

## Resolving the Optical Spectrum of Water: Coordination and Electrostatic Effects

A. Hermann,<sup>1</sup> W. G. Schmidt,<sup>2</sup> and P. Schwerdtfeger<sup>1</sup>

<sup>1</sup>*Centre of Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, North Shore City, 0745 Auckland, New Zealand*

<sup>2</sup>*Lehrstuhl für Theoretische Physik, Universität Paderborn, 33095 Paderborn, Germany*

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The optical absorption of small water clusters, water chains, liquid water, and crystalline ice is analyzed computationally. We identify two competing mechanisms determining the onset of the optical absorption: Electronic transitions involving surface molecules of finite clusters or chains cause a redshift upon molecular aggregation compared to monomers. On the other hand, a strong blueshift is caused by the electrostatic environment experienced by water monomers embedded in a hydrate shell. Concerning the recent dispute over the structure of the liquid, the present results support the conventional fourfold coordinated water, as obtained from *ab initio* molecular-dynamics simulations.

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The understanding of the properties of water in its many phases is fundamental to research in fields as diverse as corrosion, cellular biology, and atmospheric chemistry. For example, without UV protection from the ozone layer, liquid water near the surface offers little protection against UV damage to marine life, as radiation penetrates liquid water far into the vacuum UV region. Why is the onset of the optical absorption blueshifted in liquid water (or ice) compared to water molecules? In fact, the lowest absorption energy shifts from the gas-phase value of 7.4 eV ( $\lambda = 168$  nm) to 8.2 eV (151 nm) for liquid water to 8.7 eV (143 nm) for ice (in its hexagonal, cubic, and amorphous phase) [1–4]. This seems counterintuitive. Upon condensation of molecules a transition from molecular energy levels to dispersive energy bands occurs that typically reduces the gap between occupied and empty electronic states. As a result, the optical absorption is expected to redshift.

However, not only the electronic and optical properties of water are intriguing, there are even open issues concerning the structural properties of its ubiquitous liquid phase: A recent x-ray absorption (XA) study [5] indicated that the 100-year-old picture of the structure of liquid water might be wrong. While hitherto it was believed—and obtained in practically all state-of-the-art molecular-dynamics (MD) calculations, see, e.g., [6,7]—that hydrogen bonds pulled liquid water into an extended network, with each water molecule bonded to four others, the synchrotron results suggest that many water molecules are, in fact, bonded to only two neighbors.

Standard experimental approaches to the analysis of crystal structures (x-ray and neutron diffraction) can provide detailed information on ordered phases of ice, but only indirect, and often limited, information on amorphous ice and liquid water. On the theoretical side, classical and *first-principles* molecular-dynamics based on density-functional theory (DFT) have been used extensively to study water and solvation processes, see, e.g., Refs. [8,9]. However, it is not yet fully understood how accurate the

various gradient-corrected functionals in DFT describe the structural and diffusive properties of liquid water [10–12]. Furthermore, the quantitative influence of the inclusion of proton quantum effects in *ab initio* simulations remains to be established. Therefore, methodologies that solely depend on computational data may have difficulties to reliably determine the structural properties of liquid water. In these circumstances, the comparison of spectroscopic data such as the optical response with fingerprints calculated for structural candidates may be a valuable help.

Remarkably, the calculated optical absorption of liquid water, obtained recently by the superposition of many snapshot configurations of a classical MD run [13], deviates significantly from experiment: similar to gas-phase molecules, the calculated onset of the optical absorption occurs at about 7 eV. As *first-principles* calculations for the water molecule [14] and crystalline ice *Ih* [15] reproduce the measured optical absorption peaks well, this discrepancy could be indicative for the failure of the standard, tetrahedral model of liquid water. Whereas the latter is supported by recent MD simulations with an *ab initio* based force field [16], calculations of XA spectra were interpreted to support either the tetrahedral model [17,18] or twofold bonding configurations [19,20].

Here we analyze in detail the impact of the coordination and the electrostatic environment on the excited-state properties of hydrogen-bonded water monomers. We investigate small water clusters, chains of water molecules, solid ice as well as liquid water obtained from *ab initio* MD simulations. Two competing mechanisms are identified that considerably shift the excitation energies of hydrogen-bonded monomers compared to single molecules: A redshift is caused by “surface” effects for undercoordinated structures, while the local electric fields of neighboring molecules blueshift the spectrum. The optical response calculated for *ab initio* liquid water agrees remarkably well with experiment.

Structural parameters of water clusters and crystalline ice are optimized using DFT with a plane-wave basis and

the projector augmented wave (PAW) method [21] as implemented in the Vienna *ab initio* simulation package (VASP) [22,23]. Computational details are similar to Ref. [24]. *Ab initio* MD simulations are performed within VASP, using a 64 molecule unit cell at  $T = 298$  K. Preoptimized liquid water from classical MD using the TIP4P potential [25] served as input for an *ab initio* equilibration; structural snapshots were then taken every 200 fs from a 4 ps production run. The PW91 exchange correlation energy functional [26] is used as it reasonably describes hydrogen bonds in crystalline ice [24].

Based on the DFT ground-state calculations, optical absorption spectra including many-body effects are calculated. Depending on size and dimensionality of the problem, this is done by performing either GW and Bethe-Salpeter (BSE) type calculations [27], occupation-constrained DFT ( $\Delta$ SCF) calculations in VASP, or wave function based symmetry-adapted cluster configuration interaction (SAC-CI) calculations [28,29]. The GW + BSE methodology is used for infinite chains and bulk ice, utilizing the implementation outlined in Refs. [14,30].  $\Delta$ SCF (in vacuum) and SAC-CI calculations (including dipole interaction field) using augmented correlation consistent valence double-zeta basis sets [31] are performed for finite clusters. The former allow for the calculation of optical spectra over the desired energy range; for the latter, calculations had to be limited to correlating the 20 lowest single-particle excitations. The different approaches account comparably for self-energy and excitonic effects: while DFT predicts the optical gap of the water monomer at 6.16 eV, we obtain 7.24 (7.15, 7.2) eV from  $\Delta$ SCF (SAC-CI, GW + BSE), all close to the experimental value of 7.4 eV. A recent EOM-CCSD(T) calculation for the water monomer obtained 7.54 eV [32].

The calculated absorption spectra of structurally relaxed cluster geometries obtained by filling up the first coordination shell of a water molecule are shown in Fig. 1. Upon increasing cluster size, the three main excitations of the monomer are split and the absorption onset is redshifted towards smaller energies [cf. Figs. 1(a)–1(d)]. In every cluster, the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) are localized on a hydrogen-bond donating and accepting molecule, respectively. The HOMO-LUMO excitation is an intermolecular transition that occurs (most clearly for  $(\text{H}_2\text{O})_5$ ) between cluster surface states. The influence of these surface transitions can be expected to fade away with further increasing cluster size. For the infinite crystal, no surface effects occur. Instead [see Fig. 1(e)], the absorption onset is blue-shifted with respect to the monomer, and oscillator strength is shifted to a strong excitonic peak at about 9 eV. This confirms results by Hahn *et al.* and was discussed in their work in the picture of a molecular exciton that delocalizes upon the neighboring water molecules [15]. These results indicate that compact clusters are no suitable model to explain the optical absorption of liquid water, in particular, the absorption onset at 8.2 eV.

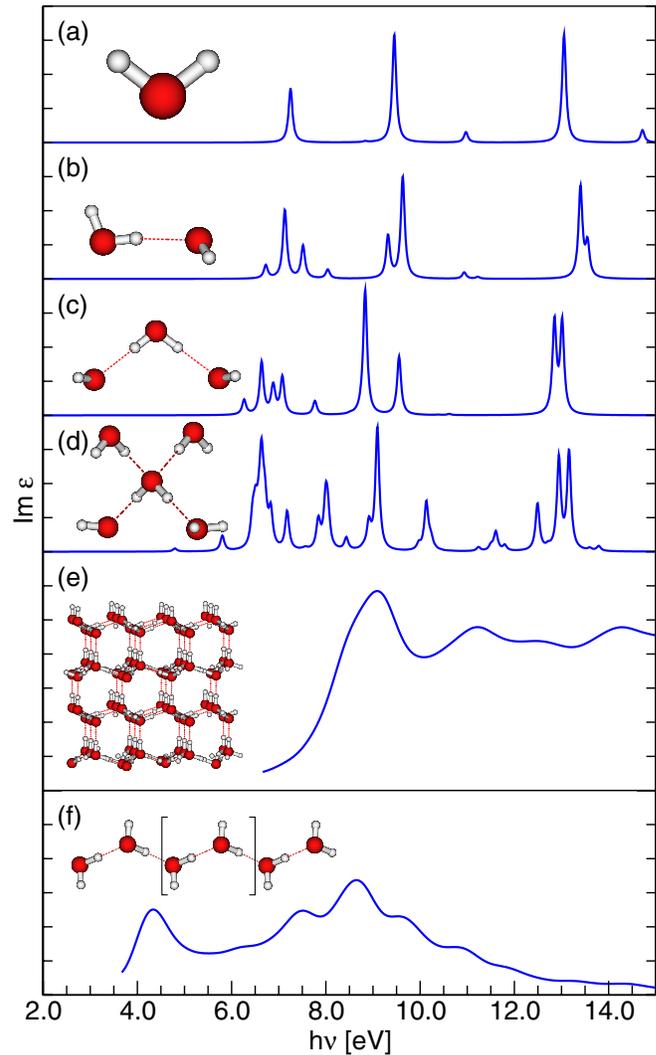


FIG. 1 (color online). Optical absorption spectra of (a)–(d) small compact water clusters, (e) hexagonal ice, (f) infinite water chain, calculated for Coulomb-correlated quasiparticles.

According to Ref. [5], most molecules of liquid water form H-bonded chains or rings. We calculated the optical response of finite chains up to  $(\text{H}_2\text{O})_7$  and of an infinite molecular chain. Similar to the clusters discussed above, the onset of the optical absorption of finite chains (spectra not shown here) is found to occur below the monomer value. This also holds for the infinite chain, where a strong excitonic peak occurs at 4.3 eV [cf. Fig. 1(f)].

The chain and cluster structures modeled so far do not experience the long-range electrostatic interaction with a surrounding aqueous environment [33]. This Coulomb interaction is taken into account in the following, using point charges. This does not only model the electrostatic contribution to the hydrogen bond, but also (at least partially) the orbital delocalization. Other contributions such as dispersive or closed shell repulsion interactions are, of course, not included. The dipole electrostatic field is constructed by placing point charges at the positions of oxygen

and hydrogen atoms both of the optimized ice structure and liquid water MD snapshots. Their magnitudes are adjusted to account for the enhanced dipole moment of water in ice [34] and the liquid [35]. Placed around a central water monomer or cluster, the optical spectra are calculated using the SAC-CI method.

Figure 2 compares the optical spectrum of water in vacuum, and in the dipole electrostatic fields of surrounding crystalline ice and *ab initio* liquid water. The electric field induced by the surrounding hydrate environment of crystalline ice shifts the absorption onset of the water monomer from 7.2 to 8.6 eV, in very good agreement with the measured data for ice Ih. Transition energies at 8.6, 10.8, (12.7), and 14.2 eV also agree well with the calculated solid state spectrum [cf. Fig. 1(e)]. Figure 3 illustrates on the single-particle level the influence of the hydrate shell on the shapes of molecular HOMO and LUMO: while the HOMO is almost unchanged (being only slightly delocalized), the LUMO is significantly quenched upon repulsive interaction with neighboring, hydrogen-bonded molecules. The high directionality of the hydrogen bonds in ice leads to strong local electric fields that effectively raise the LUMO energy and slightly lower the HOMO. Since all bound excitations in Fig. 2 are dominated by single-particle excitations into the LUMO, all are shifted similarly under the influence of the surrounding hydrate shell. It is interesting to note that the blueshift of the optical absorption upon aggregation of water molecules to ice explained by many-body effects in Ref. [15] can thus be understood already in a single-particle picture, provided the local electrostatic environment is taken into account.

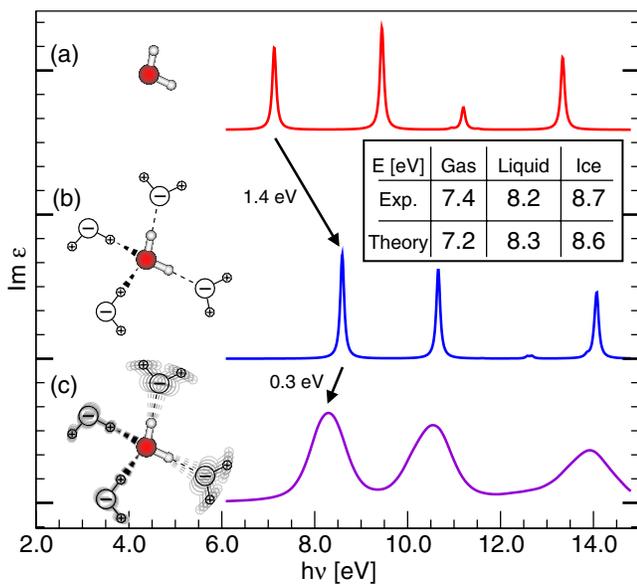


FIG. 2 (color online). Absorption spectra of a single water molecule (a) in vacuum, and in electric field of (b) surrounding crystalline ice, and (c) surrounding liquid water, from SAC-CI calculations. Inset compares onsets with experimental data [1–4].

The influence of the dipole electric field is corroborated by calculations for a water pentamer cluster (geometry fixed “as is” from crystalline ice) embedded in point charges. The absorption onset is shifted from 7.0 to 8.7 eV, see Fig. 4, again very close to the value of crystalline ice. All low-energy excitations populate the LUMO and LUMO + 1 states that are combinations of water’s molecular LUMO’s; these are quenched similarly under the influence of the hydrate shell. Note that the spectra in Fig. 1(d) and 4(a) differ in parts because of the pentamers’ different structures, but mostly because the SAC-CI method used for the latter is restricted to the 20 lowest transitions. Both spectra feature dominant peaks at 6.5–7.0 eV and 8 eV, but the higher energy region was not accessible in our SAC-CI treatment.

Based on the excellent agreement between experiment and the electrostatic environment calculations for crystalline water, we now apply this methodology to the *ab initio* liquid phase. The liquid water absorption spectrum is obtained by accumulating spectra of MD snapshot configurations until the spectral features are converged in line shape and position. The result is shown in the lower panel of Fig. 2. The first absorption peak is redshifted (with respect to crystalline ice) to 8.3 eV, very close to the experimental value of 8.2 eV. The other main peaks at 10.5 and 13.9 eV are also close to the experimentally identified maxima at 10.0 and 13.7 eV [3]. We failed to achieve a similar degree of agreement with experiment on the basis of a twofold coordinated water molecule embedded in an appropriate electrostatic environment, unless

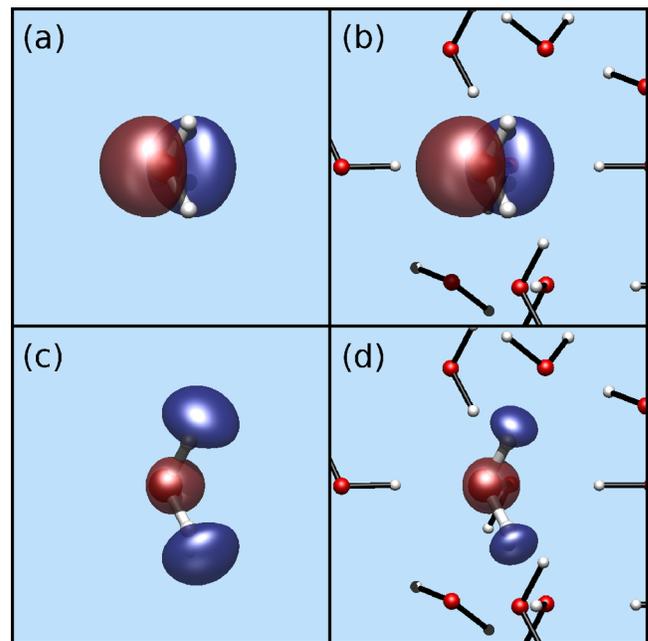


FIG. 3 (color online). Plots of single-particle orbitals: HOMO/LUMO in (a/c) vacuum, and (b/d) icelike electric field. Isosurface value 0.06 a.u. Right panel indicates positions of hydrate shell point charges.

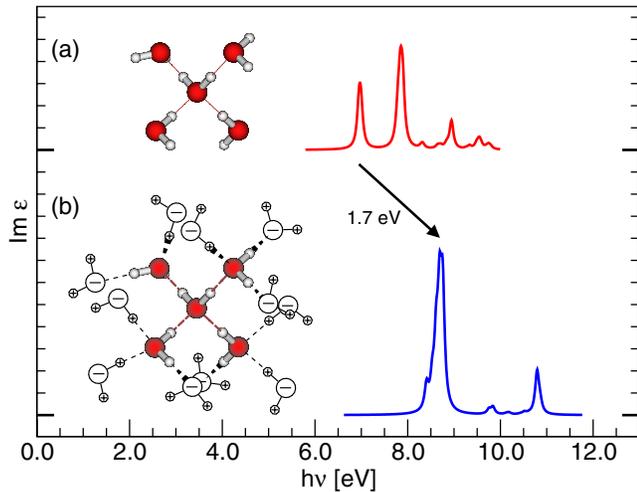


FIG. 4 (color online). Low-energy excitations of a water pentamer (a) in vacuum, and (b) in icelike electric field, from SAC-CI calculations.

the density of the liquid was drastically reduced (by at least 25%) compared to the experimental value. The excellent agreement of the optical response calculated for the *ab initio* liquid with the measured absorption certainly strongly supports the conventional picture of fourfold coordinated water molecules in the liquid. This result complements XA spectra calculations which usually probe dipole transitions of a different character [36]. However, given the large number of adjustable parameters, the possibility of alternative models cannot be ruled out completely on the basis of the optical absorption data alone.

In conclusion, *first-principles* calculations show that the onset of the optical absorption of a network of undercoordinated water monomers in vacuum is redshifted with respect to the monomer excitation. This is related to intermolecular transitions involving edge or surface molecules that give rise to low-energy absorption peaks. These are suppressed for long water chains, which, however, feature a strong excitonic peak at low photon energy. The local electric fields caused by the hydrate shell surrounding water monomers or clusters, however, are responsible for a large (more than 1 eV) competing shift of the optical absorption to higher energies. In fact, the calculations identify the local electric fields in the condensed water phases as the major force opening the optical transmission window of liquid and solid water compared to the vapor. The *ab initio* structural model of nearly fourfold coordinated molecules in the liquid phase of water is found to be consistent with the optical absorption experiments.

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