Molecular dynamics simulation of water CCl_4 mixtures

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A computer simulation of the molecular dynamics of a mixture of water and CCl_4 molecules has been carried out with site–site terms for the intermolecular potentials. These are made up of Lennard-Jones interactions for the atom–atom terms and partial charges for the electrostatics. In a subpicosecond interval of time the H bonding structure of the pure aqueous environment is disrupted by the more massive CCl_4 molecules; both in a 50% and 11% n/n emulsion. In this time interval the fine emulsion of water molecules in carbon tetrachloride has not had time to separate into water and carbon tetrachloride layers as would be expected from the immiscibility of the two macroscopic liquids. Therefore, the simulation provides a means of studying in detail the dynamics of water molecules freed of hydrogen bonding in an environment of much more massive carbon tetrachloride molecules. This provides an opportunity of investigating the effect of H bonding on the atom–atom pair distribution functions and time correlation functions of the dynamical ensemble. The most pronounced effect of distributing the water molecules in this way is seen in single molecule cross correlation such as $\langle \mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ where $\mathbf{v}$ is the linear molecular center-of-mass velocity and $\boldsymbol{\omega}$ the angular velocity of the same molecule.

I. INTRODUCTION

The molecular dynamics of water free from hydrogen bonding are known experimentally to be very different from those in pure liquid water. The first comprehensive molecular dynamics study of the dilution of water in organic solvents was carried out using far-infrared spectroscopy by Pardoe[1] and later interpreted by Evans[2] with linear three variable Mori theory. The results showed a dramatic shortening of the orientational correlation time in "free" water dissolved in organic solvents such as carbon tetrachloride, benzene, and cyclohexane compared with the orientational correlation time in the pure liquid water (about 5.0 ps). At the same time the far-infrared peak power absorption shifts from 700 cm^{-1} in pure water to about 200 cm^{-1} in dilute solution. This shows clearly the effect of H bonding on the far-infrared spectrum and on the molecular dynamics of water when freed from H bonding.

The interpretation originally given by Evans[2] of the far-infrared results of Pardoe[1] is extended in this paper to computer simulation using mixtures of water and CCl_4 molecules interacting through site–site potentials consisting of Lennard-Jones atom–atom and site–site terms. The computer simulation[3] uses classical translational and rotational equations of motion only. No attempt will be made to incorporate quantum or bond vibrational effects,[4,5] so that it is understood from the outset that those parts of the far-infrared and mid-infrared spectrum due to quantum effects or bond vibration cannot be reproduced in this paper. It deals with the interaction of rigid water molecules with rigid carbon tetrachloride molecules; so that only the classical part of the spectrum is recovered from the autocorrelation functions of this paper. Nevertheless, it is important and interesting to show that the technique of computer simulation is capable of producing detailed dynamical information on the effects of emulsifying water in carbon tetrachloride. This is seen as the starting point for future simulations involving bond vibration[6] and more detailed quantum effects using potentials from *ab initio* computations. These might be expected to build up a more complete picture of far-infrared spectra in liquid water and organic solutions thereof.

This paper is developed as follows. The first section deals with the site–site parameters and the thermodynamic conditions of the computer simulation. The initial configurations are described together with a brief description of the integration method for the equations of motion. Section II deals with the results for water–water atom–atom pair distribution functions in the pure aqueous ensemble and in the carbon tetrachloride "microemulsion." A stream line diagram is shown for the center-of-mass drift of the water molecules, and discussed in terms of the molecular dynamics. Section III then deals with the correlation functions of pure water compared with their equivalents in the microemulsion in the subpicosecond time interval. Autocorrelation functions are shown of various vectors together with cross-correlation functions in the frame of reference defined by the principal molecular moments of inertia. It is particularly significant to the dynamics that one of these cross-correlation functions (ccf's) vanishes upon emulsification in carbon tetrachloride of the water molecules to which it refers. This is as predicted in principle by group theory[7] and is strong evidence for the correctness of the computer simulation algorithm and for the direct influence of H bonding in pure water on the rotation and translation of the molecule. Other autocorrelation functions (acf's) and ccf's also show the influence of H bond breaking by microemulsification on

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the molecular dynamics of a range of molecular vectors. Section IV is a discussion of these results and of their significance in relation to naturally occurring hydrocarbon water mixtures such as hydrated methane.

II. MOLECULAR DYNAMICS ALGORITHM

The algorithm was written by the author and is an extension of the algorithm TETRA, a well tried code described in further detail elsewhere.[8] The modifications include a pair potential routine for taking into account the three types of interaction: water–water; water–carbon tetrachloride; and CCl_4–CCl_4. This operates by constructing site–site terms by the use of Lennard-Jones atom–atom and partial charge terms. The water molecule is modeled[9] with a five site potential framework. There are three Lennard-Jones atom terms, two H terms, and one O term, and two partial charges located on the lone pair water electrons. The geometry and magnitude of the partial charges is taken from the ST2 potential, so that the $-0.23\,e$ on the lone pairs is balanced by $+0.23\,e$ on the two hydrogens, the oxygen being neutral. It is reported in the literature that this potential has been fully tested against experimental atom–atom pair distribution functions for pure liquid water and the results also compared with the MCY potential of Lie and Clementi[10] and the ST2 itself.[11] However, as with all empirical and other water potentials no claim is made for the behavior of this five site potential when tested against a complete range of experimental data. Morse and Rice have shown clearly[12] that in this respect no contemporary representation of the water potential is satisfactory. However, its thermodynamic behavior is satisfactory as regards output pressure for given molar volume and room (293 K) temperature. The internal energy from the potential is comparable with that from the ST2, but its second virial behavior is untried. The advantage of the five site water potential in the present context is that interactions with carbon tetrachloride molecules may be modeled with the same Lennard-Jones hydrogen and oxygen parameters and the same partial charges. This is achieved simply by coding into the algorithm oxygen to carbon; oxygen to chlorine; hydrogen to carbon; hydrogen to chlorine; oxygen to oxygen; hydrogen to oxygen; carbon to carbon; and carbon to chlorine interactions. Charge to charge interactions are maintained between water molecules only, even in the microemulsion, because the first nonvanishing multipole moment of the carbon tetrachloride molecule is the octopole[13] and the partial charges on the chlorines are assumed to be zero. Therefore, the total potential energy over the 108 molecules of the microemulsion is built up of these site–site terms, taking care not to count terms more than once. The actual Lennard-Jones and partial charge terms are then

$$\epsilon/k(\text{O–O}) = 58.4\ \text{K};\quad \sigma(\text{O–O}) = 2.8\ \text{Å};$$

$$\epsilon/k(\text{H–H}) = 21.1\ \text{K};\quad \sigma(\text{H–H}) = 2.25\ \text{Å};$$

$$\epsilon/k(\text{C–C}) = 51.0\ \text{K};\quad \sigma\,(\text{C–C}) = 3.20\ \text{Å};$$

$$\epsilon/k(\text{Cl–Cl}) = 175.0\ \text{K};\quad \sigma(\text{Cl–Cl}) = 3.35\ \text{Å};$$

$$\sigma(\text{A–B}) = \tfrac{1}{2}[\sigma(\text{A–A}) + \sigma(\text{B–B})];$$

$$\frac{\epsilon}{k}(\text{A–B}) = \left[\frac{\epsilon}{k}(\text{A–A})\,\frac{\epsilon}{k}\,(\text{B–B})\right]^{1/2};$$

$$q_e = -q_H = -0.23|e|.$$

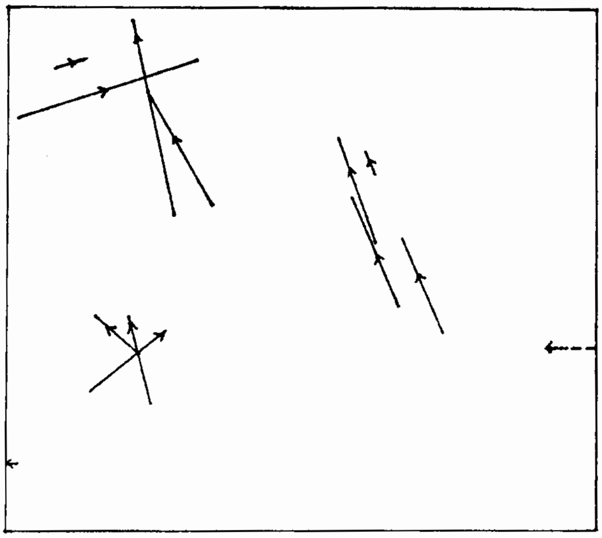

FIG. 1. Trace lines for the centers of mass of the 12 water molecules over 3285 time steps. The lines simply join the center-of-mass positions and no attempt is made to follow the irregularities (random walks) due to Brownian motion. The z positions are all plotted on the (x,y) plane. The dashed arrows show the reemergence of a molecule due to the operation of periodic boundary conditions.

The algorithm has been coded to compute the atom–atom pair distribution functions between the oxygen and hydrogen atoms in the microemulsion, so that the equilibrium structure of the water molecules dispersed in the more massive CCl_4 molecules can be compared with the equivalent in pure liquid water. This is one of the ways of showing the effect of breaking the H bonds. Atom–atom pair distribution functions for hydrogen and oxygen are obtained in this way, and also the cross pdf between oxygen and hydrogen. They are compared with their equivalents in pure liquid water.[9]

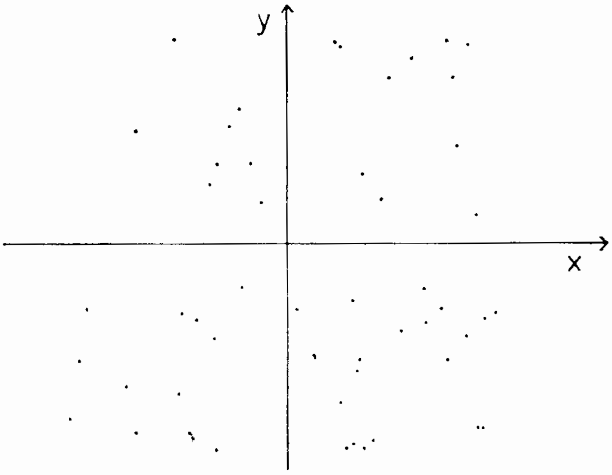

FIG. 2. Plot in the (x,y) plane of the positions of the centers of mass of the 54 water molecules after 5887 time steps, not including aproximately 2000 time steps for equilibration. The water molecules are well dispersed among the carbon tetrachloride molecules.

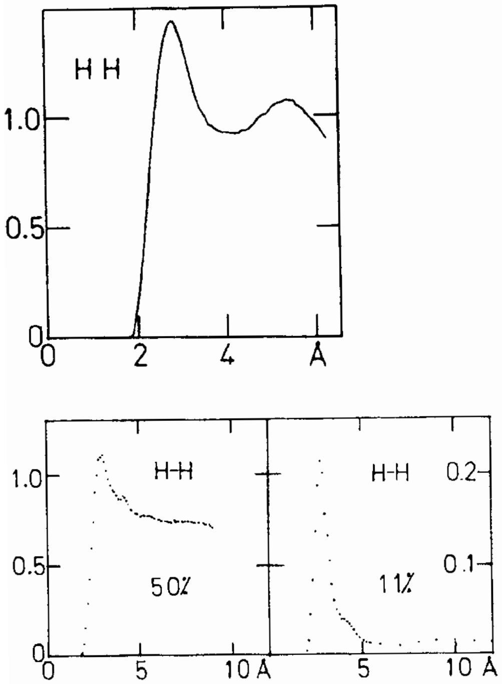

FIG. 3. H–H atom atom pdf's for pure liquid water and two microemulsions in carbon tetrachloride.

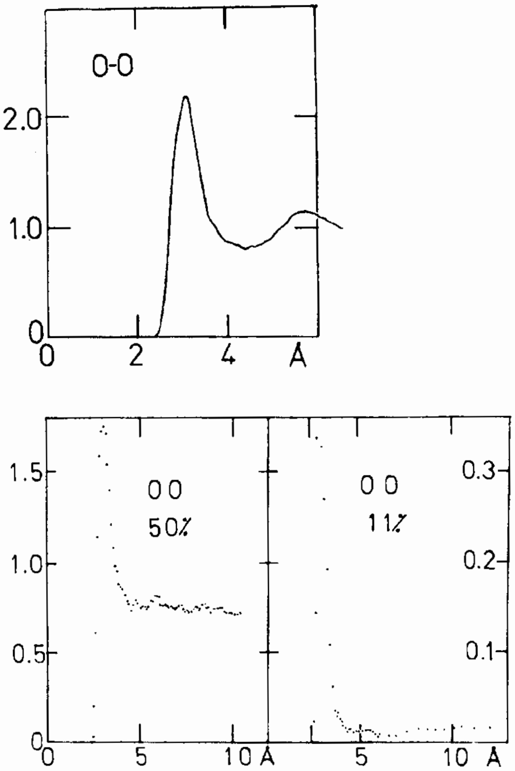

FIG. 4. O–O atom–atom pdf's as in Fig. 3.

The initial configuration to form a microemulsion was a face-centered cubic arrangement for the molecular centers of mass of both types with the water molecules arranged centrally initially surrounded by the CCl_4 molecules. Two concentrations were used, one consisting of 54 water and 54 CCl_4 molecules and the other of 12 water molecules and 96 CCl_4 molecules.

The algorithm was then started with a random number generator in the usual way and equilibrated with about 2000 time steps of 0.5 fs each. The next 6000 time steps approximately were used to construct trace lines for the centers of mass of the water molecules. These trace lines are depicted in Fig. 1 and show how the water is emulsified on the picosecond time scale by the much heavier carbon tetrachloride molecules. It is clear from Figs. 1 and 2 that the initial water cluster is broken up and the water molecules are scattered among the CCl_4 molecules. The periodic boundary conditions for both types of molecule ensure that all 108 remain in the cube as usual. Some "reentries" can be found in these figures.

The algorithm is coded to treat the two types of molecule according to the classical rotational and translational equations of motion. these are integrated as in TETRA, i.e., in two stages, the total torque on each molecule being computed from the forces on individual sites (including charge–charge sites) and the angular momentum in frame (1,2,3) then computed by numerical integration. The translational equation of motion was integrated with Verlet's method. Cut-off criteria were applied with respect to each type of interaction for intermolecular center-of-mass distance. Long range corrections were coded for the virial and total configurational energy.

Acf's and ccf's were evaluated in frames (x,y,z) and (1,2,3) with running time averages over segments of 1000 time steps each. Two segments were used for each correlation function. In the following the results for these acf's and ccf's in the microemulsion are computed from approximately 6000 time steps onwards to 8000 time steps. It is therefore assumed that the sample is statistically stationary in this time interval, the water molecules having been distributed among the carbon tetrachloride molecules as in Figs. 1 and 2.

The input molar volume was calculated from the literature molar volumes at 293 K of pure water and pure carbon tetrachloride scaled by simple averaging to the number of water molecules in the microemulsion. For example, the input molar volume for 54 water molecules was the mean of that of pure water and pure carbon tetrachloride.

III. ATOM–ATOM PAIR DISTRIBUTION FUNCTIONS

From Figs. 3 and 4 it is seen that the main effect of emulsification and H bond breaking is to remove the second peak of the H–H atom–atom pdf. In Fig. 3 are H–H pdf's for pure liquid water and at a 50% and 11% n/n concentration in the microemulsion. The first pdf peak remains at the same position as in pure liquid water but on emulsification progressively becomes relatively much more intense than the second peak, which almost disappears completely. This means that the H bonding structure has been removed to such an extent that the probability of finding an H atom given the position of the first H atom as the reference point of the pdf rapidly becomes smaller with emulsification in carbon tetrachloride. This reinforces the result illustrated in the

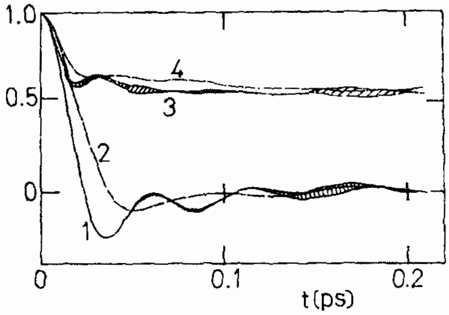

FIG. 5. Angular velocity autocorrelation functions (first and second order). Comparison for pure water and 54/54 microemulsion. (1) First order acf for pure water; (2) for the 54 water molecules of the microemulsion. (3) As for (1); second order acf $\langle \omega(t)\cdot\omega(t)\omega(0)\cdot\omega(0)\rangle / \langle \omega^4 \rangle$. (4) As for (2); second order acf.

stream lines of Fig. 1 and the positional 2D projection of Fig. 2 which both show a dispersion of the water centers of mass after approximately 6000 time steps. The atom–atom pdf's were computed from approximately 6000 to 10 000 time steps and therefore represent this state of pseudo-equilibrium and show the same structural information.

Similar results are illustrated in Fig. 4 for the O–O atom–atom pdf's. In this case the second O–O peak is seen to disappear in magnitude very quickly.

Therefore the second peak in the H–H and O–O pdf's of water represents the degree of "excess structure" in pure H bonded water over "emulsified" water and shows that relatively close packing of the molecules is required for the strong and characteristic H bonding in pure water to take effect. In other words, the characteristic mean structure only appears when all the molecules are within H bonding range and form the extended H bond lattice of pure water. In the present simulation collisions with the heavy, electrostatically neutral, CCl_4 molecules disrupt the H bond lattice completely. For a sufficiently long simulation (e.g., one million time steps) and a sufficiently big sample (e.g., about 10 000 molecules) the two types of molecule should start to separate out into layers because water is (nearly) macroscopically immiscible with carbon tetrachloride. This is why the mixtures in the present (small scale) simulation are referred to as "microemulsions" and not "solutions".

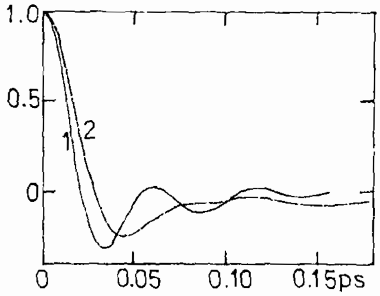

FIG. 6. Rotational velocity acf $\langle \dot{e}_2(t)\cdot\dot{e}_2(0)\rangle / \langle \dot{e}_2^2 \rangle$ for water and the 54/54 microemulsion, computed over the 54 water molecules only. (1) Pure water; (2) microemulsion.

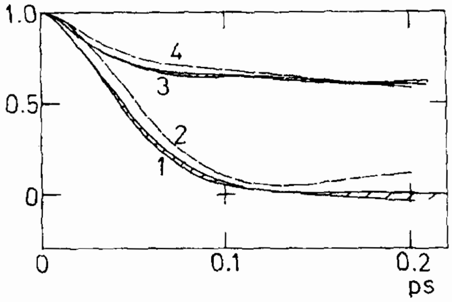

FIG. 7. As for Fig. 5, center-of-mass velocity acf.

IV. DYNAMICAL PROPERTIES, AUTO- AND CROSS-CORRELATION FUNCTIONS

The auto- and cross-correlation functions of time can be used to monitor the dynamical behavior of the system in many ways, and the known ccf's among various of the relevant molecular vectors (e.g., **v** and **ω**) are increasing rapidly.[14–20] In this section acf's and ccf's of various kinds are compared for pure liquid water and for the mixture of 54 water molecules in 54 carbon tetrachloride molecules. In view of the structureless nature of the pdf's referred to above it may be assumed that the microemulsion in this case is very weakly H bonded and that its molecular dynamics will behave accordingly. For example, the oscillations in the angular velocity acf of Fig. 5 are damped out almost completely in the microemulsion, so that H bonding is seen to be the underlying cause of these features in pure liquid water. Remove the H bonding and the oscillations are removed. Similarly in the second order angular velocity acf (curves 3 and 4 of this figure).

The important result for far-infrared spectroscopy is Fig. 6, the rotational velocity acf whose Fourier transform is, essentially speaking,[21] the far-infrared spectrum. The effect of microemulsification is similar to that on the angular velocity acf, i.e., the oscillations are removed. This means that the far-infrared spectrum from the Fourier transform of this (dynamically classical) result will shift with emulsification to peak to lower frequencies and will broaden.

This is approximately what is observed spectroscopically, as in the original data of Pardoe.[1] Caution needs to be exercized in making any direct comparison because of the quantum effects as mentioned in the Introduction and because the solutions investigated by Pardoe were very dilute (less than 0.1% mole fraction) and were true thermodynamically equilibrated solutions. In this computer simulation the emulsion has not equilibrated because the total time span of about 10 000 time steps amounts to only 5.0 ps in total. It takes many orders of magnitude longer for immiscible layers to separate. This may be observed simply by shaking a flask of water and carbon tetrachloride. Layer separation takes place slowly and is not an instantaneous clearcut process. Bearing all this in mind, then, the present computer simulation and the spectroscopic results of Pardoe show the same trend, dilution or microemulsification shifts the spectral peak to lower frequencies, and removes the oscillations in the rotational velocity acf.

The effect of microemulsification is least in the center-

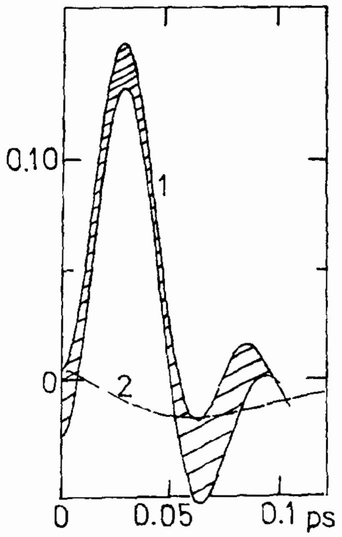

FIG. 8. The moving frame ccf element: $[\langle\omega_3(t)v_2(0)\rangle/(\langle\omega_3^2\rangle^{1/2}\langle v_2^2\rangle^{1/2})]_{(1,2,3)}$ for (1) pure water; (2) 54/54 microemulsion, computed over the 54 water molecules only.

of-mass velocity acf of Fig. 7. The acf cuts the x axis in the pure aqueous medium but in the mixture with CCl_4 the function is positive, remaining above the time axis. In both cases however the second order correlation functions reach the Gaussian limit of 2/3, providing support for the accuracy of the statistics in the present simulation.

The most pronounced effect of microemulsification is on the cross-correlation function $\langle\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle$ between the center-of-mass linear velocity of the water molecule and its own angular velocity $\boldsymbol{\omega}$. This is illustrated in Fig. 8, where curve 1 shows the cross-correlation function in pure liquid water the hatched area representing the difference between the results from two segments. Curve 2 is the same function averaged over 54 water molecules in 54 CCl_4 molecules. The significance of this result is that the T_d symmetry of the carbon tetrachloride molecules means that this moving frame ccf vanishes for all t in pure carbon tetrachloride liquid but the C_{2v} symmetry of the water molecule means that it exists (curve 1) in pure water. Therefore the much reduced amplitude of the ccf in Fig. 8 is consistent with the overall symmetry of the mixture and is strong support for the correctness of the computer simulation method.

Note that the ccf is computed over the 54 water molecules only, but the symmetry effect of the 54 CCl_4 molecules is clear through the amplitude effect in Fig. 8 despite the fact that the CCl_4 molecules are not directly involved in the running time averaging used to compute curve 2; only the water molecules themselves. This is clear evidence for the link between hydrogen bonding and cross-correlation functions of this type. When the H bonds are broken the amplitude of the ccf is reduced almost to zero (curve 2).

Further support for these symmetry effects and for the reliability of the algorithm comes from the computation of other types of cross-correlation function illustrated in Figs. 9 and 10. This is the type

$$\langle\boldsymbol{\omega}(t)\times\mathbf{A}(t)\mathbf{A}^T(0)\rangle_{(1,2,3)},$$

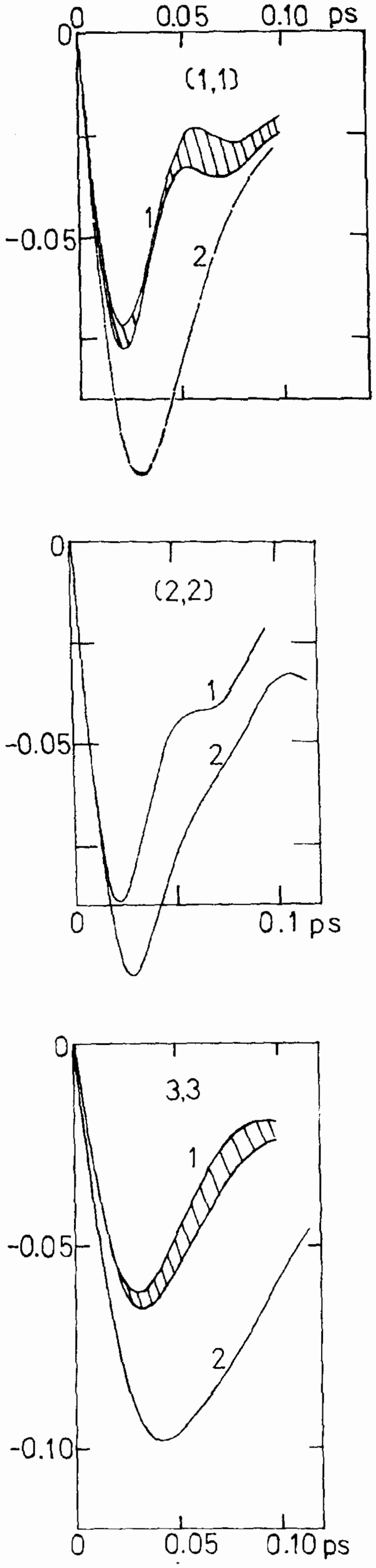

FIG. 9. (a) The moving frame ccf element: $[\langle[\mathbf{r}(t)\times\boldsymbol{\omega}(t)]_1r_1(0)\rangle/(\langle r^2\rangle\langle\omega^2\rangle^{1/2})]_{(1,2,3)}$ computed (1) for pure water; (2) over the 54 water molecules in the 54/54 microemulsion. (b) Element (2,2); (c) element (3,3).

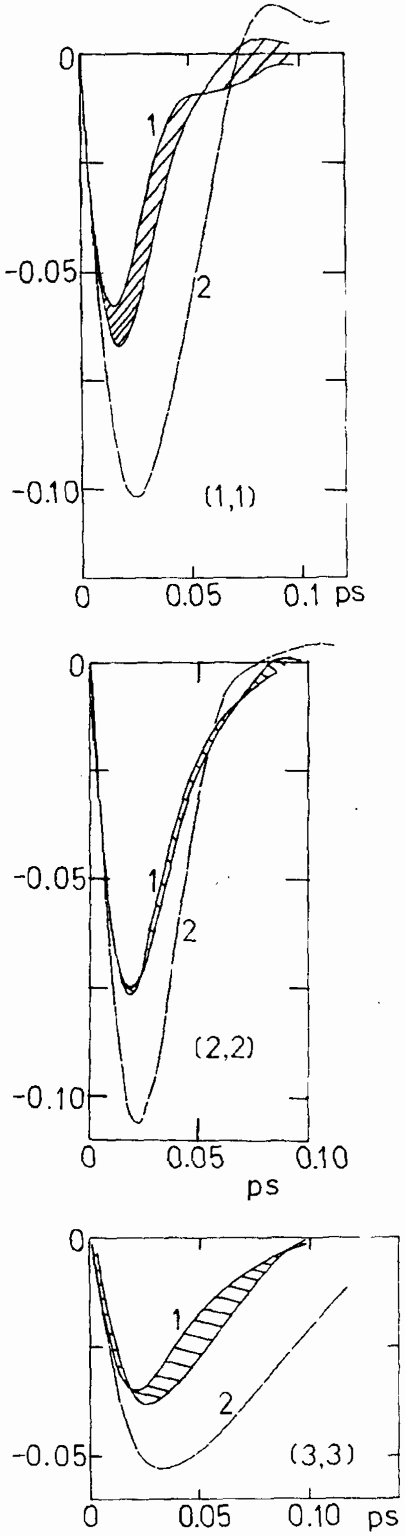

FIG. 10. (a) The moving frame element: $[\langle(\mathbf{v}(t)\times\boldsymbol{\omega}(t))_i v_i(0)\rangle / (\langle v^2\rangle\langle\omega^2\rangle)^{1/2}]_{(1,2,3)}$ (b) (2,2) element; (c) (3,3) element.

and is nonzero in frame (1,2,3) for $t>0$ both in T_d symmetry molecules (CCl_4) and in C_{2v} symmetry (H_2O). In consequence the ccf's of this type computed over the 54 water molecules in the microemulsion are much less affected by amplitude loss than in the case of Fig. 8. This is again support for the correctness of the main data generating and subsidiary running time average algorithms coded for this work and is an interesting indication of the way the symmetry properties of the CCl_4 molecules affect those of the 54 water molecules over which the running time averaging is constructed. This is evidence for the conclusion that cross-correlation functions, even over single molecules, are very sensitive to the symmetry of the environment, and of the point group symmetry of the molecules of the environment (in this case CCl_4) even though the running time averaging is confined to the 54 water molecules alone. It is easy to imagine that the properties of ccf's of this type will be sensitive in consequence to the environmental fluctuations in phase changes and in critical and flow phenomena of various kinds.

V. CONCLUSIONS

A computer simulation of the molecular dynamics of carbon tetrachloride water "microemulsions" has shown that the H bonding of a group of water molecules set up initially as a bonded cluster is broken up quickly on the subpicosecond time scale by the surrounding carbon tetrachloride molecules. This is counter to intuition, because of the H bonding the water cluster might have been "expected" to remain bonded, but evidently, the structural and dynamic data show that the H bonding is almost completely dispersed, even in the relatively "concentrated" 50/50 mixture. The main conclusion that can be drawn from this is that the microscopic properties of liquid mixtures on a subpicosecond time scale cannot be inferred by simple intuitive extrapolation from the corresponding macroscopic mixture properties as observable in the laboratory.

ACKNOWLEDGMENT

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