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Liquid water dynamical partial charges and infrared intensities

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Abstract

In this paper we present a study of the atomic polar tensors (APT) and dynamical charges in liquid water. An exact sum rule is used to relate dynamical partial charges to the total intensity of the infrared (IR) spectrum. It was then possible to evaluate, from experimental data, these charges through isotopic substitution data. These were compared with calculated values from a Density Functional Theory based first-principle simulations and both show an hydrogen charge increase when going from the gas phase to the liquid phase, as expected. The hydrogen APT tensor is then studied in more details from simulation and shown to be highly anisotropic, a feature attributed to the electronic nature of the hydrogen bond. The anisotropy of the hydrogen APT tensor is finally related to the ratio of IR band intensities in liquid water.

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I. INTRODUCTION

Hydrogen bonding is at the origin of the unusual properties of liquid water[1]. Breaking hydrogen bonds by a temperature increase or evaporation costs energy and this leads to water high heat capacity and latent heat. This makes oceans important heat reservoirs while the cycle of water through evaporation and rain constitutes a large part of energy transfer between the hot and cold regions. Another property induced by hydrogen bonding in liquid water is its high dielectric constant. This plays also a crucial role in the solvation of ions by screening the coulomb interaction.

Hydrogen bonding in liquid water does not simply reduces to coulombic interaction between dipolar molecules but induces a charge density reorganisation with respect to the electron density of isolated water molecules. The common picture is that hydrogen bonding enhances the molecular dipole of water in the liquid phase by making the hydrogen atoms and the oxygen atom more positively and more negatively charged respectively. The molecular dipole moment in liquid water has for example be estimated to be around 3 D from ab initio Molecular Dynamics simulations[2]; comparison of neutron scattering and x-ray scattering liquid water form-factors also point in the same direction with a dipole moment around 2.9 D[3].

In this paper we will study the effect of hydrogen bonding on atomic dynamical charges in liquid water.

These dynamical charges are derived from the atomic polar tensor[4] of an atom I , defined as the derivative of the system total dipole moment (or polarization) with respect to infinitesimal displacement of the atom I [5]:

$$APT_I = \frac{\partial \vec{M}}{\partial \vec{R}_I}, \quad (1)$$

where \vec{M} is the system total dipole moment and \vec{R}_I the vector position of atom I . Note that the atomic polar tensor is a 3×3 tensor. Commonly the Born charge, Z_I , of an atom I is defined[4] from the trace of this tensor as

$$Z_I = \frac{1}{3} \text{Tr} \frac{\partial M^\beta}{\partial R_I^\alpha} = \frac{1}{3} \sum_\alpha \frac{\partial M^\alpha}{\partial R_I^\alpha} \quad (2)$$

where $\alpha = x, y, z$. Indeed if one assumes that the system is composed of ions with fixed

charges q_I so that the system dipole moment can be written as

$$\vec{M} = \sum_I q_I \cdot \vec{R}_I, \quad (3)$$

the atomic polar tensor is then a diagonal matrix with q_I on the diagonal and we recover that the Born charge is equal to the ionic charge q_I , $Z_I = q_I$. Recently different authors have studied dynamical *molecular* charges in liquid water[6, 7]; we will rather here study the hydrogen and oxygen dynamical charges separately.

In the general case, the Atomic Polar Tensor englobes the electronic density rearrangements induced by the displacement of the atom I . Figure 1 show the electronic density rearrangement in a water dimer following a small displacement to the right of the hydrogen involved in the H-bond (see section III). There is an increase of density in front of the H and a decrease behind, corresponding to an atomic charge density surrounding the H and being translated with it: this composes the main electronic part of the APT tensor of the central H. However it can be seen from Fig. 1 that electronic rearrangments occur also elsewhere in the system, in particular with a decrease of charge density close to the oxygen on the right. The APT tensor, and the atomic charges we will derive from it, does not arise only from the bare atom charge density but also from electronic rearrangments far from it; in that sense the APT tensor can be seen as a dressed quantity. Note for example that in a condensed phase system it contains a contribution from the polarization response of the surrounding dielectric medium around the moving atom. This dressing could be seen as a defect for an atomic charge derived from the APT tensor: in the following we will argue that this dressing crucial for the case of hydrogen bonded systems and in fact we can learn about the electronic structure of the H-bond from it.

A main aspect of the APT tensor is that it relates to the infrared spectrum of the system. From the fluctuation-dissipation theorem, the infrared spectrum is proportional to the Fourier-transform of the current-current auto-correlation function[8]:

$$I(\omega) \propto \int dt \langle \vec{M}(0) \vec{M}(t) \rangle e^{i\omega t} \quad (4)$$

$$\propto \int dt \langle \vec{j}(0) \vec{j}(t) \rangle e^{i\omega t}, \quad (5)$$

with $\vec{j}(t) = \frac{d\vec{M}(t)}{dt}$. For the frequencies corresponding to infrared spectroscopy one will assume that the Born-Oppenheimer approximation is valid so that the system total dipole is again

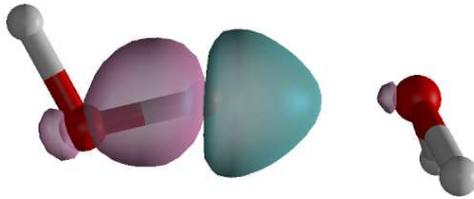


FIG. 1: Electronic rearrangement in a water dimer following a small displacement of the central hydrogen to the right. In blue: increase of charge density, in pink: decrease of charge density.

considered as a function of the ionic coordinates. In that case, the current $\vec{j} = \frac{d\vec{M}}{dt}$ can be written through a chain rule as

$$\vec{j} = \frac{d\vec{M}}{dt} = \sum_I \frac{\partial \vec{M}}{\partial \vec{R}_I} \vec{V}_I, \quad (6)$$

involving the APT tensors. The infrared spectrum is thus

$$I(\omega) \propto \int dt \sum_{I,J} \left\langle \frac{\partial \vec{M}}{\partial \vec{R}_I}(0) \frac{\partial \vec{M}}{\partial \vec{R}_J}(t) \vec{V}_I(0) \vec{V}_J(t) \right\rangle e^{i\omega t}. \quad (7)$$

The APT tensors thus enter directly in the infrared spectrum expression, mainly defining the band intensities. This link between the APT tensor and the infrared intensity was previously used to interpret the low frequency region of the IR spectrum of liquid water[7].

In the present work, we study this relationship between IR intensities and dynamical charges in the case of liquid water. An exact sum rule is used to relate a contraction of the APT, with dimension of a charge, to the total integrated intensity of the IR spectrum. It is then shown that isotopic substitution further allows for an experimental evaluation of these charges. They were compared with calculated values from Density Functional Theory based first-principle simulations. The anisotropy of the hydrogen APT tensor is then studied in more details from simulation and related to the ratio of IR band intensities in liquid water.

The remaining of the paper is organised as follows. The next section discusses the sum rule for the integrated infrared intensity. Section III describes the details of the First-Principle Molecular Dynamics simulations performed. Results are presented and discussed in section IV and we finally conclude in section V. Detailed derivation of the sum rule for the integrated infrared intensity is given in an appendix.

II. SUM RULE

The link between the APT tensor and the infrared spectrum can be made precise thanks to an exact sum rule. Indeed it can be shown that the integral of the infrared absorption is equal to (see for example[9]):

$$I_{tot} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega \chi''(\omega) = \frac{1}{3V} \sum_I \frac{1}{m_I} \left\langle \frac{\partial M^\beta}{\partial R_I^\alpha} \frac{\partial M^\beta}{\partial R_I^\alpha} \right\rangle, \quad (8)$$

where m_I is the mass of atom I . It was first proposed for systems in the gas phase (where a correction for rotation is necessary) using the harmonic approximation[9, 10]. The validity of that sum rule turns out to be much more general: it is valid for a classical or a quantum system and does not depend on any assumption on the potential energy surface (e.g. harmonicity) and is thus very general. A proof of that sum rule for classical and quantum systems is given in Appendix.

This sum rule is equivalent to the usual f -sum rule in optics and expresses the total infrared absorption, or plasma frequency, as a sum of atomic terms proportional to the atom inverse mass and to the sometimes called King charge, defined as the equilibrium average

$$\xi_I^2 = \frac{1}{3} \left\langle \frac{\partial M^\beta}{\partial R_I^\alpha} \frac{\partial M^\beta}{\partial R_I^\alpha} \right\rangle, \quad (9)$$

where an Einstein notation is used. This charge is different from the Born charge in that it involves all elements $\frac{\partial M^\beta}{\partial R_I^\alpha}$ of the APT tensor; this will be important in case where the APT tensor is not isotropic as we will discuss later in the case of H-bonding.

The $1/m_I$ factors appearing in eq. (8) suggest that isotopic substitutions can be used to determine individual partial charges, $|\xi_I|$, generalizing the case of isolated molecules[10]. Let us first rewrite eq. (8) as:

$$I_{tot} = \sum_I \frac{n_I}{m_I} \langle \xi_I^2 \rangle, \quad (10)$$

where I designates the particle type of mass m_I and concentration n_I (atomic or ionic species); all particles of this type are chemically equivalent and their partial charge is ξ_I . For an atomic or ionic crystal I labels the crystal sites; for a pure molecular liquids I labels the atoms in the solvent molecule. When an isotopic substitution of a particle of type I is made the difference of integrated IR intensities can be very well approximated by

$$\Delta I_{tot} \approx n_I \langle \xi_I^2 \rangle \times \left(\frac{1}{m_I^a} - \frac{1}{m_I^b} \right), \quad (11)$$

	I_{tot} (cm ⁻²)
CH ₃ OH	50357
CH ₃ OD	31535
CD ₃ OH	47405
CD ₃ OD	28956

TABLE I: Total integrated IR intensities of four isotopomers of methanol, from data of ref. [11]

where m_I^a and m_I^b are the masses of the two isotopes. This only assumes that the average charge $\bar{\xi}_I = \sqrt{\langle \xi_I^2 \rangle}$, which is a static property, depends only slightly on the isotope considered.

Before considering the case of liquid water, we illustrate the application of the sum rule (8) with isotopic substitutions from experimental data of the infrared spectrum of methanol and its isotopomers. Recently, accurate and quantitative determination of the IR spectra of four isotopomers, CH₃OH, CH₃OD, CD₃OH and CD₃OD, of liquid methanol has been achieved over a very large range of frequencies.[11] The total integrated IR intensities for these four isotopomers of methanol are given in table I. These allow for the determination of the average effective partial charges for the hydrogen bonded to the oxygen, H(O), and for the three hydrogens bonded to the carbon, H(C). From $I(\text{CH}_3\text{OH}) - I(\text{CH}_3\text{OD})$ we find $\xi_{\text{H(O)}} = 0.63 e$ and $\xi_{\text{H(C)}} = 0.14 e$ from $I(\text{CD}_3\text{OH}) - I(\text{CH}_3\text{OH})$. These values are quite consistent with what is usually expected from chemical intuition. Furthermore equation (10) and the assumption that the atomic charges do not depend on the isotopic substitution imply

$$I(\text{CD}_3\text{OD}) = I(\text{CD}_3\text{OH}) + I(\text{CH}_3\text{OD}) - I(\text{CH}_3\text{OH}); \quad (12)$$

this relation is verified with 1.3% accuracy.

III. NUMERICAL METHODS

A. Liquid phase computations

Liquid phase simulations were performed with density functional based first-principle Molecular Dynamics[12] (FPMD). FPMD has proven successful in reproducing water structure and dynamics[13, 14, 15, 16]. The simulated system was a periodically replicated

box containing 32 water molecules at experimental density. The gradient-corrected BLYP functional was used in conjunction with Trouiller-Martins (TM) pseudo-potentials and a plane-wave basis-set with an energy cut-off of 70 Ry. A small fictitious electron mass of 80 A.U. was used with a timestep of 2 A.U. This was necessary in order that the fictitious electron dynamics does not alter vibration frequencies. With these settings, the fictitious kinetic energy was negligible with respect to the ionic, physical, kinetic energy. The system was first equilibrated at 350 K using a chain of three Nosé thermostat for 5 ps and then constant energy simulation was performed for 10 ps. We have chosen such temperature slightly higher than the temperature of the experimental data we will compare our results with, because it has been demonstrated that water described by FPMD has a fusion temperature too high[17]. Liquid water at 300 K from FPMD appears too structured with a too low diffusion constant[16, 17, 18, 19, 20]. Taking the diffusion constant as "thermometer", FPMD water at 350 K corresponds approximately to experimental water at 300 K[20]. All computations were performed using the CPMD package[21].

B. APT tensor and infrared spectrum

The APT tensor was calculated for each atom every 1.935 fs from a ≈ 5 ps long dynamics, using a finite difference approach. The APT tensor can be rewritten through the Maxwell relation:

$$\frac{\partial M^\beta}{\partial R_I^\alpha} = \frac{\partial F_I^\alpha}{\partial \mathcal{E}^\beta} = \frac{\partial^2 E_{tot}}{\partial \mathcal{E}^\beta \partial R_I^\alpha} \quad (13)$$

where $\vec{\mathcal{E}}$ is an applied uniform electric field and \vec{F}_I the force acting on particle I . This allows for the calculation of the $3N$ elements of the system APT tensor through only three responses calculations to an external electric field ($\beta = x, y, z$). To this aim we have applied small electric fields in all six directions ($\pm x, \pm y, \pm z$) of 0.001 A.U. The coupling between the external electric field and the electronic system through the macroscopic polarization of the periodically replicated cell[22, 23] is defined using the Berry phase approach of Resta[2, 24].

The infrared spectrum was calculated as the Fourier transform of the autocorrelation function of the total current using harmonic quantum-classical corrections:

$$I(\omega) = \frac{\beta}{3V} \int dt \langle \vec{j}(0) \vec{j}(t) \rangle e^{i\omega t}, \quad (14)$$

with $\vec{j}(t) = \frac{d\vec{M}(t)}{dt}$, β the inverse temperature and V the system volume. The current was

then evaluated from the APT tensors through chain rule (6) Because harmonic corrections amount to consider the classical response of the system to an applied electric field, the integrated intensity sum rule remains valid.

C. Gas phase calculations

Water dimer calculations were similar to liquid water. We have employed a simulation box of 15 A.U. and electrostatic interaction between replicates was avoided using the Hockney method. The geometry of the system was first optimized. APT tensors of all atoms in the dimer were then obtained from application of finite electric fields.

Electron density reorganisation upon displacement of the central hydrogen was also computed from finite difference: the central proton was moved 0.1 A.U. in a direction parallel to the H...O axis.

IV. RESULTS

A. Infrared charges in liquid water

We have collected literature data[25, 26, 27] for the IR spectra of H₂O and D₂O over the whole range of infrared frequencies: from 15 cm⁻¹ to 15000 cm⁻¹ for H₂O and 8000 cm⁻¹ for D₂O. In the latter case, a scaling of data for the low frequency region was necessary to combined with the high frequency data, collected at different temperature. From the integrated intensities of the infrared spectra of H₂O and D₂O, the experimental partial charge on the hydrogens of water was found to be 0.55 *e*.

From our FPMD simulation we have obtained effective partial charges $\xi_H = 0.59 e$ and $|\xi_O| = 1.00 e$ repectively for the hydrogens and oxygen of water. The agreement reached between the experimental charges and the simulation results is very good, but partially due to the choice of effective temperature for the simulation.

A clear enhancement of the water hydrogen infrared charge from gas phase, where $\xi_H = 0.24 e$, to liquid phase is observed. This evidences the larger charge displacements in liquid water due to hydrogen bonding, both from simulation and experiment, which is a success of using charges directly related to infrared spectroscopy.

In the remainder of this paper, we will now study in more details the nature of the charge displacements through analysis of the anisotropy of the APT tensors. While it would seem that a drawback of defining partial charges from experimental data is that they are inevitably dressed, we will show that this dressing of the charges contains valuable information once retrieved.

B. Anisotropy of the hydrogen APT

The calculated water oxygen and hydrogen infrared King charges discussed above do not satisfy electro-neutrality. This is at contrario to the Born charges that are required to satisfy electro-neutrality through the so-called acoustic sum rule. King charges and Born charges are thus not equal for liquid water. The Born charge represents the isotropic part of the APT tensor; a different King charge then means that anisotropic contributions to the water APT are non zero.

To characterize better the APT which is a non symmetric 3×3 tensor we performed singular value decomposition of the APT tensors, writing

$$APT = U \Xi V^T, \quad (15)$$

where U and V are 3×3 unitary matrices and Ξ is a diagonal matrix with non-negative diagonal elements. The singular values, diagonal elements ξ_1 , ξ_2 and ξ_3 of Ξ , have the dimension of a charge and their differences can be used to characterize the anisotropy of the atomic polarisability tensor. The infrared King charge ξ_I^2 is then the average of the three singular values squared.

A graphical representation of that decomposition can be given defining ellipsoids whose principal axis are aligned with the right-singular vectors and have a length given by the associated singular value. Figure 2 displays such ellipsoids for the APT tensors of the water dimer. Physically, these ellipsoids show the magnitude of the dipole moment change upon a small displacement of the associated atom in the direction of the principal axis. For completion, but of less direct interest here, we would like to mention that these ellipsoids represent the envelop of forces acting on the atom upon application of a normalised electric field along any direction.

It is evident from figure 2 that the central hydrogen APT tensor is highly anisotropic,

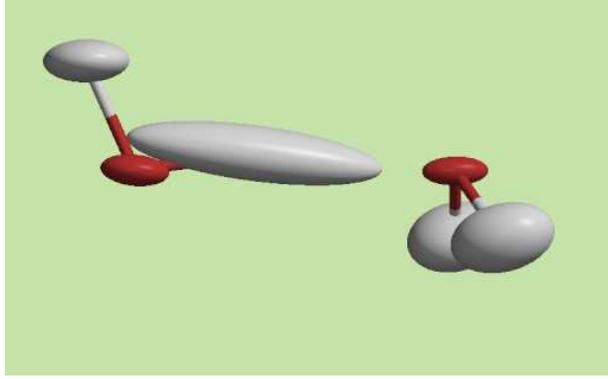


FIG. 2: Ellispoidal representation of the APT tensors (see text) in the water dimer.

with an ellipsoid exhibiting a marked prolate shape. The response of the total dipole moment with respect to a displacement of the central hydrogen along the H-bond is seen to be much larger than for displacements perpendicular to it. This indicates in the latter case a large accompanying flow of charge along the H-bond. The situation is similar in liquid water, see fig. 3 where many of the hydrogen APT ellipsoids display the typical prolate shape encountered in the water dimer. The average singular values are found to be in the FPMD simulations: $\xi_1 = 0.93 e$, $\xi_2 = 0.34 e$ and $\xi_3 = 0.24 e$.

The water hydrogen APT tensor depend strongly on the geometry of the hydrogen bond and figure 4 displays the mean hydrogen APT singular values function of the O-O distance of the H-bond in which the hydrogen is involved. The hydrogen infrared King charge as a function of O-O distance is also shown on this figure. The largest singular value appears the most sensitive to the strength of the H-bond while the other two are nearly independent of it, with values around the gas phase value ($0.24 e$) for all O-O distances. For very short H-bonds the highest singular value can even be larger than $1 e$. This indicates that globally electrons counter flow the hydrogen displacement along the H-bond in that case, instead of flowing with it! On the other hand, for broken H-bonds the hydrogen APT tensor is nearly isotropic with singular values equal to $\xi_1 = 0.45 e$, $\xi_2 = 0.36 e$ and $\xi_3 = 0.25 e$.

C. Relation to band intensities in the IR spectrum

While the largest singular value seems associated to OH stretch motion, the other two are related to bending motion of the H-bond. If these motions were uncorrelated a partial sum rule for each band would be valid. The infrared intensity integrated for one band only

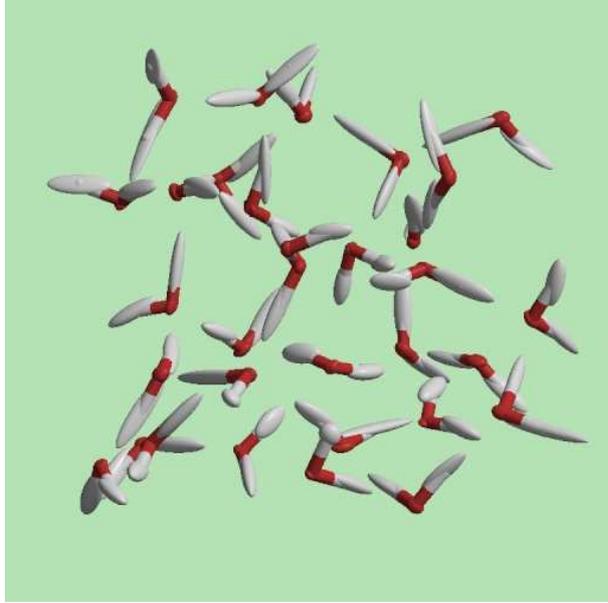


FIG. 3: Ellipsoidal representation of the APT tensors (see text) for a snapshot of a simulation of 32 water molecules.

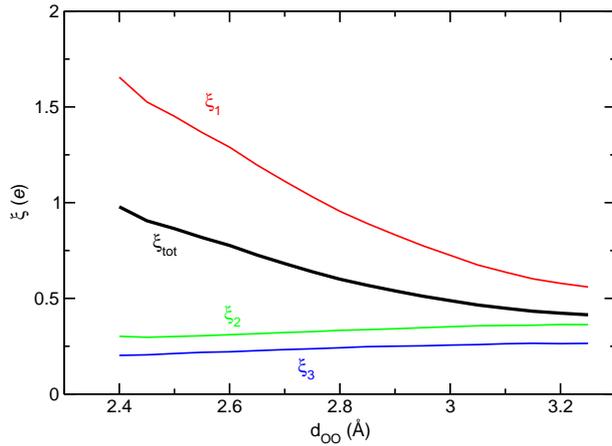


FIG. 4: Mean singular values and global infrared charges of the hydrogen APT tensors as a function of the H-bond length (O-O distance).

would then be equal to the infrared charge of the underlying vibration. Assuming that this is approximately true for the OH-stretch whose frequency is much higher than other vibrational modes in the system we can integrate the infrared intensity in the OH-strech region as is illustrated in figure 5. The integration from 2500 cm^{-1} to 4000 cm^{-1} of the calculated infrared spectrum gives a OH-stretch infrared charge of $0.85 e$ compared to the average largest singular value $\xi_1 = 0.93 e$. Using experimental data we get for the OH-strech

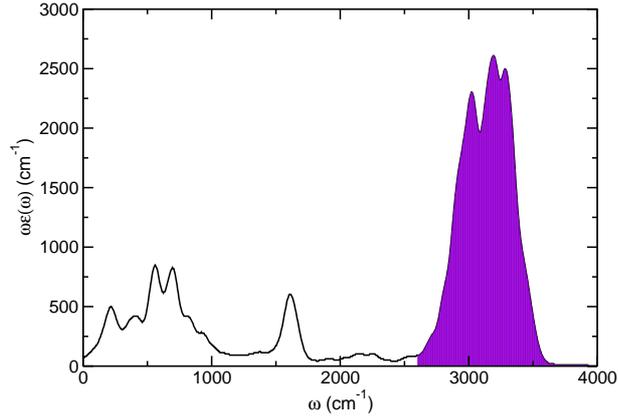


FIG. 5: Simulated IR spectrum of an assembly of 32 water molecules. The integration region under the OH-stretch band used to define the charge of this mode is highlighted in purple.

a charge of $0.75 e$. Here as well we find from experimental data that the water hydrogen APT tensor is highly anisotropic. Assuming that the two smaller singular values are nearly equal we get from experimental data $\xi_2 \approx \xi_3 \approx 0.41 e$ ($\xi_2 \approx \xi_3 \approx 0.30 e$ from FPMD). The large anisotropy of the hydrogen APT tensor then gives rise to the characteristic shape of liquid water IR spectrum with a very intense OH stretch band with respect to the rest of the spectrum.

The OH stretch charge is greatly enhanced when going from the gas phase to the liquid phase while the two other singular values for the water hydrogen APT are much smaller. This can explain why the molecular dipole defined from the APT tensor appears small[6]. The molecular dynamical dipole is the derivative of the total dipole moment with respect to a rotation of the molecule. In such rotation, the hydrogen move perpendicularly to the H-bond so that the molecular dipole probes only the two lower singular values.

To further evidence the effect of the anisotropy of the APT tensors in liquid water on the infrared spectrum we have calculated the later in two different ways[28]: using the full APT tensors to calculate the instantaneous current in the sample,

$$\vec{j} = \frac{d\vec{M}}{dt} = \sum_I \frac{\partial \vec{M}}{\partial \vec{R}_I} \vec{V}_I, \quad (16)$$

or using only the Born charge, the isotropic part of the APT tensor, in its place:

$$\vec{j}^{iso} = \sum_I Z_I \vec{V}_I, \quad (17)$$

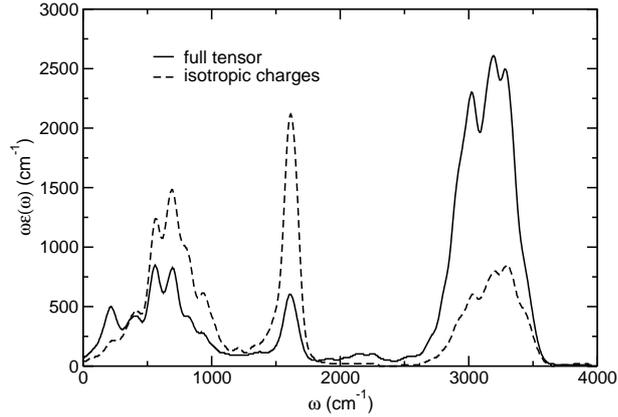


FIG. 6: Simulated IR spectrum of an assembly of 32 water molecules. Solid line: using the full APT tensor, dashed line: defining the instantaneous current from the trace only of the APT tensor (see text).

for the same FPMD trajectory. The second case is very similar to classical MD simulations where atoms bear a simple point charge (although it should be noted that in the present calculation the born charges Z_I depend on time). Like previously we have used the standard harmonic quantum-classical correction as this one preserve the sum rule discussed above. The two spectrum (full and iso) are represented figure 6 along with the experimental spectrum figure 7[25]. It is clear from this figure that an isotropic APT leads to an OH stretch intensity at maximum lower than that of the bending and libration bands while it should be found much higher. The bending and libration bands appear then too intense when using an isotropic APT tensor. Only the full, anisotropic, APT tensors can capture the right shape of the liquid water infrared spectrum. The libration band is the signature of rotations and its small intensity is thus related to the two lowest singular values and to the small molecular dynamical dipole.

It would then appear that the failure to reproduce infrared band intensities for liquid water with non-polarizable force-fields simulation is not due to quantum-classical corrections but to the lack of a physical effect, namely the charge reorganisation following atomic displacements, giving rise to strongly anisotropic hydrogen APT's.

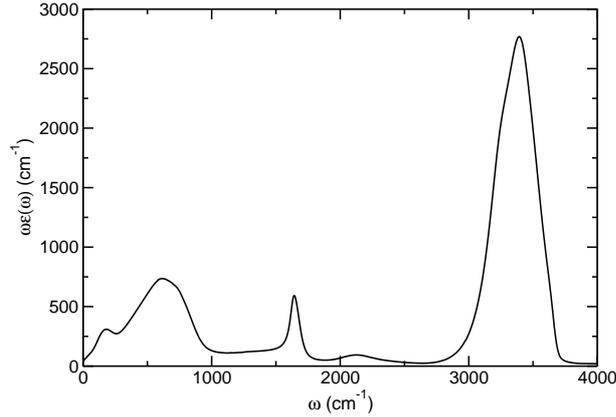


FIG. 7: Experimental IR spectrum of liquid water.

V. CONCLUSION

We have shown in this paper that by using an exact sum rule on the infrared spectrum it is possible to evaluate experimentally a partial dynamical charge for hydrogen atoms in liquid water, dynamical charge derived from the APT tensor. This infrared King's charge, is estimated from experimental data to be $0.55 e$ and $0.59 e$ from ab initio MD. This hydrogen King charge is remarkably enhanced with respect to its gas phase value, as a result of hydrogen bonding. This shows that the use of dynamical charge makes it possible to quantify from an experimentally accessible probe charge transfers induced by H-bonding.

It was found however from the first-principle simulations that the hydrogen APT tensor in liquid water is highly anisotropic. This originates from large charge rearrangements when the hydrogen is moved along the hydrogen bond. Such structure of the APT tensor is at opposite to the picture of a simple point charge carried by the hydrogen atom.

We have then shown that the anisotropy of the hydrogen APT tensor can also be inferred from the infrared spectrum of liquid water, namely through the very strong OH-stretch band. To this respect, first-principle simulations were shown to very successfully reproduce infrared band intensities of liquid water. That anisotropy of the APT tensor is expected to have diverse consequences, e.g. through modifying the magnitude of the interaction between OH-stretches, with respect to a simple point charge picture, with influence on the lifetime of vibrational excitations or the spatial extend of the coupling between OH vibrators.

Finally, as all charges derived from the APT tensor, the infrared King charge is a dressed quantity and, as exemplified above, can not simply be used to fix simple point charge models.

However being observables the APT tensors can be computed for any kind of model, like polarizable models or charge transfer models, and can be used in this respect for fitting purposes.

APPENDIX A: DERIVATION OF SUM RULES

We state here a general sum rule for the imaginary part of the susceptibility of a classical or quantum system, in the case where both the perturbation and the observable depend only on positions (not on momenta). We then particularize that sum rule to the case of infrared spectroscopy, in order to obtain the generalized Crawford's sum rule used here to relate integrated infrared intensities to dynamical partial charges.

1. Generalized f -sum rule

The linear response of an observable B of a system of N particles in contact with a thermostat at temperature T subject to a time-dependent force $X(t)$ conjugated to the quantity A (the first order perturbation of the hamitonian of the system then being $-AX(t)$) is written as[8]

$$B(t) = \int_0^{+\infty} \Phi(\tau)X(t - \tau)d\tau, \quad (\text{A1})$$

where $\Phi(t)$ is called the response function. The associated susceptibility $\chi(\omega) = \int_0^{+\infty} e^{i\omega t}\Phi(t)dt$ can be shown to satisfy the sum rule (eq. (3.7.8) of ref. [8])

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega \left[\chi''(\omega) - \frac{\Phi(+0)}{\omega} \right] = \dot{\Phi}(+0), \quad (\text{A2})$$

where χ'' is the imaginary part of χ .

In the case where both A and B are functions only of the positions $\{\mathbf{q}_i\}$, $i = 1, \dots, N$ of the particles ($A = A(\{\mathbf{q}_i\})$ and $B = B(\{\mathbf{q}_i\})$), equation (A2) can be shown to yield the following sum rule, valid both for a classical or a quantum system:

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega \chi''(\omega) = \sum_i \frac{1}{m_i} \left\langle \frac{\partial B}{\partial q_i^\alpha} \frac{\partial A}{\partial q_i^\alpha} \right\rangle, \quad (\text{A3})$$

where m_i is the mass of particle i . This equation is the main result of this appendix. It relates the average rate of energy absorption over the whole range of frequencies to a sum of equilibrium atomic properties.

For a classical system, the demonstration of eq. (A3) relies on the equipartition theorem for an equilibrium state. Indeed, in that case the response function $\Phi(t)$ can be written as the correlation between B and \dot{A} :

$$\Phi(t) = \beta \langle B(t) \dot{A}(0) \rangle \quad (\text{A4})$$

($\beta = k_B T$ and $\langle \rangle$ denotes an average over the unperturbed system). Equation (A2) becomes

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega \chi''(\omega) = \beta \langle \dot{B}(0) \dot{A}(0) \rangle \quad (\text{A5})$$

(since $\beta \langle B(t) \dot{A}(0) \rangle$ is an odd function of time, $\Phi(+0) = 0$). We then have

$$\dot{A} = \sum_i \frac{\partial A}{\partial q_i^\alpha} \dot{q}_i^\alpha = \sum_i \frac{\partial A}{\partial q_i^\alpha} \frac{p_i^\alpha}{m_i} \quad (\text{A6})$$

and similarly for B , where \mathbf{p}_i is the momentum of particle i ($\alpha = x, y, z$ and the Einstein notation was used). Thus

$$\begin{aligned} \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega \chi''(\omega) &= \beta \sum_{ij} \left\langle \frac{\partial B}{\partial q_i^\alpha} \frac{p_i^\alpha}{m_i} \times \frac{\partial A}{\partial q_j^\beta} \frac{p_j^\beta}{m_j} \right\rangle. \\ &= \beta \sum_{ij} \left\langle \frac{\partial B}{\partial q_i^\alpha} \frac{\partial A}{\partial q_j^\beta} \right\rangle \left\langle \frac{p_i^\alpha}{m_i} \frac{p_j^\beta}{m_j} \right\rangle \end{aligned} \quad (\text{A7})$$

using the decorrelation of positions and momenta at equilibrium. Finally from the equipartition theorem we further have

$$\frac{1}{2m_i} \langle p_i^\alpha p_j^\beta \rangle = \frac{k_B T}{2} \delta_{ij} \delta_{\alpha\beta} \quad (\text{A8})$$

which leads to equation (A3).

On the other hand, for a quantum system we have (eq. (4.2.14) of ref. [8])

$$\Phi(t) = \frac{i}{\hbar} \langle [\hat{B}(t); \hat{A}(0)] \rangle, \quad (\text{A9})$$

where now $A \equiv \hat{A}$ and $B \equiv \hat{B}$ are operators and $[;]$ denotes their commutator. Then (eq. (4.2.35) of ref. [8])

$$\dot{\Phi}(+0) = \frac{-1}{\hbar^2} \langle [[\hat{\mathcal{H}}; \hat{B}(0)]; \hat{A}(0)] \rangle, \quad (\text{A10})$$

Using the assumption that both \hat{A} and \hat{B} are functions only of the position operators, $\hat{A} = A(\{\hat{\mathbf{q}}_i\})$ and $\hat{B} = B(\{\hat{\mathbf{q}}_i\})$, we have from $[\hat{q}_i^\alpha; \hat{q}_j^\beta] = 0$: $[\hat{A}; \hat{B}] = 0$ and $[\hat{\mathcal{H}}; \hat{B}] = [\hat{T}; \hat{B}]$,

with $\hat{\mathcal{T}} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_i}$ being the kinetic operator. From $[\hat{\mathbf{p}}_i; \hat{B}] = -i\hbar \frac{\partial \hat{B}}{\partial \hat{\mathbf{q}}_i}$ and adding and subtracting $\frac{1}{2m_i} \sum_i \hat{\mathbf{p}}_i \hat{B} \hat{\mathbf{p}}_i$ to $[\hat{\mathcal{H}}; \hat{B}]$ we obtain

$$\dot{\hat{B}} = \frac{i}{\hbar} [\hat{\mathcal{H}}; \hat{B}] = \frac{1}{2} \sum_i \left(\frac{\partial \hat{B}}{\partial \hat{q}_i^\alpha} \hat{p}_i^\alpha + \hat{p}_i^\alpha \frac{\partial \hat{B}}{\partial \hat{q}_i^\alpha} \right) \quad (\text{A11})$$

which is the quantum analog of eq. (A6) for the operator \hat{B} . Combining equations (A10) and (A11) with $[\hat{\mathbf{p}}_i; \hat{A}] = -i\hbar \frac{\partial \hat{A}}{\partial \hat{\mathbf{q}}_i}$, we finally recover the desired sum rule eq. (A3).

2. Application to infrared spectra

For infrared (IR) or optical spectroscopy, the time-dependent perturbation is $-\mathbf{M}\mathcal{E}(t)$ where \mathbf{M} is the *total* dipole moment of the system and $\mathcal{E}(t)$ is the time-dependent $\mathbf{k} = 0$ component of the Maxwell electric field applied on the (infinite) system. The measured signal is the induced polarization $\mathbf{P} = \mathbf{M}/V$ in the system (V being its volume). The system is assumed to be isotropic without lack of generality so that \mathbf{P} is colinear with the applied field and the signal is averaged over all possible orientations. The integrated absorption spectrum of the system is given by

$$I_{tot} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega \chi''(\omega) = \frac{1}{3V} \sum_i \frac{1}{m_i} \left\langle \frac{\partial \hat{M}^\beta}{\partial \hat{q}_i^\alpha} \frac{\partial \hat{M}^\beta}{\partial \hat{q}_i^\alpha} \right\rangle, \quad (\text{A12})$$

where the index i denotes the particles, atoms or ions, in the system. Note that the derivatives $\frac{\partial \hat{M}^\beta}{\partial \hat{q}_i^\alpha}$ in principle depend on boundary conditions; since the perturbation applied on the infinite system is the Maxwell electric field, those are to be taken at zero field.[29] This equation is identical to Crawford's G-sum rule, up to a rotational correction, which was originally developed for isolated molecules in the harmonic approximation[9]. Here its very general validity is deduced from linear response theory. In practice the upper limit ω_M of the integration in eq. (A12) should be much higher than the typical frequencies of atomic motions but still much lower than the lowest optical transition. In insulators, a wide range of frequencies satisfy these conditions and I_{tot} is largely independent of ω_M over that range.

When ω_M is large enough so that the optical spectrum is included in the integration, electrons have to be considered at the same level as the nuclei and, based on the large difference of masses, one recovers from eq. (A12) the well-known optical f -sum rule

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega \chi''(\omega) = \frac{N}{3V} \frac{e^2}{m_e} \quad (\text{A13})$$

which relates the integrated optical spectrum to the number of electrons in the system times e^2 , with e being the elementary charge. In analogy with the f -sum rule, $\frac{1}{3V} \sum_i \frac{1}{m_i} \langle \frac{\partial \hat{M}^\beta}{\partial \hat{q}_i^\alpha} \frac{\partial \hat{M}^\beta}{\partial \hat{q}_i^\alpha} \rangle = \Omega_p^2$ is the square of an infrared plasma frequency Ω_p . Indeed, using Kramers-Krönig relations, the sum rule (A12) is equivalent with the asymptotic behavior of the real part of the dielectric constant:[30]

$$\chi'(\omega) = \chi_\infty - \frac{\Omega_p^2}{\omega^2}, \quad (\text{A14})$$

where χ_∞ is the electronic susceptibility of the system.

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- [1] B. Cabane and R. Vuilleumier, *Comptes Rendus Geosciences* **337**, 159 (2005).
 - [2] P. L. Silvestrelli and M. Parrinello, *Phys. Rev. Lett.* **82**, 3308 (1999).
 - [3] Y. S. Badyal, M.-L. Saboungi, D. L. Price, S. D. Shastri, D. R. Haeffner, and A. K. Soper, *J. Chem. Phys.* **112**, 9206 (2000).
 - [4] C. Falter, W. Ludwig, A. A. Maradudin, M. Selmke, and W. Zierau, *Phys. Rev. B* **32**, 6510 (1985).
 - [5] We assume here that the system is at all times in its electronic ground state so that the total dipole moment can be formally written as a function of the atomic positions.
 - [6] A. Pasquarello and R. Resta, *Phys. Rev. B* **68**, 174302 (2003).
 - [7] M. Sharma, R. Resta, and R. Car, *Phys. Rev. Lett.* **95**, 187401 (2005).
 - [8] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics*, vol. II (Springer Verlag, 1991), 2nd ed.
 - [9] J. B. R. Crawford, *J. Chem. Phys.* **20**, 977 (1952).
 - [10] W. T. King, G. B. Mast, and P. P. Blanchette, *J. Chem. Phys.* **56**, 4440 (1972).
 - [11] J. E. Bertie and S. L. Zhang, *J. Mol. Struct.* **413-414**, 333 (1997).
 - [12] R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
 - [13] K. Laasonen, M. Sprik, M. Parrinello, and R. Car, *J. Chem. Phys.* **99**, 9080 (1993), URL <http://link.aip.org/link/?JCP/99/9080/1>.
 - [14] M. Sprik, J. Hutter, and M. Parrinello, *J. Chem. Phys.* **105**, 1142 (1996).
 - [15] P. Silvestrelli and M. Parrinello, *J. Chem. Phys.* **111**, 3572 (1999).

- [16] J. VandeVondele, F. Mohamed, M. Krack, J. Hutter, M. Sprik, and M. Parrinello, *J. Chem. Phys.* **122**, 014515 (pages 6) (2005), URL <http://link.aip.org/link/?JCP/122/014515/1>.
- [17] P. H.-L. Sit and N. Marzari, *J. Chem. Phys.* **122**, 204510 (pages 9) (2005), URL <http://link.aip.org/link/?JCP/122/204510/1>.
- [18] J. C. Grossman, E. Schwegler, E. W. Draeger, F. Gygi, and G. Galli, *J. Chem. Phys.* **120**, 300 (2004), URL <http://link.aip.org/link/?JCP/120/300/1>.
- [19] E. Schwegler, J. C. Grossman, F. Gygi, and G. Galli, *J. Chem. Phys.* **121**, 5400 (2004), URL <http://link.aip.org/link/?JCP/121/5400/1>.
- [20] M. V. Fernández-Serra and E. Artacho, *J. Chem. Phys.* **121**, 11136 (2004).
- [21] *Cpmd*, Copyright IBM Corp 1990-2001, Copyright MPI für Festkörperforschung Stuttgart (1997-2004).
- [22] P. Umari and A. Pasquarello, *Phys. Rev. Lett.* **89**, 157602 (2002).
- [23] P. Umari and A. Pasquarello, *Int. J. Quant. Chem.* **101**, 666 (2005).
- [24] R. Resta, *Phys. Rev. Lett.* **80**, 1800 (1998).
- [25] J. E. Bertie and Z. Lan, *App. Spec.* **50**, 1047 (1996).
- [26] J. E. Bertie, M. K. Ahmed, and H. H. Eysel, *J. Phys. Chem* **93**, 2210 (1989).
- [27] H. R. Zelsmann, *J. Mol. Struc.* **350**, 95 (1995).
- [28] A. Pasquarello and R. Car, *Phys. Rev. Lett.* **79**, 1766 (1997).
- [29] P. Ghosez, J.-P. Michenaud, and X. Gonze, *Phys. Rev. B* **58**, 6224 (1998).
- [30] M. Altarelli, D. L. Dexter, , H. M. Nussenzveig, and D. Y. Smith, *Phys. Rev. B* **6**, 4502 (1972).