approximation and thus an atomic model. Adopting a numerical implementation of time-dependent density functional theory (TD-DFT) based on Voronoi cells the ionization of water molecules in intense laser fields was studied in [23]. In that implementation only next-neighbor-cell interactions were considered. This approach will be in the following named TDVFD as in [23]. Considering two 2-dimensional cuts it was found that within the TDVFD approach the overall ionization is dominated by ionization from the HOMO, but at specific directions the HOMO-1 contribution can locally exceed the one from the HOMO. In [24] the ionization from the HOMO of water was calculated within the molecular Ammosov–Delone–Krainov (MO-ADK) approximation. At least along the considered two-dimensional cut the dependence of the ionization rate on the relative orientation between laser field and molecular plane as obtained by the MO-ADK model was shown to agree qualitatively, though not quantitatively, with the TDVFD results in [23].

The high-harmonic radiation of water molecules was recently investigated experimentally [25] and theoretically within a variant of the strong-field approximation in which the recombination dipole matrix element is related to single-photon ionization cross-sections [26]. Already earlier, a theoretical investigation within the strong-field approximation was reported in [27]. In accordance with the in [23] predicted overall dominance of the HOMO ionization (first step of the three-step model), the theoretical investigation of isotope effects on the high-harmonic generation of water was restricted to the HOMO in [27]. It was concluded that practically no isotope effect is present and thus no nuclear motion is visible from the high-harmonic radiation, if the ratio of the high-harmonic spectra from H<sub>2</sub>O and D<sub>2</sub>O is analyzed. The reason is the absence of (substantial) excitation of vibrational motion, if ionization from the water HOMO is considered. This is due to the fact that the potential surfaces of the neutral water molecule and the formed ion (in its electronic ground state) are very similar. The time-resolved imaging of nuclear motion using high-harmonics requires on the other hand vibrational excitation and thus different potential surfaces of the neutral and the ion [9,28–30]. Nevertheless, a recent mixed experimental and theoretical study [6] has shown a pronounced isotope effect in water harmonics. It is explained by high-harmonic generation from the HOMO-1 which, in contrast to the one from the HOMO, is accompanied by substantial vibrational excitation. As it becomes clear from the present study, the good visibility of the high-harmonic radiation from the HOMO-1 (relative to the one from the HOMO) is, within the terminology of the three-step model, also due to the second and third step, while ionization (in an isotropic ensemble) occurs dominantly from the HOMO, at least for not too high intensities.

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