



A cluster model of liquid water and its IR spectroscopic response

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Abstract

IR spectra of liquid water were modeled for a cluster of 214 molecules, using combined MD and ab initio DFT-BPW91/6-31G** computations. The model reproduced well the experimental absorption profile in the range of 0–4000 cm^{-1} , positions, bandwidths and magnitudes of the absorption maxima for the OH stretching, bending and molecular librational modes. A band corresponding to the transitional motion is reproduced with a bigger error. The procedure can be applied universally and was also used for simulation of absorption spectra of liquid methanol.

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1. Introduction

Apart from the importance to terrestrial chemistry and physics, liquid water is a convenient testing system for solvent models because of the strong intermolecular interactions. Presumably, a representation describing satisfactorily its properties is also applicable for other solvents and solvated systems. Particularly, this work suggests an extension of precise ab initio simulations of vibrational spectra to multi-molecular systems.

Molecular dynamics (MD) simulations provided useful insights into physical properties of water, including the absorption spectra [1–4]. In the past decade, it has been recognized that these simulations can become simpler and more universal if

coupled with ab initio calculations [5,6]. The time correlation function and the instantaneous normal mode analysis approaches enabled a consistent simulation of H_2O and D_2O absorption spectra profiles and were found most advantageous for the lower-frequency modes [7]. A different approach is adopted in continuum solvent models, such as the dipole Onsager [8] or advanced self-consistent field models attempting to accommodate realistic molecular shape and solvent properties [9,10]. Finally, one of the most advanced approaches is represented by the Car–Parinello molecular dynamics (CPMD) [11] that enabled to explain many structural properties of water [12] and related systems [13], and has been extended for simulations of the infrared spectra [14,15]. The CPMD method provided good prediction of most spectral features, namely in the lower-frequency region. For many systems, however, it is still too robust and time-demanding, with a

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restriction to a rather limited number of density functionals given by its computer implementation.

Proper treatment of the solvent was found necessary, for example, in the prediction of the Raman optical activity spectra of zwitterionic peptides non-existent in vacuum [16,17], or in the assessment of accurate vibrational frequencies of the amide group [18]. The hydrogen bonding significantly influences protein IR spectral intensities [18,19] and its proper simulation can enhance otherwise conceptually difficult baseline subtraction, i.e., the separation of the solvent and solute signals. The interaction with the solvent also influences the energetic and conformational equilibria of studied molecules [20].

Fully ab initio solvent models, involving explicitly individual molecules, appear most appealing for analytical spectroscopy. They are not dependent on empirical parameters, unlike the MD approach, nor they omit specific solvent interaction, namely the hydrogen bonds, unlike the continuum models. However, such models are quite demanding on computer power and some simplifications have to be always introduced. In this study, a relatively minor contribution of the longer-range atomic interactions to the spectra is omitted, which enables to divide target system into smaller units and thus significantly cut the computational cost. For example, time of a typical ab initio (DFT) enumeration of second energy derivatives may be proportional to N^5 , N being the number of atoms [21]. However, the separation into the units scales linearly, since their number is proportional to the system size (N) and the time needed for computation on each of them is constant. By experience, the longer-range interactions can be neglected even in covalently bond systems [22,23]. Using the optimization in the normal mode coordinates [24], geometries obtained by an MD simulation could be partially relaxed and then directly used in ab initio computations of the spectra. Harmonic approximation was adopted, similarly as for the MD models where the spectra are obtained by a Fourier (harmonic) transformation of the time-dependent variables. As shown below, such a model reproduces main absorption spectral features found in liquid water and methanol.

2. Method

Geometry of approximately cubic ‘droplet’ consisting of 214 water molecules was optimized using the TINKER MD program package [25] and the Amber [26] force field. A Tinker example file according to [27] was used as the starting structure. Then the droplet was divided into 125 mutually overlapping units, with the aid of the MCM95 program (written in house, [28]). This ‘brute force’ division was based on a propagation of a cubic elementary cell sized 7 Å, using 3.5 Å steps as indicated in Fig. 1. Molecular fragments (H, OH, O) in the smaller cubes were automatically deleted and each smaller cluster was partially optimized in the normal mode coordinates [24], fixing modes with wavenumbers smaller than 200 cm^{-1} , at the BPW91/6-31G** level. Thus geometries of the units still approximately mimicked those in the droplet, but the higher-frequency vibrational modes (most contributing to the spectrum) could be relaxed. For all the partially relaxed structures harmonic force fields and dipole derivatives were calculated by the GAUSSIAN program [29] at the same BPW91/6-31G** level. The BPW91 functional [30,31] proved to be extraordinarily successful for IR spectra simulations of various

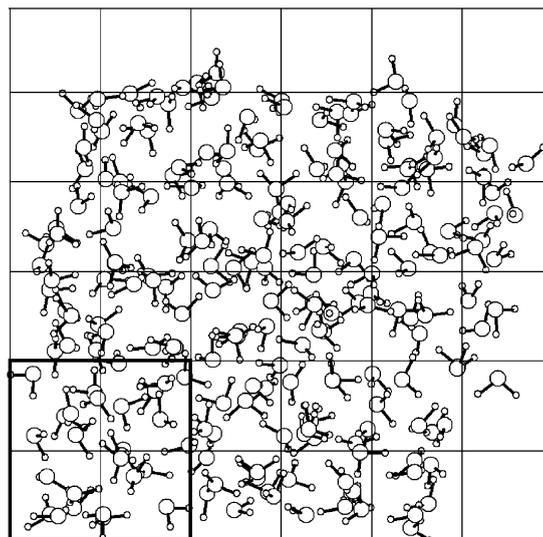


Fig. 1. The division of the water droplet into 125 overlapping cubes. The ‘elementary cube’ is emphasized by the thick line.

systems previously [32–34]. Also, recent studies [35] indicate that the Perdew–Wang exchange–correlation functional can at least approximately reproduce the dispersion forces, for which current DFT methods are usually not suitable. Finally, the force field and the dipole derivative tensors were transferred in the Cartesian coordinates [23] to the droplet, providing the harmonic vibrational frequencies and intensities [36].

3. Results and discussion

3.1. The IR spectral profile

The calculated molar absorption coefficient was obtained from the intensities using an arbitrary Lorentzian bands with a bandwidth of 15 cm^{-1} , and is compared to the experimental profile from [39] in Fig. 2. Since the system was not completely relaxed at the BPW91/6-31G** level, 274 from the total of 1926 harmonic frequencies were obtained as imaginary. The number of these imaginary frequencies is relatively small and their contribution to the absorption intensity negligible. As most of them have absolute values smaller than 200 cm^{-1} , larger error may thus potentially arise only in the lowest-frequency region.

The experimental absorption maximum around 200 cm^{-1} has been attributed to a translational motion of water molecules and reproduced on the basis of MD modeling [2,3,14]. This is in agreement with the dynamic visualization of the normal mode displacement observed for the cluster, although the translational and librational modes cannot be cleanly separated. Instead of the maximum, a broad shoulder at 400 cm^{-1} appears in the simulated spectra in Fig. 2.

Better match was obtained for the rest of the wide band at the $300\text{--}1100\text{ cm}^{-1}$ region. The experimentally observed intensity maximum for these vibrations dominated by the librational motion of hydrogen-bonded molecules at $\sim 690\text{ cm}^{-1}$ corresponds to the simulated peak approximately at 740 cm^{-1} . The sharper drop of the intensity observed around 860 cm^{-1} is predicted by the calculations at frequencies by about 90 cm^{-1} higher.

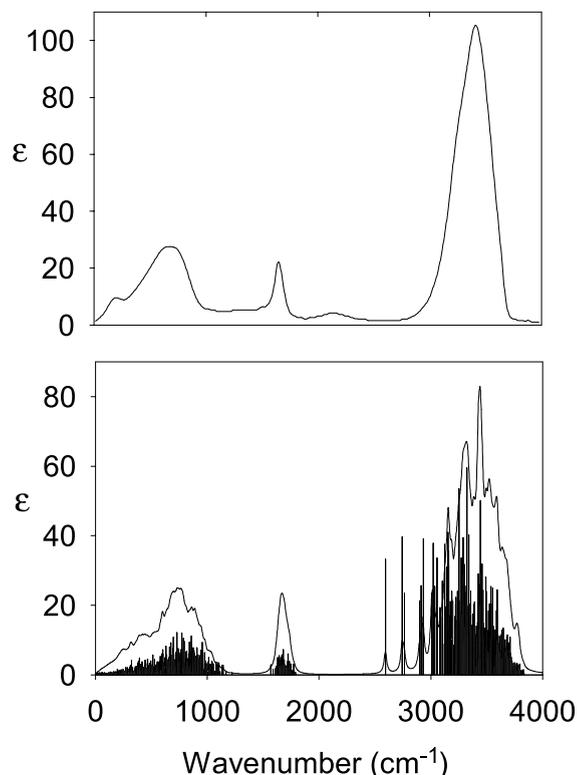


Fig. 2. Experimental (top, redrawn from [39]) and calculated (bottom) absorption profile of liquid water. Line representation of relative intensities of individual transitions is included for the latter.

The experimental anharmonic ‘background’ absorption at the region of $1000\text{--}1500\text{ cm}^{-1}$ and the broader peak around 2140 cm^{-1} cannot be reproduced, similarly as it cannot be obtained by the Fourier analysis of the MD data. Presumably, an inclusion of the anharmonic forces will be a next step in future simulations of vibrational spectra of liquids and solvated systems.

The peak of the bending molecular vibration, experimentally at 1640 cm^{-1} , calculated at 1666 cm^{-1} , is well-reproduced, with respect to its position, bandwidth and intensity. So is the OH stretching maximum at 3414 (calculated at 3432) cm^{-1} . The bending peak is rather symmetric, while the OH intensity sharply diminishes at higher wavenumbers, which is correctly reproduced by the model. Supposedly, for a bigger ensemble of molecules even smoother and more realistic spec-

tral shape could be obtained, especially for the region 2500–4000 cm^{-1} . However, this is limited by the computer power, since the computations for the current model lasted about 4 month if normalized to a single processor (Intel PIII, 1 GHz) time.

The integral intensity of all the OH stretching transitions excellently agrees with the experimental observations. The experimental dipole derivative for this mode has been determined [39] as $|\delta\mu/\delta Q|^2 = 19.06 (\text{D}\text{\AA}^{-1} \text{amu}^{-1/2})^2$, the calculated value is $19.88 (\text{D}\text{\AA}^{-1} \text{amu}^{-1/2})^2$. In Table 1, more usual molar intensities are listed for the main transition groups. The experimental numbers were estimated from band areas, and the frequencies and intensities are compared to calculations for a molecule in vacuum, with the COSMO [9] solvent correction ($\epsilon_r = 78$, ‘water in water’), and for the cluster. Clearly, the cluster computation is not only superior to the vacuum results, but also provides much more realistic frequencies and intensities than the continuum solvent model. Especially the complex OH stretching intensity enhancement, as discussed in Fig. 3, would be difficult to obtain with the electrostatic continuum models.

3.2. Isotopic substitution

Heavy water (D_2O) is often used as a solvent since it provides a broader frequency window in the mid IR region. Generation of the deuterated spectra for the cluster is a trivial task computa-

tionally and provides a tests of its reliability. Indeed, the IR spectra shown in Fig. 4 reproduce most of the isotopic effects observed experimentally [3,7]. Under the deuteration, the O–D stretching and D–O–D bending intensity maxima shift to about 2490 and 1290 cm^{-1} , which compares well with the experimental values of 2500 and 1195 cm^{-1} . The librational intermolecular band shifts to lower wavenumbers (from 740 cm^{-1} for H_2O to 560 cm^{-1} for D_2O) and its intensity decreases by about 40%. Although the ‘center’ positions can be determined only with errors both for the experimental and simulated broad uneven bands, the overall agreement with the experiment, exhibiting a shift from 690 to 500 cm^{-1} with a 30% intensity drop, is very good. In the 0–300 cm^{-1} region the calculation also reproduces correctly the experimentally confirmed independence of the absorption signal on the deuteration. This contradicted to the earlier free-rotator models and was explained by a confinement of the molecules [37].

3.3. Temperature effects and model variations

Temperature, similarly as the anharmonic effects, cannot be directly incorporated in the model. Experimental water IR spectra change only mildly with temperature [39] and the harmonic approximation seems to be appropriate for most of molecular motions [7]. However, the influence of the Boltzmann population of the excited states could be included and lead to an absorption decrease smaller than 30% only at the 0–300 cm^{-1} region.

Table 1
Absorption frequencies and intensities in liquid water

	BPW91/6-31G** calculation			Exp. [39]
	Vacuum	COSMO, $\epsilon_r = 78$	Cluster	
	Absorption maxima (cm^{-1})			
O–H stretching	3824, 3708	3772, 3677	3432	3414
H–O–H bending	1639	1586	1666	1640
Librations	–	–	740	690
Translations	–	–	~415	~200
	Intensities (km/mol)			
O–H stretching	14.9 + 0.4	89.8 + 18.3	829.0	794
H–O–H bending	62.6	104.7	69.3	44
Librations	–	–	113.0	271
Translations	–	–	30.4	29

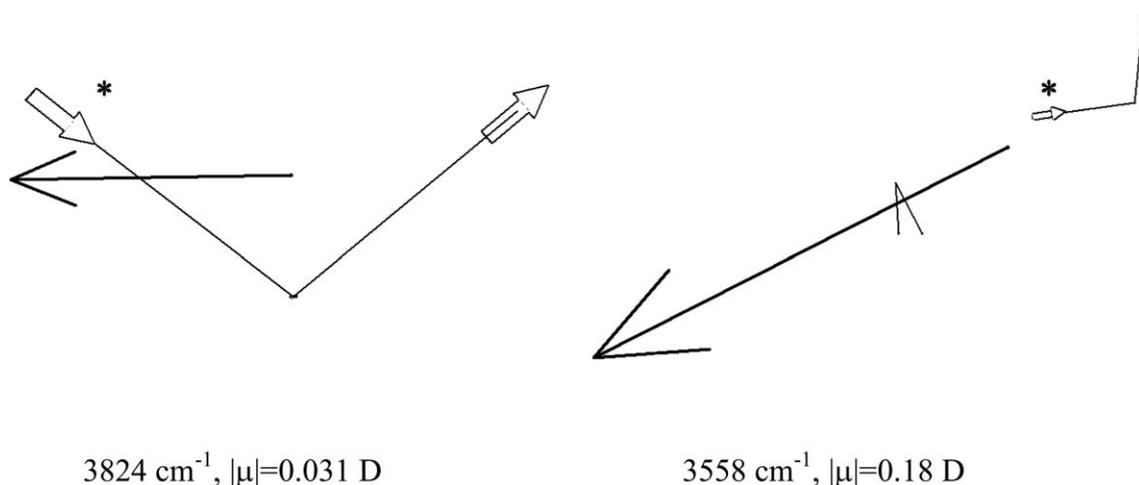


Fig. 3. Calculated (BPW91/6-31G**) contribution of one hydrogen atom (marked by asterisk *) to the transition electric dipole moment of the stretching vibration. Full arrows denote the dipole, white arrows the atomic displacements. Compared to an isolated molecule (left), the dipole in a dimer (right) is longer because (1) the OH stretching frequency is smaller, (2) the displacement is bigger, (3) polarizability (change of dipole normalized to the displacement) increases and, finally, (4) the displacement and the transition dipole moment are more collinear. Note, that observed absorption is proportional to the square of the dipole, which further magnifies the effect.

Proper selection of the ab initio level appears more important, for example the PM3 force field (Fig. 5a) uniformly overestimates transitional frequencies, in spite of its qualitatively correct pattern. If the ab initio relaxation of the subunits is omitted, as for trace b, a much worse absorption profile is obtained, lacking namely low-frequency wing in the O–H stretching region. Thus the relaxed DFT model provides the best match with the experi-

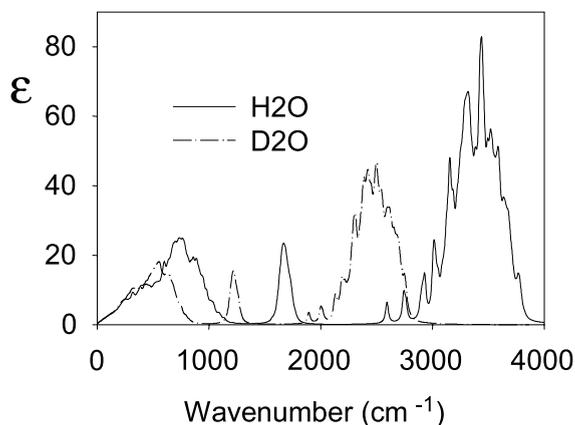


Fig. 4. Calculated IR spectra of normal and heavy water.

ment, although due to the limited size of the cluster and the surface effects different shapes of the droplet provide still somewhat different spectra (Figs. 5c, d).

The inhomogeneous line widths generated by the statistical disorder (see the line representation

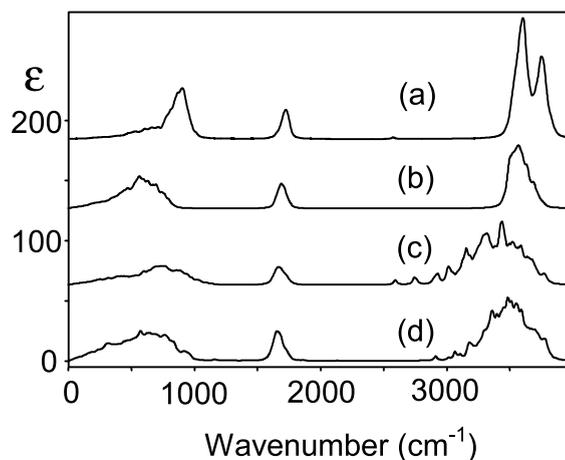


Fig. 5. Simulated spectra of the $(\text{H}_2\text{O})_{214}$ cluster at the PM3 level (a), and at the BPW91/6-31G** level for rigid (b) and relaxed (c, d) geometries. Simulation (d) correspond to (c), but was based on a different (more regular) shape of the cluster.

in Fig. 2) appear as realistic approximations to the experiment. The width of the hydrogen stretching band is somewhat too large, but it can be further improved with a fine tuning of the simulation parameters as for the spectrum in Fig. 5d. This particular success of the model probably reflects the difference of time scales between molecular dynamics and vibrational transitions, by other words the light sees water as a static system. For example, the wavenumber of 1000 cm^{-1} is associated with the time period of $T \sim 10^{-14}\text{ s}$, which is presumably less than a time needed for a re-arrangement in the structure. Such approximation, however, may not be valid for the lowest-energy modes, where CPMD or quantum MD simulations are more appropriate.

3.4. Liquid methanol

Liquid methanol IR spectra were simulated in order to confirm a general applicability of the model. A cube consisting of 120 molecules was subjected to a MD run (NPT-assemble, 1000 steps with 1 fs for $T = 298\text{ K}$, then 5000 steps at 600 K, and, finally, 1000 steps at 298 K) under periodic boundary conditions. The cube with a size of 20.04 \AA was then divided into 80 smaller cubes sized 9 \AA , so that spectral parameters could be calculated for each of them and transferred back onto the $(\text{CH}_3\text{OH})_{120}$ cluster. Nice examples of solvent effects can thus be seen in Fig. 6, where the cluster spectrum is compared to a vacuum computation for one molecule. The OH stretching mode for an isolated molecule at 3771 cm^{-1} appears as a broad band around 3530 cm^{-1} , in agreement with experimental values of 3700 and 3360 cm^{-1} [38]. The shape of the C–H stretching bands (2800 – 3200 cm^{-1}) does not well compare to the experiment because of the anharmonic interactions. On the other hand, the OH and C–H bending modes (at 1461 and 1335 cm^{-1} for single molecule) form a broader band centered around 1420 cm^{-1} , well-matching an experimental maximum at 1466 cm^{-1} . The C–O stretching mode at 1035 cm^{-1} in the cluster (1034 experimentally) is least influenced by the clustering. By contrast, the maxima at 631 (experimentally at 670 cm^{-1}) and 340 cm^{-1} appear exclusively as results of the intermolecular interac-

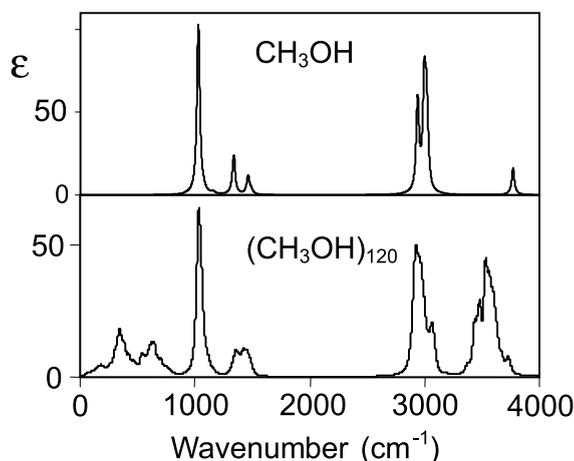


Fig. 6. Calculated (BPW91/6-31G**) absorption spectra of methanol molecule (top) and the cluster (bottom).

tions and can be attributed to the rotation of the OH group coupled with the hydrogen bond stretching.

4. Conclusions

The static ab initio cluster model provides realistic band shapes and positions of most of the vibrational transitions observed in liquid water and methanol. Unlike most of the previous simulations of liquids, it is not dependent on ad hoc parameters and can be universally applied for arbitrary solvent or solvated systems. Calculated frequencies are less accurate in the lower-frequency region (0 – 300 cm^{-1}).

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