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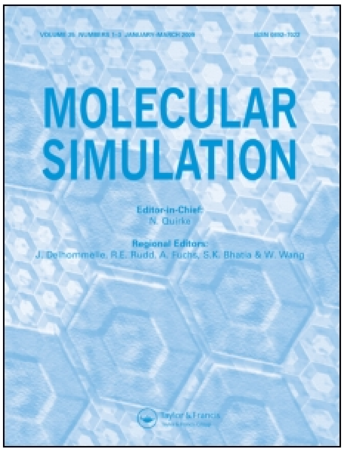

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ROTATION-VIBRATION COUPLING IN LIQUID WATER INVESTIGATED BY MOLECULAR DYNAMICS SIMULATION

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The standard rotation-vibration decoupling approximation for liquid water is tested using a method based on the split of the molecular dipole fluctuation correlation function into pure rotational, pure vibrational and crossed terms. Our results corroborate the total decoupling between vibrational and rotational motions in liquid water at ambient conditions and provide a tool able to test the reliability of this approximation for molecular liquids at different states.

Keywords: Molecular dynamics; liquid water; rotation-vibration coupling; dipole moment

1. INTRODUCTION

Theoretical approaches for the study of different properties and systems usually require to assume one or more approximations. These approximations are normally based on reasonable hypotheses and their validity is frequently proved a posteriori. If the property under study is accessible by experimental techniques, the assumed approximation can be directly tested. Otherwise, computer simulation can provide alternative ways for testing the approximation. Molecular dynamics (MD) simulation is a powerful tool

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that is not only able to reproduce the microscopic structural and dynamic properties of physical systems but it also can be very helpful to check the reliability of the theoretical approximations.

In most of spectroscopic studies of solids, liquids and gases the influence of the crossed vibration-rotation correlation terms is ordinarily neglected [1]. This hypothesis could be questionable for molecular liquids, especially for hydrogen-bonded systems like water. However, to our knowledge, this approximation has not been tested in the case of liquid water. The extent of the coupling between the translational and rotational molecular motions in condensed phase water was analysed by DiCola *et al.* [2]. These authors studied proton dynamics in supercooled water and compared the MD simulation results using the SPC/E potential model with the quasielastic neutron scattering results. They observed a substantial coupling between rotational and translational dynamics in the time scale of about 1 ps, for both supercooled and ambient states.

We have investigated the validity of the rotation-vibration decoupling approximation in the case of liquid water by MD simulation. Among the molecular models for liquid water, SPC is one of the most popular. In the rigid version [3] it is assumed the existence of three point charges located in the atomic sites, interacting each other through effective forces which keep the atoms close to their equilibrium positions. One of the SPC flexible versions is the model introduced by Toukan and Rahman in 1985 [4]. That model was reparameterized in order to reproduce the infrared frequency spectrum of water at room temperature [5]. The latter, which is the model employed in this work, incorporates intramolecular interactions which include both harmonic and anharmonic terms.

MD simulations allow us to analyse translation, rotation and internal vibration of the different molecules in a liquid from a classical point of view. In recent years, detailed MD studies of molecular motions for water at states along the coexistence curve [6] and for supercritical states [7] have been carried out. It is important to note that infrared (IR) and Raman spectroscopy as well as neutron scattering measurements are the most relevant experimental tools to study the internal microscopic dynamics in liquids. Moreover, molecular motions resulting from classical MD simulations can be related to these experimental properties [8–11].

The method proposed in this paper is based on the study of the fluctuations of the molecular dipole moment. This quantity, which is sensitive to changes in both rotational and vibrational motions is associated with the IR spectroscopic properties [12]. Furthermore it is well known that, in the gas phase, the vibrational-rotational band shape can be used to analyse whether the dipole moment change is produced along or across the axis of a linear molecule [13]. For a nonlinear molecule like water, we can perform an analogous treatment since the changes in the instantaneous dipole moment direction are directly connected to both the variations of the geometry of the molecule (vibrations) and to the molecular spatial orientation (rotations). When considering a condensed phase, the influence of the environment on the molecular motions should have a significant contribution to the dipole moment fluctuations.

2. MOLECULAR DYNAMICS SIMULATION

We performed a MD simulation of 216 flexible water molecules at 298 K and 1.0 g/cm^3. We assumed the flexible SPC potential of Ref. [5]. It is important to point out that this model allows us to reproduce the main trends of the experimental frequency bands of the water infrared spectrum, as shown in Ref. [9].

We considered usual periodic boundary conditions and the Ewald sum rule was employed in order to compute the long-ranged Coulombic interactions. A leap-frog Verlet integration algorithm with coupling to a thermal bath was used [14]. The integration time-step was 0.5 fs. Translational and internal degrees of freedom were equilibrated separately [15] to get quickly the corresponding temperature. We have performed a MD run of 150 ps after an equilibration period of 20 ps.

3. DISCUSSION

The theoretical treatment of the microscopic motions for a nonrigid molecular model is based on the observation that all atoms can move about their equilibrium positions [1]. In the Hamiltonian formulation, we can write the total energy of a system of N molecules as a sum over all the degrees of freedom of the kinetic energy plus the potential energy contribution. The kinetic energy includes translational, rotational, vibrational and coupled rotational-vibrational terms (Coriolis energy). The standard theoretical approach for the total energy of a molecular system includes the energy of the rigid rotating bodies plus the vibrational energy of the nonrotating molecules whereas the rotational-vibrational coupling term is ordinarily neglected (see Ref. [1] for instance).

In MD simulations, the study of the microscopic rotations and vibrations is usually performed through the calculation of the spectral densities

$S_{O,H}(\omega)$ of the atomic velocity autocorrelation functions $C_{\mathbf{v}_{O,H}}(t)$ [16]:

$$S_{O,H}(\omega) = \frac{1}{2\pi}\int_0^\infty dt\, C_{\mathbf{v}_{O,H}}(t)\,\mathrm{e}^{-i\omega t}, \tag{1}$$

where

$$C_{\mathbf{v}_{O,H}}(t) \equiv \langle \mathbf{v}_{O,H}(0)\mathbf{v}_{O,H}(t)\rangle. \tag{2}$$

The spectral density $S_H(\omega)$ found for liquid water at ambient conditions (see Ref. [5] for instance) shows three different and separated bands. The band centred about 500 cm^{-1} is related to molecular rotations and can be decomposed into three different contributions according to an orthogonal coordinate system corresponding to instantaneous molecular plane [16]. The bands centred about 1650 and 3400 cm^{-1} are associated with the bending and stretching vibrations, respectively. Furthermore, it is possible to connect the $C_{\mathbf{v}_H}(t)$ correlation function with the absorption coefficient obtained by IR spectroscopy [9]. This procedure has proved to be very useful to study the spectral bands separately but it does not provide any information about the importance of the vibrational-rotational coupling contribution. So we will consider an alternative but equivalent approach which is based on the direct calculation of the correlation function corresponding to the molecular dipole moment fluctuations. This is a suitable method to study the rotation-vibration coupling since the fluctuations of the molecular dipole moment as well as the contributions to these fluctuations from the molecular rotations and vibrations can be independently determined.

The IR spectral density (roughly the absorption coefficient) can be calculated [10] through the Fourier transform of the *dipole moment fluctuation* time correlation function $C_{rv}(t)$:

$$C_{rv}(t) = \left\langle \frac{1}{N}\sum_{j=1}^{N}[\delta\boldsymbol{\mu}_j(0)\cdot\delta\boldsymbol{\mu}_j(t)]\right\rangle, \tag{3}$$

where

$$\delta\boldsymbol{\mu}_j(t) = \boldsymbol{\mu}_j(t) - \boldsymbol{\mu}_j^{\mathrm{eq.}} \tag{4}$$

and the dipole moment $\boldsymbol{\mu}_j$ of the water molecule j ($j = 1, \ldots, N = 216$) is

$$\boldsymbol{\mu}_j(t) = e\,(\mathbf{r}_j^H(t) + \mathbf{r}_j^{H'}(t) - 2\,\mathbf{r}_j^O(t)). \tag{5}$$

Here $\boldsymbol{\mu}_j^{\mathrm{eq.}}$ is the equilibrium (averaged) value of the dipole moment, e is the electron charge and the $\mathbf{r}_j(t)$ are the atomic positions. It is important to note that the correlation function $C_{rv}(t)$ is defined as the correlation at different times of the dipole moment fluctuation $\delta\boldsymbol{\mu}_j(t)$. This property is not equivalent to the single dipole moment correlation function $\langle\boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle$, that was studied in Ref. [16].

The dipole moment can be straightforwardly rewritten as:

$$\boldsymbol{\mu}_j(t) = \mu_j(t)\cdot\boldsymbol{u}_j(t) \tag{6}$$

where $\boldsymbol{\mu}_j(t)$ is the module of the dipole moment and $\boldsymbol{u}_j(t)$ is a unit vector along $\boldsymbol{\mu}_j(t)$. Using that notation we can define the following time correlation functions:

$$\begin{aligned} C_r(t) &= \langle\boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\rangle \\ C_v(t) &= \langle\delta\mu(0)\delta\mu(t)\rangle \end{aligned} \tag{7}$$

One of these functions ($C_r(t)$) is directly connected to the orientational changes of the molecular dipole moment (*pure rotations*) whereas the other ($C_v(t)$) corresponds to the fluctuations of the module of the molecular dipole moment (*pure vibrations*). Let us note that:

$$\begin{aligned} C_{rv}(t) &= \left\langle\frac{1}{N}\sum_{j=1}^{N}[\mu_j(0)\boldsymbol{u}_j(0)-\boldsymbol{\mu}_j^{\mathrm{eq.}}]\cdot[\mu_j(t)\boldsymbol{u}_j(t)-\boldsymbol{\mu}_j^{\mathrm{eq.}}]\right\rangle \\ &= \left\langle\frac{1}{N}\sum_{j=1}^{N}[\mu_j(0)\mu_j(t)\ \ \boldsymbol{u}_j(0)\cdot\boldsymbol{u}_j(t)-\boldsymbol{\mu}_j^{\mathrm{eq.}}\cdot\boldsymbol{\mu}_j(t)-\boldsymbol{\mu}_j^{\mathrm{eq.}}\cdot\boldsymbol{\mu}_j(0)+(\boldsymbol{\mu}_j^{\mathrm{eq.}})^2]\right\rangle \\ &= C_v(t)\,C_r(t)+\{\text{coupling terms}\}. \end{aligned} \tag{8}$$

Consequently, the rotation-vibration approximation can be written as:

$$C_{rv}(t) \simeq C_v(t)C_r(t) \equiv C_{r\times v}(t). \tag{9}$$

In order to analyse the reliability of the rotation-vibration decoupling approximation we have calculated the four time-correlation functions appearing in Eq. (9) for liquid water at 298 K and $1.0\,\mathrm{g/cm^3}$. The pure rotation and pure vibration autocorrelation functions are shown in Figure 1a and Figure 1b respectively. The $C_{r\times v}(t)$ and $C_{rv}(t)$ results are compared in Figure 1c. We observe that the contribution of the rotation-vibration coupling is very small and the decoupling approximation is well fulfilled. This can be associated to the different time scales characteristic of the rotational and vibrational motions. So, whereas the oscillation period of $C_v(t)$ is 0.006 ± 0.001 ps (Fig. 1b), the relaxation time of $C_r(t)$ is more than one order

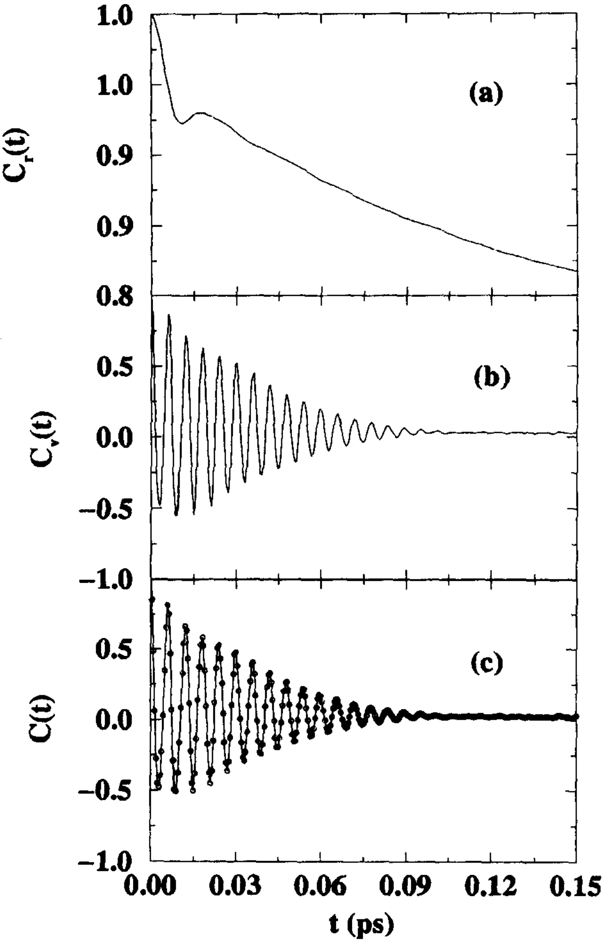

FIGURE 1 Vibration-rotation approximation: (a) Pure rotation correlation function $C_r(t)$; (b) Pure vibration correlation function $C_v(t)$ and (c) Approximation comparison: $C_{rv}(t)$ (continuous line) *vs.* $C_{r \times v}(t)$ (circles).

of magnitude bigger. When considering an exponential long time behaviour for $C_r(t)$,

$$C_r(t) \propto \exp\left\{-\frac{t}{\tau}\right\} \tag{10}$$

we find $\tau = 0.1038 \pm 0.0005\,\text{ps}$. However, we must to point out that the validity of the decoupling approximation has been only checked in liquid water at ambient conditions.

4. CONCLUDING REMARKS

It is generally assumed that molecular rotations and vibrations in liquids are not coupled. However that assumption has not been experimentally checked and only some work was done [2] concerning to the translational and rotational motions. Using molecular dynamics simulation, we have investigated the extent of the rotation-vibration coupling in liquid water at ambient conditions by calculating a set of time correlation functions which are related to the fluctuations of the molecular dipole moment. We have found a very different behaviour for the two types of motions, *i.e.*, the dipole moment rotations relax very smoothly whereas the initial vibrational decay is much faster and fast oscillations are observed after this initial decay. The clear separation of time scales explains the lack of correlation between the associated motions. It is interesting to remark the generality of the methodology proposed, which can be applied to different systems made up of polar molecules with internal vibrations in liquid, gas or solid phases.

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References

[1] Wilson, E. B., Decius, J. C. and Cross, P. C. (1955). "Molecular Vibrations", Dover Publications Inc., New York.

[2] DiCola, D., Deriu, A., Sampoli, M. and Torcini, A. (1996). "Proton dynamics in supercooled water by molecular dynamics simulations and quasielastic neutron scattering", *J. Chem. Phys.*, **104**, 4223.

[3] Berendsen, H. J. C., Postma, J. P. M., van Gunsteren, W. F. and Hermans, J. (1981). "Interaction models for water in relation to protein hydration", In: *Intermolecular forces*, Pullman, B., Ed., Reidel, Dordretch, Holland, pp. 331–342.

[4] Toukan, K. and Rahman, A. (1985). "Molecular-dynamics study of atomic motions in water", *Phys. Rev. B*, **31**, 2643.

[5] Martí, J., Padró, J. A. and Guàrdia, E. (1994). "Molecular dynamics calculation of the infrared spectra in liquid H_2O-D_2O mixtures", *J. Mol. Liq.*, **62**, 17.

[6] Martí, J., Padró, J. A. and Guàrdia, E. (1996). "Molecular dynamics simulation of liquid water along the coexistence curve: Hydrogen bonds and vibrational spectra", *J. Chem. Phys.*, **105**, 639.

[7] Martí, J. (1999). "Analysis of the hydrogen bonding and vibrational spectra of supercritical model water by molecular dynamics simulations", *J. Chem. Phys.*, **110**, 6876.

[8] Madden, P. A. (1986). "Simulation of properties of spectroscopic interest", In: *Molecular Dynamics Simulation of Statistical Mechanical Systems*, Edited by Ciccotti, G. and Hoover, W. G., North Holland, Amsterdam.

[9] Martí, J., Guàrdia, E. and Padró, J. A. (1994). "Dielectric properties and infrared spectra of liquid water: Influence of the dynamic cross correlations", *J. Chem. Phys.*, **101**, 10883.
[10] Bansil, R., Berger, T., Toukan, K., Ricci, M. A. and Chen, S. (1986). "A molecular dynamics study of the OH stretching vibrational spectrum of liquid water", *Chem. Phys. Lett.*, **132**, 165.
[11] Ricci, M. A., Ruocco, G. and Sampoli, M. (1989). "Raman spectra of water in the translational and librational regions. III. Temperature evolution by computer simulation with the TIP4P potential", *Mol. Phys.*, **67**, 19.
[12] Madden, P. A. (1991). "Molecular motions in liquids", In: *Les Houches, Session LI, 1989: Liquids, Freezing and Glass Transition*, Edited by Hansen, J. P., Levesque, D. and Zinn Justin, J., Elsevier Science Publishers.
[13] Colthup, N. B., Daly, L. H. and Wiberley, S. E. (1990). *Introduction to Infrared and Raman spectroscopy*, Academic Press, Inc., San Diego.
[14] Berendsen, H. J. C., Postma, J. P. M., van Gunsteren, W. F., DiNola, A. and Haak, J. R. (1984). "Molecular dynamics with coupling to an external bath", *J. Phys. Chem.*, **81**, 3684.
[15] Wallqvist, A. and Telemann, O. (1991). "Properties of flexible water models", *Mol. Phys.*, **74**, 515.
[16] Martí, J., Padró, J. A. and Guàrdia, E. (1993). "Computer simulation of molecular motions in liquids: Infrared spectra of water and heavy water", *Mol. Simul.*, **11**, 321.