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Molecular-dynamics simulation of liquid water with an *ab initio* flexible water-water interaction potential. II. The effect of internal vibrations on the time correlation functions

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A computer simulation of liquid water using the *ab initio* Matsuoka-Clementi-Yoshimine-Lie (MCYL) potential has been analyzed in comprehensive detail with use of pertinent autocorrelation and cross-correlation functions of the water molecule's vibrational, rotational, and translational dynamics. The autocorrelation functions (ACF's) of dynamical quantities such as atom velocity, center-of-mass velocity, molecular angular momentum, molecular angular velocity, molecular dipole moment, and molecular rotational velocity vectors have been computed with 3400 configurations generated in a simulation with 343 molecules in the laboratory frame and in the frame of the principal molecular moments of inertia. Furthermore, cross-correlation functions (CCF's) of many different kinds have been computed in both frames in order to study in detail the mutual effects of vibration, rotation, and translation at the single-molecule level. In some respects the inclusion of vibrational effects in the MCYL potential does not significantly change the pattern of dynamical information summarized in these time correlation functions. The rotation-translation CCF's which were obtained recently by Evans *et al.* from a rigid empirical model for the intermolecular pair potential energy in liquid water appear once more from the *ab initio* MCYL potential with the same symmetry and time dependence. This is a strong corroborative evidence for the correctness of the methods used in both cases. However, the inclusion of vibrational effects by Lie and Clementi in their MCYL potential leads in this work to considerable further insight obtained by a detailed study of cross-correlation functions between vibration and rotation and between vibration and center-of-mass translation.

I. INTRODUCTION

Since the publication of a quantum-chemical potential for water-water interaction by Matsuoka, Clementi, and Yoshimine (referred to as MCY potential in the literature) in 1976,[1] there has been widespread interest in the use of this potential to study structures and dynamics of water, ice, and solutions.[2–13] The potential was obtained by carrying out large-scale configuration-interaction calculations over the localized molecular orbitals in order to recover the most of the intermolecular correlation energies. One limitation of the potential is due to the assumption that the water geometry is *fixed* from experimental data. Thus, for example, the potential is not capable of predicting geometrical changes between the vapor and liquid phases. This potential has recently been extended to remove this limitation by Lie and Clementi[14] by incorporating another *ab initio* intramolecular quantum-mechanical potential[15] into the MCY potential. The extended potential [henceforth referred as Matsuoka-Clementi-Yoshimine-Lie (MCYL) potential] uses no empirical parameters other than the atomic masses, electron charge, and Planck constant, hence is a true *ab initio* potential from atomic- and molecular-physics point of view.

The appearance of the MCYL potential has made possible the investigation of intramolecular modes of motion of water molecules and their effect on its translational and rotational dynamics. For the first time, therefore, it is possible to see how the three fundamental types of molecular motion mutually interact in the aqueous environment at normal temperature (300 K). The simulation of the molecular dynamics of rigid water molecules, using an empirical site-site plus charges potential, has revealed the presence of a well-defined statistical cross correlation between the angular velocity and the linear center-of-mass velocity of the same water molecule a time t later in the rotating frame of the molecular principal moments of inertia (1,2,3).[16,17] Further, higher-order cross-correlation functions (CCF's) were discovered in this frame involving dynamically noninertial quantities, such as the molecular Coriolis acceleration $2\mathbf{v}\times\boldsymbol{\omega}$, where $\mathbf{v}$ is the molecular center-of-mass velocity and $\boldsymbol{\omega}$ its angular velocity.[18–22] The existence of these higher-order CCF's in the (1,2,3) frame is governed essentially by the molecular point-group symmetry[23] (in this case C_{2v}) and is further proof of the intricate and ineluctable interrelation between basic dynamical velocities and accelerations at the single-molecule level. The recent work has demonstrated in detail how the fundamental modes of rigid molecule dynamics, translation of the center-of-mass and molecular angular velocity, combine to form a pattern of statistical correlation functions whose time dependence can now be determined by computer simulation methods.[23–29] Recent work has shown that CCF's involving the noninertial dynamical variables also exist in the laboratory frame

(x,y,z) and form a well-defined set of nonvanishing functions of time in that frame.[18–22] This paper aims to use 3400 configurations from the simulation of Lie and Clementi[14] to investigate for the first time the effect on CCF's of intramolecular stretching and bending motions, of which there are three in water.

In Sec. II the autocorrelation functions (ACF's) of a number of dynamical quantities are given, including those of the molecular center-of-mass velocity, the angular velocity, the angular momentum, the dipole orientation, and its second time derivative (the rotational velocity). Where relevant, these are illustrated in frames (x,y,z) and (1,2,3).

In Sec. III, the analysis of the large number of CCF's obtained in this work is carried out firstly in terms of the symmetry of the various dyadics in frames (x,y,z) and (1,2,3) and secondly in terms of rotation-translation, rotation-vibration, and translation-vibration coupling in both frames. Cross reference and comparison is made to the data available from the work of Evans[16,17] using his own empirical model of water referred to already in this paper. For this purpose some higher-order CCF's have been computed in this work for the MCYL potential to compare directly with Evans's work using as few as 500 configurations and 108 molecules. This serves the twin purposes of checking for any possible artifacts arising from sample size and/or number of configurations used in the running time averages of the latter. The various CCF's are classified into those which describe the various types of cross correlations possible; and cross reference is made among members of each class or group of CCF's in order to gain insight into the nature of the single-molecule dynamics in its aqueous environment. Finally, in Sec. IV the relation of this work to the available experimental data is discussed and suggestions are made as to which experimental probe should be used to isolate a given type of cross correlation.

II. TIME AUTOCORRELATION FUNCTIONS

A. Orientational autocorrelation functions

The dipole-orientation correlation function has been obtained and found to agree with the result obtained by Lie and Clementi.[14] Figure 1 is the rotational velocity ($\dot{\mathbf{e}}_1 = \omega \times \mathbf{e}_1$, where ω is the angular velocity and $\mathbf{e}_1$ the unit dipole vector) ACF for the molecular dipole moment, and is essentially the Fourier transform of the contribution of molecular libration to the far-infrared spectrum of liquid water.[2] Note that it is not the complete spectrum because contributions are expected from the proper modes of vibration. The results of Fig. 1 are similar to those obtained by Evans *et al.* using an empirical rigid site-site potential.[16,17] The far-infrared spectrum from the ACF of Fig. 1 is similar to that illustrated by Evans.[16] The minimum in the ACF of the MCYL potential is slightly deeper, and there is slightly more structure in the 0.0–0.1-ps region, but otherwise vibration does not affect significantly the molecular librational motion of the water molecule. The results of Evans *et al.* were obtained with only 500 configurations and 108 molecules,[16,17] thus the number of configurations and sample size do not seem to be a significant effect on the ACF's. The same is true for the other ACF's in this paper, except for the linear velocity ACF of atoms, which is significantly more oscillatory due to internal vibrations in the MCYL potential.

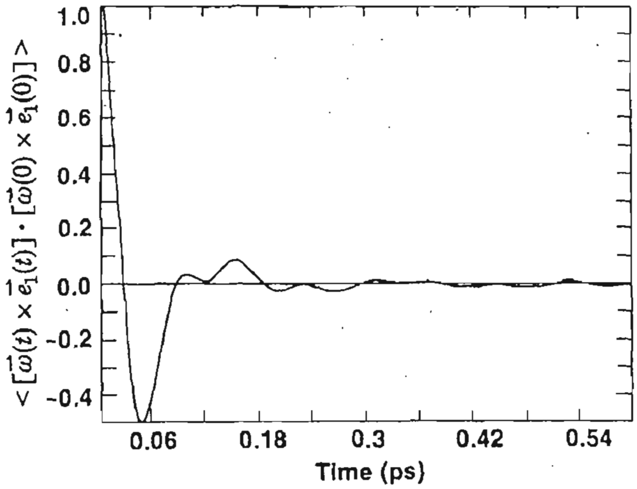

FIG. 1. Normalized rotational velocity autocorrelation functions of the water molecule.

It is significant that the angular velocity ACF shown in Fig. 2(a) is essentially identical with the rotational velocity ACF in normalized time dependence. This is a consequence of the far slower time dependence of the orientational ACF compared with the rotational velocity ACF (Fig. 1). In other words librational motion is a far faster process than molecular rotational diffusion. This is reflected in the fact that the Debye relaxation time of liquid water[30] is about 50 times longer than the correlation time of the molecular libration.[31,32]

Figures 2(b)–2(d) illustrate the anisotropy of the angular velocity ACF in frame (1,2,3), the frame of the principal molecular moments of inertia. In these figures the 3 component of this frame is the axis perpendicular to the plane of the molecule and passing through the center of mass; the 2 component is the axis in the plane of the molecule approximately parallel to the oxygen-center-of-mass line, and perpendicular to the 3 axis, and the 1 axis is that mutually perpendicular to 3 and 2. The anisotropy data in Fig. 2 can be obtained in principle from NMR spin-spin and spin-rotation relaxation. The present computer simulation results suggest that the time dependence about each axis of the frame (1,2,3) is different; implying that the angular diffusion of the water molecule is different in each direction.

There is also an anisotropy in the linear center-of-mass velocity ACF in frame (1,2,3) of the principal molecular moments of inertia. Components 1 and 2 of the normalized ACF are very similar in time dependence to that of the complete ACF in this frame, but the ACF of component 3 is different. The center-of-mass linear libration or "cage" effect is much less pronounced in the 3 axis of the rotating frame. It is noteworthy that the

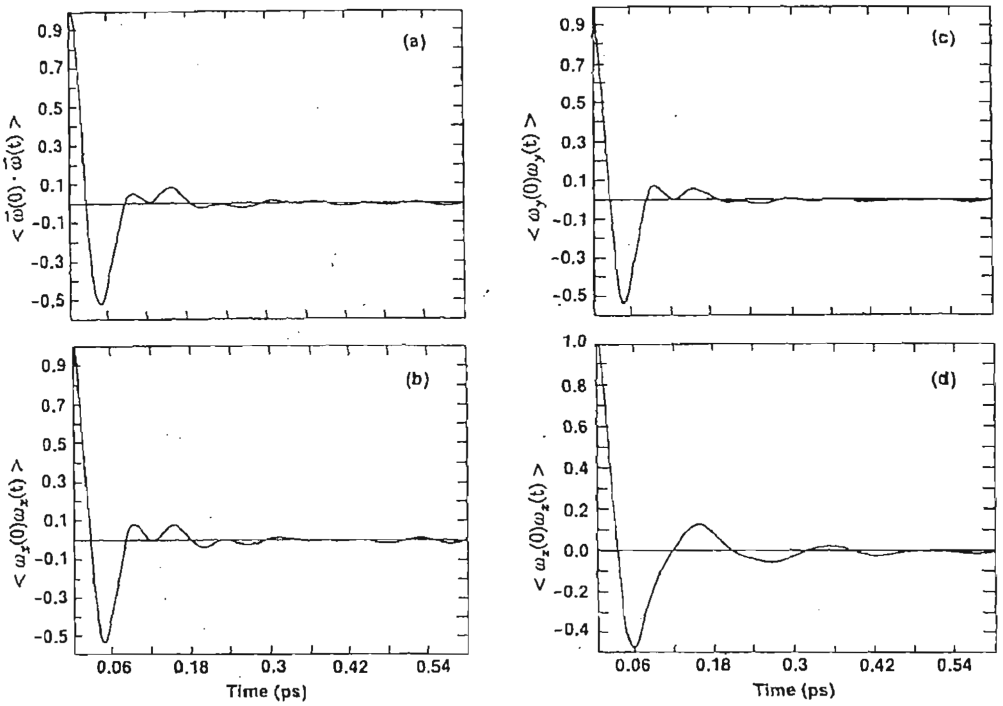

FIG. 2. Normalized angular velocity autocorrelation functions of liquid water in the frame of the principal molecular moments of inertia.

time dependence is almost identical with that of the complete ACF in the laboratory frame (x,y,z). This is more oscillatory than that obtained by Evans *et al.*[16,17] with the rigid site-site potential, but similar to that from the rigid MCY potential.[33] Therefore, vibration has little direct effect on the center-of-mass linear velocity ACF in either frame of reference.

The ACF's of the noninertial linear velocity $\omega\times\mathbf{r}_{\mathrm{c.m.}}$ and (Coriolis) acceleration $\omega\times\mathbf{v}_{\mathrm{c.m.}}$ in the frame (1,2,3), which appear in the rotating-frame analysis of molecular diffusion recently developed by Evans and described in detail elsewhere,[18,22] are again similar in time dependence to the equivalents obtained by Evans from his rigid site-site potential.[16,17]

Finally, in this section we note that the ACF's of H and O atom velocities reported by Lie and Clementi[14] have been checked to have the same time dependence from the independent algorithms developed in this work. These ACF's in the rotating frame of reference (1,2,3) have a similar but not identical time dependence. The ACF of the H atom velocity is the only one having highly oscillatory features due to bond vibration.

III. TIME CROSS-CORRELATION FUNCTIONS

Considerable extra insight into the molecular dynamics of the water molecule in an aqueous environment is obtainable by the computer simulation of time cross-correlation functions. The term is interpreted in the broadest sense here to include cross correlations between off diagonal elements of tensor products of two dynamical quantities in either frame of reference. This section is divided into three subsections for ease of reference: vibration-translation, vibration-rotation, and rotation-translation couplings.

A. Vibration-translation coupling

Statistical time cross correlation between vibration and center-of-mass translation can be used as in Fig. 3 to illustrate the interdependence of each mode of molecular motion. The vibration is defined through the linear velocity in frame (1,2,3) of the hydrogen atom, and the translation as that of the molecular center-of-mass in the same (rotating) frame of reference. The nine elements of the tensor product

$$\underline{C}_1=\left[\frac{\langle \mathbf{v}_H(t)\mathbf{v}^T_{\mathrm{c.m.}}(0)\rangle}{\langle \mathbf{v}_H^2\rangle^{1/2}\langle \mathbf{v}^2_{\mathrm{c.m.}}\rangle^{1/2}}\right]_{(1,2,3)} \tag{1}$$

were obtained. The 12 and 21 off diagonal elements of this tensor exist above the background uncertainty level ("noise"). The other off diagonal elements vanish in the noise, but the three diagonal elements exist, so that the overall symmetry of the vibration-translation matrix is

$$\begin{bmatrix} + & + & 0 \\ + & + & 0 \\ 0 & 0 & + \end{bmatrix}.$$

The time dependence of each diagonal element is illustrated in Fig. 3. It is seen from Figs. 3 and 4 that the off diagonal and diagonal elements are very anisotropic in the rotating frame. Center-of-mass translation is coupled to H-atom vibration in different ways, depending on the axis under consideration. The coupling in the 22 component [Fig. 3(b)] is oscillatory at the frequency of the H atom vibration, because the 2 axis is the one that approximately bisects the molecule through the oxygen-center-of-mass axis. The 11 component [Fig. 3(a)] shows the fact oscillations of Figs. 4(a) and 4(b) superimposed on the slower oscillations of the O-atom vibrations. Finally, the 33 component [Fig. 3(c)] is free of vibrational oscillations because the 3 axis is perpendicular to the plane of the molecule. We shall see later that this element is nearly identical in time dependence with the off diagonal element 13 of the rotating-frame CCF between molecular angular velocity and linear center-of-mass velocity. It is also significant that only the off diagonal elements [Figs. 4(a) and 4(b)] not involving the 3 axis of the principal molecular moments of inertia frame (1,2,3) survive. There is no coupling of the atom and center-of-mass linear velocities between vector components parallel and perpendicular to the plane of the molecule. Coupling occurs for vector components which are both either in the plane or perpendicular to the plane of the molecule. These results differ significantly from their equivalents obtained from any rigid water molecule approximation.

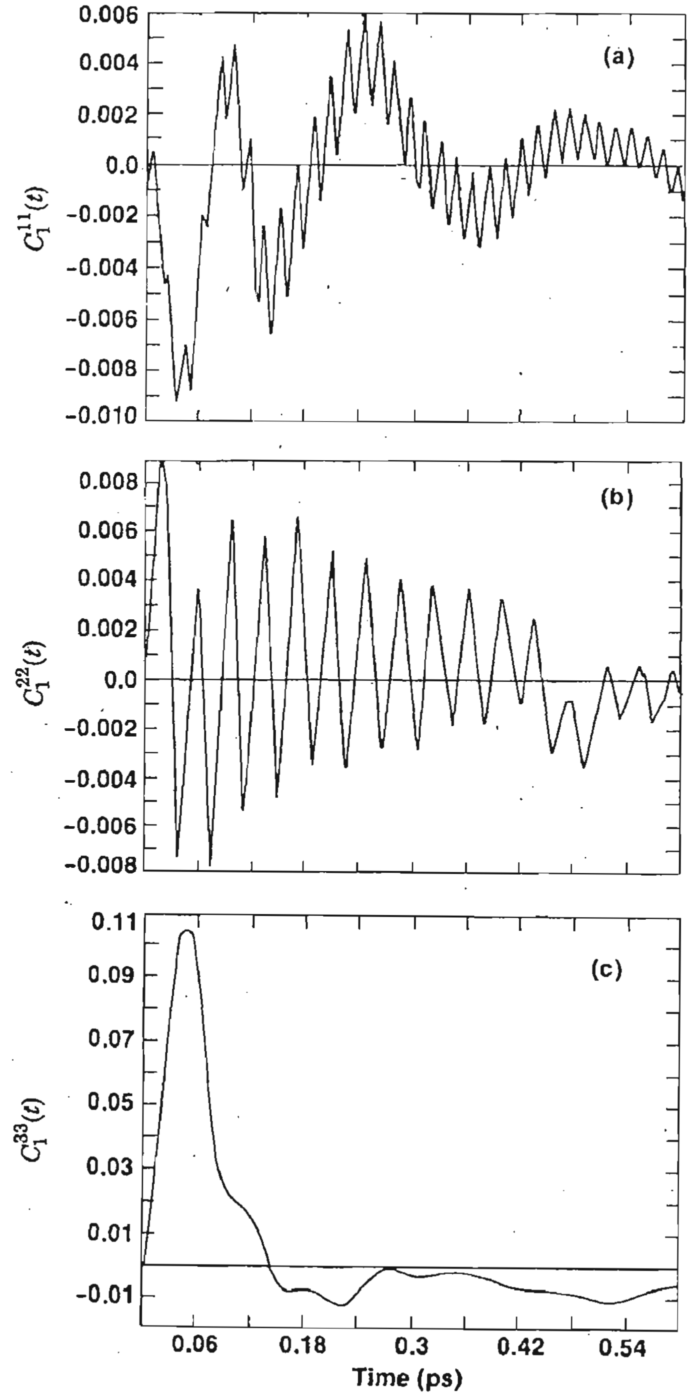

FIG. 3. Elements of the normalized cross-correlation functions $\underline{C}_1(t)$. Superscripts indicate the components of the tensor.

B. Vibration-rotation coupling

The effect of vibration can be studied by considering the normalized tensor product

$$\underline{\mathbf{C}}_2 = \left[\frac{\langle \mathbf{v}_H(t)\omega^T(0)\rangle}{\langle \mathbf{v}_H^2\rangle^{1/2}\langle \omega^2\rangle^{1/2}} \right]_{(1,2,3)} . \qquad (2)$$

Figure 5 shows the time dependence of the four off-diagonal elements of this CCF tensor in frame (1,2,3). The diagonal elements in this case vanish in the noise, so that the overall symmetry of the matrix is

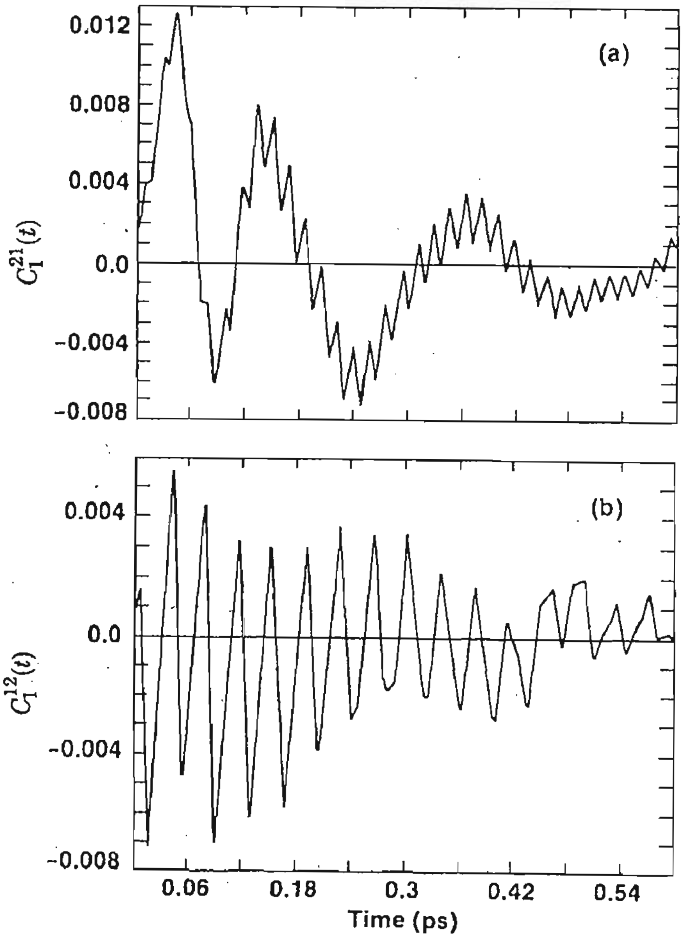

FIG. 4. Elements of the normalized cross-correlation functions $\underline{C}_1(t)$. Superscripts indicate the components of the tensor.

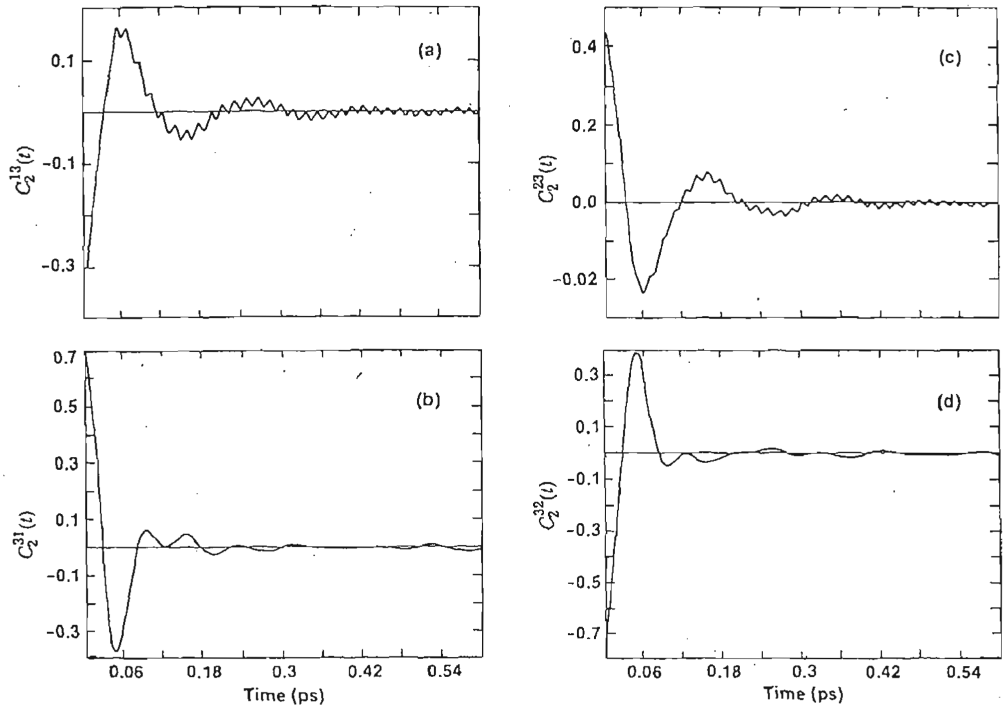

FIG. 5. Elements of the normalized cross-correlation functions $\underline{C}_2(t)$. Superscripts indicate the components of the tensor.

$$\begin{bmatrix} 0 & 0 & + \\ 0 & 0 & + \\ + & + & 0 \end{bmatrix} .$$

This situation is opposite to the symmetry of the vibration-translation matrix described already. Figure 5 shows that the 31 and 32 components of the CCF are essentially perfect mirror images of each other in time dependence, while there is some residual asymmetry in the otherwise mirror-image behavior of the 23 and 13 components. Since the molecule can only vibrate in the molecular plane, we see that the effect of vibrations shows up in the 13 and 23 components as small ripples.

Figures 6(a) and 6(b) confirm the symmetry of Fig. 5 for the equivalent CCF matrix between the molecular angular velocity in frame (1,2,3) and the linear velocity of the oxygen atom. In this case the whole matrix is dominated by the 31 element [Fig. 6(a)]. Due to the fact that the amplitude of the oxygen vibration is much smaller than that of hydrogen, no ripples have been seen here. The 13 element [Fig. 6(b)] seems to be signal, but its amplitude is ten times smaller. All the other seven elements vanish in the noise, so that the overall symmetry is

$$\underline{C}_3 = \left[\frac{\langle \mathbf{v}_0(t) \omega^T(0) \rangle}{\langle v_0^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2}} \right]_{(1,2,3)} = \begin{bmatrix} 0 & 0 & + \\ 0 & 0 & 0 \\ + & 0 & 0 \end{bmatrix} . \quad (3)$$

It is very interesting to cross reference Figs. 3(c) and 6(a), which illustrate the time dependence of the 33 component of the vibration-translation matrix and the 31 component of the oxygen linear translation to molecular angular velocity CCF matrix, respectively. The time dependence of these elements is seen to be essentially the same, with slightly different maxima. Furthermore, Fig. 6(c) shows that the 13 component of the CCF for molecular angular velocity to molecular center-of-mass linear velocity in frame (1,2,3) is identical with the component in Fig. 6(a). This can be explained by the proximity of the oxygen atom to the molecular center of mass. Thus there is a clear interrelation among the CCF tensors of vibration-translation, vibration-rotation, and, in Fig. 6(c), rotation-translation.

C. Rotation-translation coupling

The relevant matrix is the tensor product between the molecular angular velocity in frame (1,2,3) and the molecular center-of-mass velocity in the same frame

$$\underline{C}_4 = \left[\frac{\langle \mathbf{v}_{\text{c.m.}}(t) \omega^T(0) \rangle}{\langle v_{\text{c.m.}}^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2}} \right]_{(1,2,3)} . \quad (4)$$

Figures 6(c) and 6(d) shows that the matrix is dominated by the 13 element, but that there is a trace of a signal in the mirror-image element 31 [Fig. 6(d)]. The existence of these two elements is allowed by group theory.[23] It is significant and important to note that the result of Fig. 6(c), obtained from the MCYL potential with 3400 configurations for 343 molecules, is almost identical in time dependence and amplitude with the equivalent element obtained by Evans[16,17] from his site-site model of rigid water, using only 500 configurations for 108 molecules. This is convincing evidence for the reality of these cross-correlation functions from two wholly independent computer simulations of liquid water. The pattern of the rotation-translation CCF matrix is

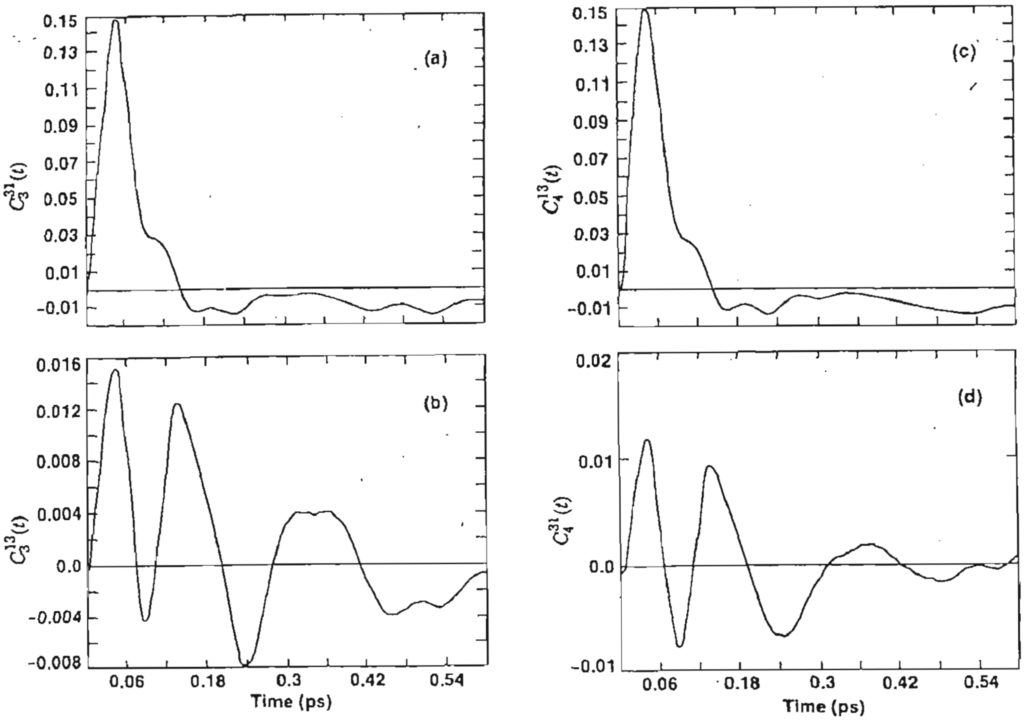

FIG. 6. Elements of the normalized cross-correlation functions $\underline{C}_3(t)$ and $\underline{C}_4(t)$. Superscripts indicate the components of the tensor.

$$\begin{bmatrix} 0 & 0 & + \\ 0 & 0 & 0 \\ + & 0 & 0 \end{bmatrix}_{(1,2,3)}$$

and this corroborates the simulation by Evans.[16,17] In both simulations the matrix is dominated by the equivalent of the 13 component. Therefore, there is little or no effect of vibration on rotation-translation coupling. This means that the large amount of data now available from the previous work of Evans and coworkers[16,29] on rotation-translation in a variety of rigid molecule symmetries is essentially valid as it stands for their flexible counterparts. This is an important step forward in our understanding of these subtle phenomena in the liquid state of molecular matter.

Nonvanishing (diagonal) elements also exist for the "higher-order" CCF matrix between the molecular noninertial Coriolis linear acceleration in frame (1,2,3) and the center-of-mass velocity, i.e., the matrix

$$\underline{C}_5 = \left[\frac{\langle \mathbf{v}_{\text{c.m.}}(t) \times \omega(t) \mathbf{v}_{\text{c.m.}}^T(0) \rangle}{\langle \mathbf{v}_{\text{c.m.}}^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2}} \right]_{(1,2,3)} . \tag{5}$$

The diagonal elements of $\underline{C}_5$ can be compared directly with those provided by Evans[16,17] in the literature from his rigid-site potential. Again the rigid and flexible water potentials provide similar results, but not quite identical for this higher-order CCF. The time dependence for the MCYL potential is slightly more oscillatory, and the negative minimum in the 33 element is deeper in the MCYL potential than in the Evans potential.

IV. LABORATORY FRAME CROSS-CORRELATION FUNCTIONS

The computation of CCF's in the laboratory frame provides a check on the correctness of the algorithms used in this work. For example, the CCF matrix between molecular center-of-mass linear velocity and molecular angular velocity must be a null matrix in the laboratory frame because the response of each vector to parity inversion symmetry is opposite for an isotropic liquid medium. This is corroborated in this work by the individual computation of all nine elements of the matrix. The elements all vanish in the noise. Similarly any laboratory frame CCF involving atom velocity and angular velocity also vanishes by the parity rule in the laboratory frame, and this was also checked by computing each element individually. Each vanished in the noise of the simulation for all t, as required by fundamental symmetry rules in the laboratory frame of reference.

On the other hand, the existence of off-diagonal elements of tensor products involving the same vector at $t=0$ and $t=t$ is not forbidden by symmetry in the laboratory frame. In this work we have checked individually the off-diagonal elements of the tensor products

$$\underline{C}_6 = \left[\frac{\langle \mathbf{v}_{\text{c.m.}}(t) \mathbf{v}_{\text{c.m.}}^T(0) \rangle}{\langle \mathbf{v}_{\text{c.m.}}^2 \rangle^{1/2} \langle \mathbf{v}_{\text{c.m.}}^2 \rangle^{1/2}} \right]_{(x,y,z)} \tag{6}$$

and

$$\underline{C}_7 = \left[\frac{\langle \omega(t) \omega^T(0) \rangle}{\langle \omega^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2}} \right]_{(x,y,z)} \tag{7}$$

involving the molecular center-of-mass linear velocity and the molecular angular velocity in the laboratory frame. The diagonal elements of course exist, because these are the components of the ACF's in the laboratory frame. However, little is known about the time dependence of the off-diagonal elements in the laboratory frame. Figures 7(a) and 7(b) provide evidence for the existence of the z-x component in the laboratory frame of the linear molecular center-of-mass tensor product and the z-y component of the molecular angular velocity tensor product, respectively. The latter is particularly striking, because its time dependence seems to be identical with that of the equivalent ACF. The former is much smaller in amplitude, and its $t=0$ value seems to be precisely zero. These elements are not symmetry forbidden in the laboratory frame, even in a perfectly isotropic sample, and their existence in the diffusing asymmetric top seems to be confirmed by this work. Figure 7(b) shows that the z component of molecular angular velocity in frame (x,y,z) is correlated to the y component at the same instant in time, i.e.,

$$\left[\frac{\langle \omega_z(t)\omega_y(0)\rangle}{\langle \omega_z^2\rangle^{1/2}\langle \omega_y^2\rangle^{1/2}}\right]_{(x,y,z)} .$$

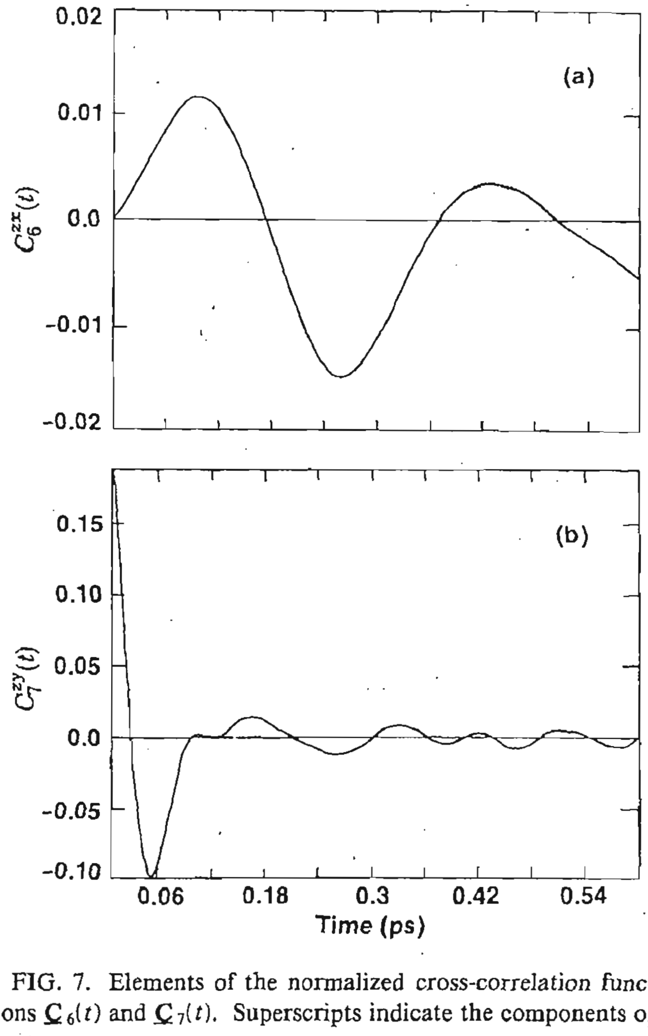

FIG. 7. Elements of the normalized cross-correlation functions $\underline{C}_6(t)$ and $\underline{C}_7(t)$. Superscripts indicate the components of the tensor.

All other off diagonal elements of the matrix vanish in the noise. This kind of cross correlation can arise in principle from cooperativity of the molecular angular motion about the z axis of the laboratory frame, or from molecular spin induced by rotation-translation coupling in frame (1,2,3). The origin of these new types of cross correlation requires further careful analysis.

Finally, we mention the existence in the laboratory frame of the diagonal elements only of the CCF tensor between the linear velocity of the hydrogen atom at time t and the linear velocity of the molecular center of mass at $t=0$ for the same molecule. In great contrast to the equivalent result in the rotating frame, discussed already, these diagonal elements have essentially the same time dependence, because of the overall isotropy of the system in the laboratory frame. These elements reach a normalized maximum value of only about 0.03. However, translation-vibration coupling in the laboratory frame is weak in contrast with the situation in the rotating frame.

V. EXPERIMENTAL OBSERVATIONS

In this section we suggest briefly ways of probing the new results presented in this paper by experiment. The original paper of Lie and Clementi[14] compares the simulation with many conventional experimental sources of information on the thermodynamics, structure, and autocorrelations. However, the experimental investigation of cross-correlation function is a considerably more difficult undertaking. At present there exist two indirect methods of investigating rotation-translation coupling both suggested by Evans.[34,35] One involves electric field-induced birefringence and the other a careful comparison of the properties of an enantiomer and its racemic mixture. For water, only the first method is relevant. The agreement between the two independent computer simulations requires the effort to be made to use the Kerr-effect method (electric-field-induced birefringence) to try to see the new CCF's experimentally using the method suggested in the literature.[34]

Rotation-vibration coupling and the closely allied phenomenon of vibration-translation coupling as seen in this work can in principle be investigated by a careful analysis of the infrared or Raman rotation-vibration absorption in liquid water. In steam the (quantized) mutual effects of vibration on rotation can be studied in detail using high-resolution spectra, and this is well known. However, the extension of this type of investigation to the liquid state is much less well pursued. The results of the present simulation, and the cross-correlation functions of this paper may therefore catalyze some more experimental studies into mode-mode coupling in liquid water at the single-molecule level.

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[1] O. Matsuoka, E. Clementi, and M. Yoshimine, J. Chem. Phys. **64**, 1351 (1976).

[2] G. C. Lie, E. Clementi, and M. Yoshimine, J. Chem. Phys. **64**, 2314 (1976).

[3] J. C. Owichi and H. A. Scheraga, J. Am. Chem. Soc. **99**, 7403 (1977).

[4] R. W. Impey, M. L. Klein, and J. R. McDonald, J. Chem. Phys. **74**, 647 (1981).

[5] D. C. Rapaport and H. A. Scheraga, Chem. Phys. Lett. **78**, 491 (1981).

[6] R. W. Impey, P. A. Madden, and I. R. McDonald, Mol. Phys. **46**, 513 (1982).

[7] D. C. Rapaport, Mol. Phys. **50**, 1151 (1983).

[8] M. Neumann, J. Chem. Phys. **82**, 5663 (1985).

[9] M. D. Morse and S. A. Rice, J. Chem. Phys. **76**, 650 (1982).

[10] M. Townsend, M. D. Morse, and S. A. Rice, J. Chem. Phys. **79**, 2496 (1983).

[11] G. Nielson and S. A. Rice, J. Chem. Phys. **80**, 4456 (1984).

[12] G. Bolis, G. Corongiu, and E. Clementi, Chem. Phys. Lett. **86**, 299 (1982).

[13] H. Tanaka, K. Nakanishi, and H. Touhara, J. Chem. Phys. **82**, 5184 (1985) and references therein.

[14] G. C. Lie and E. Clementi, Phys. Rev. A **33**, 2679 (1986).

[15] R. J. Bartlett, I. Shavitt, and G. D. Purvis, J. Chem. Phys. **71**, 281 (1979).

[16] M. W. Evans, J. Mol. Liq. **32**, 173 (1986).

[17] G. J. Evans, M. W. Evans, P. Minguzzi, G. Salvetti, C. J. Reid, and J. K. Vij, J. Mol. Liq. **34**, 285 (1987).

[18] M. W. Evans, Phys. Rev. Lett. **55**, 1551 (1985).

[19] M. W. Evans and G. J. Evans, Phys. Rev. Lett. **55**, 818 (1985).

[20] M. W. Evans, Phys. Rev. A **34**, 468 (1986).

[21] M. W. Evans and G. J. Evans, Phys. Rev. A **33**, 1903 (1986).

[22] M. W. Evans, J. Chem. Phys. **86**, 4096 (1987); D. H. Whiffen (private communication).

[23] M. W. Evans, Phys. Rev. A **34**, 2302 (1986).

[24] M. W. Evans and G. J. Evans, in *Dynamical Processes in Condensed Matter*, edited by M. W. Evans, *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1985), Vol. 63.

[25] M. W. Evans and G. J. Evans, in *Dynamical Processes in Condensed Matter*, edited by M. W. Evans, *Advances in Chemical Physics*, edited by M. W. Evans, P. Grigolini, and G. Pastori Parravicini (Wiley, New York, 1985), Vol. 63.

[26] M. W. Evans, Phys. Rev. Lett. **50**, 351 (1983).

[27] J. P. Ryckaert, A. Bellemans, and G. Ciccotti, Mol. Phys. **44**, 979 (1981).

[28] W. T. Coffey, M. W. Evans, and P. Grigolini, *Molecular Diffusion* (Wiley, New York, 1984).

[29] M. W. Evans, J. Chem. Soc., Faraday Trans. 2 **81**, 1463 (1985); D. Hennequin, P. Glorieux, E. Arimondo, and M. W. Evans, *ibid.* **83**, 463 (1987).

[30] D. Bertolini, M. Cassettari, M. Ferrario, P. Grigolini, and G. Salvetti, in Ref. 11, p. 277ff.

[31] M. W. Evans, J. Chem. Soc., Faraday Trans. 2 **72**, 2138 (1976).

[32] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Liquid Water* (Oxford University Press, Cambridge, 1969).

[33] M. Wojcik and E. Clementi, J. Chem. Phys. **85**, 6085 (1986).

[34] M. W. Evans, Physica **131B&C**, 273 (1985).

[35] M. W. Evans, Phys. Rev. A **30**, 2062 (1984).