

Molecular dynamics of water in a strong electric field: Electric-field-induced translational anisotropy

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(Received 24 February 1987)

The molecular dynamics of water in an anisotropic environment are investigated with autocorrelation and cross-correlation functions in the laboratory and moving frames of reference. The anisotropy is generated by an uniaxial electric field which destroys the invariance of the Hamiltonian to symmetry operations in the laboratory frame of reference, thus making possible the appearance of new time correlations in this frame. The effect of the electric field is recorded systematically in terms of the symmetry of cross-correlation tensors and the anisotropy induced in autocorrelation functions. The field-induced anisotropy in the diagonal elements of the center-of-mass velocity autocorrelation function suggests a new experimental method of detecting directly the effect of rotation-translation coupling on the single-molecule level.

I. INTRODUCTION

The recent discovery of fundamental cross-correlation functions (CCF's) directly in the laboratory frame of reference has prompted their further investigation in anisotropic liquids, where symmetry restrictions are less stringent.¹⁻⁸ These cross-correlation functions involve simultaneously molecular rotational and translational motions, so that the analytical methods available at present for the description of molecular diffusion quickly become intractable, even for spherical-top symmetries. The technique of computer simulation has revealed a major shortcoming in theories of molecular diffusion which eliminate from the start the interdependence of fundamental modes of motion such as rotation and translation.

The fluctuation-dissipation theorem of linear-response theory⁹ supposes that the measuring field applied to the sample in a spectroscopic investigation does not induce any new correlation which does not exist in the original Hamiltonian prior to the application of the field. Recent computer simulations have shown, however, that in the presence of any external field of force that makes the liquid anisotropic, new time cross-correlation functions appear directly in the laboratory frame itself. There are no Green-Kubo relations for these CCF's, nor do they appear in generalizations such as the Onsager reciprocity relations.¹⁰⁻¹² In rough analogy with the uncertainty principle of quantum mechanics, a measuring field used by a spectroscopist (e.g., an electric field in dielectric relaxation) always perturbs the quantity which the spectroscopist seeks to measure. The stronger the disturbance, the less likely are the experimental data to relate meaningfully to equilibrium dynamics. This leaves computer simulations as a method of investigation which does not disturb the sample in this way, and which does not introduce uncertainty of a fundamental nature into the measuring process.

In techniques such as nonlinear dielectric spectroscopy,

where very strong fields are applied¹³⁻¹⁶ to the sample, the nature of the molecular dynamics in the presence of the field differs fundamentally from those in its absence. It is partly the aim of this paper to illustrate this difference for liquid water under a strong, uniaxial z-axis electric field. The argument is based on the response to the field of laboratory-frame CCF's involving simultaneously dynamical quantities such as the molecular center-of-mass linear velocity v , the molecular angular velocity ω , and the position of the molecular center of mass r . The argument is supplemented by consideration of analogous CCF's in the moving frame of reference (1,2,3), defined by the three axes of the principal molecular moments of inertia, and by reference to anisotropic autocorrelation functions in both frames.

The results show that in order to interpret the results from nonlinear dielectric spectroscopy the technique of molecular-dynamics simulation must be used to attempt to match the experimental data from a given model or *ab initio* pair potential. The configurations generated in this way may then be utilized self-consistently to reveal the nature of dynamical cross correlations in the presence of an arbitrarily strong probe field. This is likely to be intractable with contemporary analytical methods of any kind because of the twin problems described already of rotation-translation and other cross mode correlation and inapplicability of conventional response theory.

II. MOLECULAR-DYNAMICS SIMULATION METHODS

A standard constant volume simulation algorithm^{17,18} was adapted for investigating the effect of an electric field by incorporating the extra torque

$$\mathbf{T}_q = -\boldsymbol{\mu} \times \mathbf{E},$$

where $\boldsymbol{\mu}$ is the molecular dipole moment and \mathbf{E} the electric field strength, into the forces loop. This automatically

generates the correct dependence on the external torque of the other molecular-dynamical quantities, such as angular velocity, linear velocity, and center-of-mass position. The effect of this extra torque on the temperature is offset as in previous work with a temperature rescaling method during the equilibration stage. This effectively removes the increase in temperature due to the imposed external field.

The intermolecular pair potential used in this simulation was a site-site Lennard-Jones potential combined with charge-charge interactions between the lone pairs of electrons and at the hydrogen sites, as previously described by one of the authors.¹⁹ The system studied consists of 108 water molecules in a cube with periodic boundary conditions at room temperature and experimental density. The time step used in the integration of the equations of motion is 5×10^{-16} sec. The position and velocity vectors of all the water molecules are dumped every two time steps for correlation-function calculations. The data reported in this paper are for a total simulation time of 3.0 psec.

The instantaneous response of the sample to the application of the field is the generation of a rise transient. The sample achieves equilibrium in the presence of the field (field on equilibrium) and in this state the time correlation functions of interest are computed by running time averaging using an efficient routine which eliminates data transfer from storage disk to core. The effect of the external electric field on the sample dynamics can then be evaluated by comparison of time correlation functions in the presence and the absence of the field.

III. RESULTS AND DISCUSSION

A. Time cross-correlation functions

The most significant difference between the field-on and field-off dynamics is that in the field-on condition the (x,y) and (y,x) components of the laboratory-frame cross-correlation tensor¹⁹

$$C_1^{ij}(t) = \left\langle \frac{\langle v_i(t) \omega_j(0) \rangle}{\langle v_i^2(0) \rangle^{1/2} \langle \omega_j^2 \rangle^{1/2}} \right\rangle_{(x,y,z)}$$

exist for $t > 0$, and are illustrated in Fig. 1. These elements were first simulated in liquid dichloromethane¹⁶ and are not amenable to treatment with standard linear or nonlinear response theory. In other words this theory does not take into account the ineluctable generation of these cross-correlation functions once a field is applied. This is true whether the field is weak or strong, so that the conventional method of relating a spectrum to a time correlation function is invalidated. The Kubo integral relations as used by Whitehead *et al.*²⁰ for the complex permittivity and the orientational autocorrelation function (ACF) take no account of the appearance of CCF's (Fig. 1) once the measuring field (the ac field of dielectric spectroscopy) is switched on. There can be no measurement without the field, and as soon as it is applied the cross-correlation functions appear directly in the laboratory frame of reference. Note that the two curves in Fig. 1 should be the perfect mirror image of each other, due to the axial symmetry, if more statistics were used.

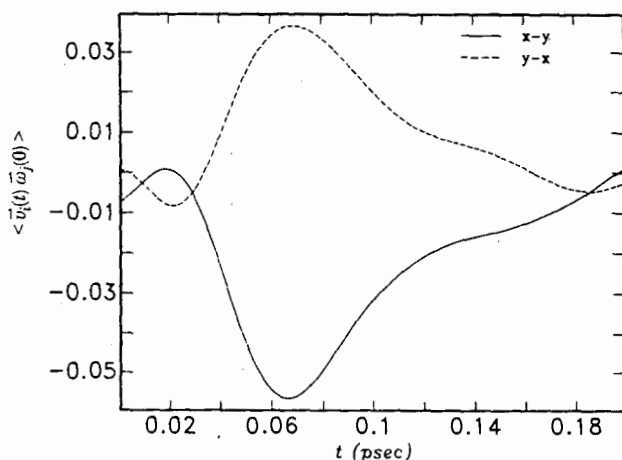


FIG. 1. Normalized laboratory frame C_1^{ij} , where $i,j=x,y,z$, generated by a z-axis electric field.

An attempt has been made by Evans²¹ to remedy the defect in conventional diffusion theory applied directly in the time domain, but this did not go as far as to make the necessary developments in the fluctuation-dissipation theorem of response theory. This is the theorem which effectively links spectra (e.g., dielectric loss and dispersion) to time correlation functions. It is used conventionally with no account of the field-induced CCF's as illustrated in Fig. 1, which were not known to exist prior to the computer simulations with which they were first discovered.¹⁶ These simulations were carried out exclusively in the time domain and need no considerations of linear response in order to obtain the correlation functions. On the other hand, the conventional experimental method of obtaining correlation functions is through the measurement of spectra, and always needs the intermediary of response theory to relate through the fluctuation-dissipation theorem to the frequency-dependent and temporal functions under investigation. There is no way of circumventing this, and the results of Fig. 1 catalyze further thought into whether field-induced CCF's in the laboratory frame undermine completely conventional wisdom in this area of physical chemistry.

A further problem for accepted theory and experimental practice is posed by the laboratory-frame CCF's of Figs. 2 and 3, which were recently shown to exist analytically and confirmed by computer simulation in spherical-top molecules. Their existence in liquid water treated to the intense external z-axis field used in this work confirms the need to develop fundamentally the theory of rotational diffusion, which has no means at present of establishing their time dependence, either in the laboratory frame or the moving frame (1,2,3) defined by the three principal molecular moments of inertia.

The CCF's of Figs. 2 and 3 are

$$C_2^{ij} = \left\langle \frac{\langle [\mathbf{v}(t) \times \boldsymbol{\omega}(t)]_i [\mathbf{v}(0) \times \boldsymbol{\omega}(0)]_j \rangle}{\langle [\mathbf{v}(0) \times \boldsymbol{\omega}(0)]_i^2 \rangle^{1/2} \langle [\mathbf{v}(0) \times \boldsymbol{\omega}(0)]_j^2 \rangle^{1/2}} \right\rangle_{(x,y,z)}$$

and

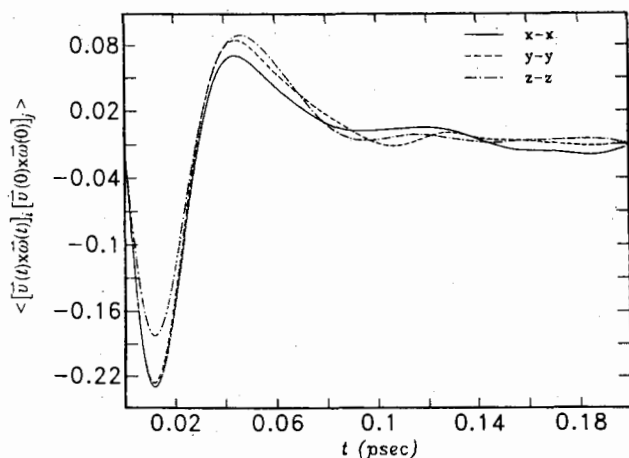


FIG. 2. Normalized laboratory frame C_2^{ij} , where $ij=x,y,z$, generated by a z-axis electric field.

$$C_3^{ij} = \left[\frac{\langle [\mathbf{v}(t) \times \boldsymbol{\omega}(t)]_i [\mathbf{T}_q(0) \times \mathbf{v}(0)]_j \rangle}{\langle [\mathbf{v}(0) \times \boldsymbol{\omega}(0)]_i^2 \rangle^{1/2} \langle [\mathbf{T}_q(0) \times \mathbf{v}(0)]_j^2 \rangle^{1/2}} \right]_{(x,y,z)}$$

There is a subtle difference, however, between the basic defect in diffusion theory and the fundamental defect in fluctuation-dissipation theory illustrated for liquid water in Fig. 1. This is because the CCF's of Figs. 2 to 3 also exist in the absence of an external field, even in spherical-top molecules, and those of Fig. 1 vanish in the absence of

$$C_6^{ij} = \left[\frac{\langle [\mathbf{r}(t) \times \boldsymbol{\omega}(t) \times \boldsymbol{\omega}(t)]_i [\mathbf{r}(0) \times \boldsymbol{\omega}(0)]_j \rangle}{\langle [\mathbf{r}(0) \times \boldsymbol{\omega}(0) \times \boldsymbol{\omega}(0)]_i^2 \rangle^{1/2} \langle [\mathbf{r}(0) \times \boldsymbol{\omega}(0)]_j^2 \rangle^{1/2}} \right]_{(1,2,3)}$$

which vanish by symmetry in the laboratory frame of reference but which contain simultaneously positional, rotational, and/or translational dynamical quantities. The derived ideas of conventional "rotational" diffusion theory are not applicable to these time correlation functions. The

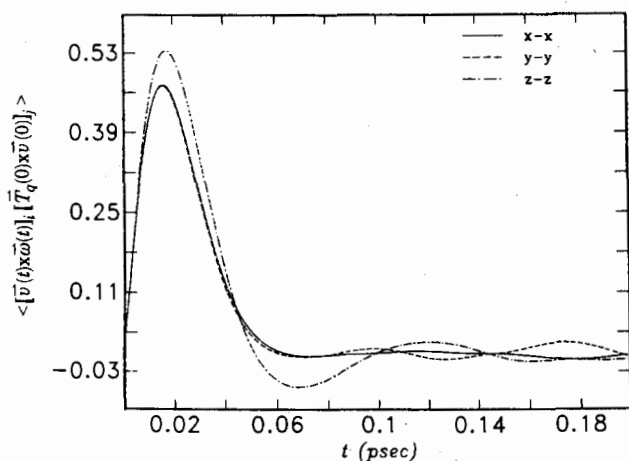


FIG. 3. Normalized laboratory frame C_3^{ij} , where $i,j=x,y,z$, generated by a z-axis electric field.

the field for all symmetries, including chiral symmetries. A complete analytical theory of diffusion would have to explain these results entirely self-consistently. Any treatment based on the Langevin equation¹⁰ or Kramers diffusion equation is likely to fail because of the intricately nonlinear nature of asymmetric top rotation translation, and because of the fundamental difficulty with response theory. There is a further difficulty introduced by the number of parameters, e.g., the simplest Perrin treatment of asymmetric top "rotational" diffusion requires three friction coefficients, and although this theory was introduced more than 50 years ago, these friction coefficients have rarely, if ever, been measured experimentally. This is probably just as well because the Perrin theory²² and all derivatives of rotational diffusion theory are fundamentally defective, being unable to account for the results of Figs. 1 to 3.

In the moving frame of reference defined by the three principal molecular moments of inertia axes, further CCF's are symmetry allowed and three types are illustrated in Figs. 4 to 6. These are

$$C_4^{ij} = \left[\frac{\langle [\mathbf{v}(t) \times \boldsymbol{\omega}(t)]_i \mathbf{v}_j(0) \rangle}{\langle [\mathbf{v}(0) \times \boldsymbol{\omega}(0)]_i^2 \rangle^{1/2} \langle \mathbf{v}_j^2(0) \rangle^{1/2}} \right]_{(1,2,3)}$$

$$C_5^{ij} = \left[\frac{\langle [\mathbf{r}(t) \times \boldsymbol{\omega}(t)]_i \mathbf{r}_j(0) \rangle}{\langle [\mathbf{r}(0) \times \boldsymbol{\omega}(0)]_i^2 \rangle^{1/2} \langle \mathbf{r}_j^2(0) \rangle^{1/2}} \right]_{(1,2,3)}$$

and

complexity into which the elegant and simple Debye theory degenerates when applied to the simultaneous rotation and translation of the asymmetric top is obvious from the attempts in the literature. Note that this is also true of Kramers equations,²³ and even of accepted contem-

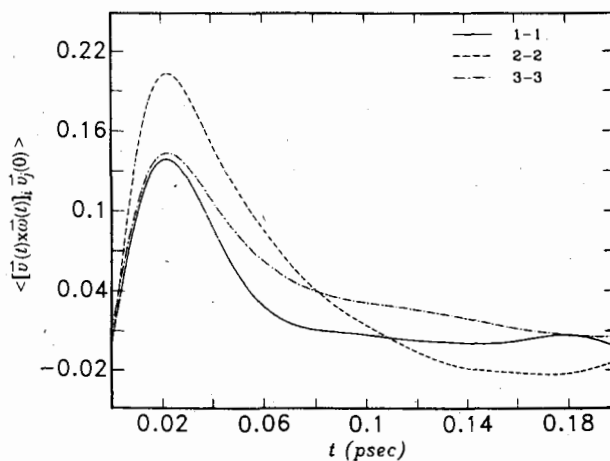


FIG. 4. Normalized moving frame C_4^{ij} , where $i,j=1,2,3$, generated by a z-axis electric field.

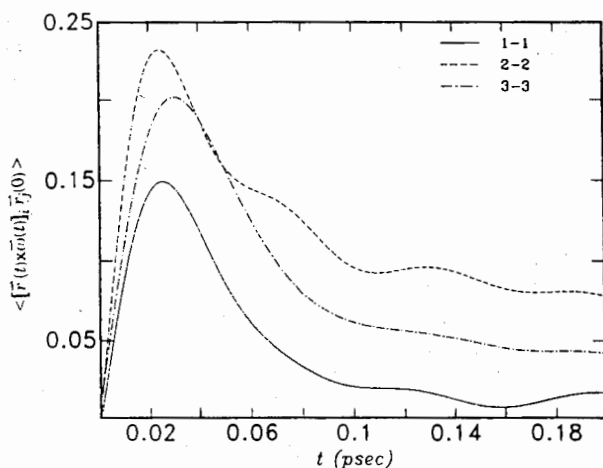


FIG. 5. Normalized moving frame C_3^{ij} , where $i, j = 1, 2, 3$, generated by a z-axis electric field.

porary theory such as that of the itinerant oscillator or reduced model theory. These approaches are of course able to explain diverse phenomena self-consistently, but only within a restrictive framework of hypothesis. That this is more restrictive than computer simulation seems to be clear from the facts illustrated in Figs. 1 to 6. Thus computer simulation is probably the most effective contemporary means of understanding molecular properties of the liquid state of matter. Not only is the simulation method able to provide time correlation functions by direct running time averaging, but it is also safe to Fourier transform these time functions into spectra with conventional Kubo relations at field-off equilibrium.

B. Time autocorrelation functions

Moreover, computer simulation is able to supply ideas for the experimental measurement of the effect of cross mode coupling in the laboratory as illustrated in Fig. 7. In this figure the anisotropy in the x , y , and z components of the linear center-of-mass velocity ACF's is illustrated

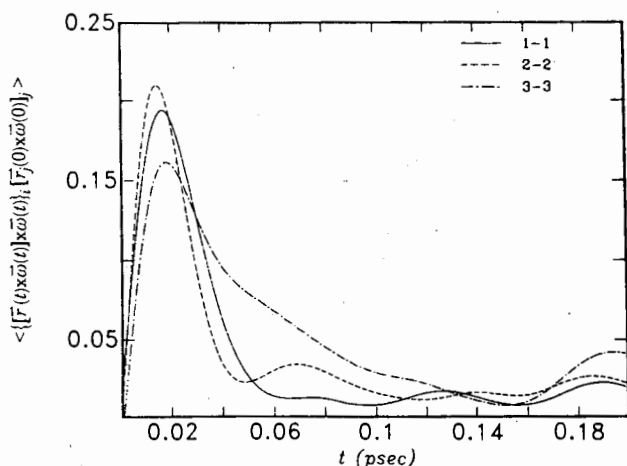


FIG. 6. Normalized moving frame C_6^{ij} , where $i, j = 1, 2, 3$, generated by a z-axis electric field.

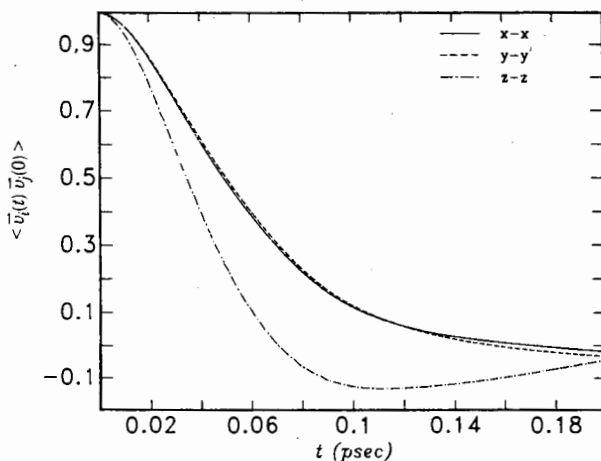


FIG. 7. Normalized x , y , and z components of the molecular center-of-mass linear velocity autocorrelation functions in the laboratory frame when an electric field is applied in the z direction.

in the laboratory frame of reference. The time dependence of the z component is clearly different from those of the other two, and cannot be explained with conventional "translational" or "rotational" diffusion theory because the anisotropy in the linear center-of-mass velocity ACF is introduced by an external torque which exerts no direct body force on the molecular center of mass in any of the three directions x , y , and z . There may be two causes for this anisotropy. The first is obviously due to space inhomogeneity caused by the partial dipole alignment to the z -axis electric field. The other might be through single-molecule cross mode coupling as illustrated in Figs. 1 to 6.

We propose to name this new phenomenon "electric-field-induced translational anisotropy." It is in the class of phenomena typified by the Kerr effect (electric-field-induced birefringence); the Faraday effect (magnetic-field-induced birefringence); and the Buckingham effect (electromagnetic-field-induced birefringence). However, it differs fundamentally from these three established effects in the literature in that it appears in the linear center-of-mass molecular diffusion coefficients through the influence of an external torque. This torque may be induced by an electric, magnetic, or electromagnetic field of force. In the simulation of this paper we have used an uniaxial electric field for simplicity of illustration. However, there is no objection in principle to using an ac field. In experimental terms the new phenomenon means that under the influence of an externally imposed torque, the linear center-of-mass diffusion in the laboratory frame becomes anisotropic. This anisotropy can be seen experimentally by measuring the linear diffusion coefficient in the z and x directions of the laboratory frame. Figure 7 means that the diffusion coefficients should be different due to cross mode coupling on the single-molecule level as illustrated in Figs. 1 to 6. The linear diffusion coefficients in the z and x directions can be measured by Brillouin scattering or inelastic neutron scattering, or by ultrasound and hypersound dispersion in the two directions of the laboratory frame. Tracer diffusion analysis might also be applic-

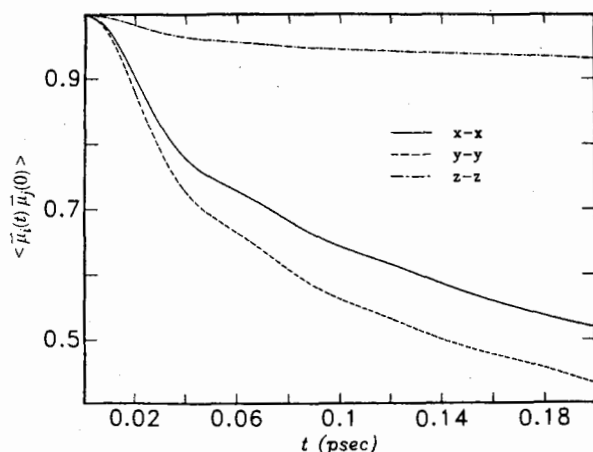


FIG. 8. Normalized x , y , and z components of the orientational autocorrelation functions in the laboratory frame as an illustration of the Kerr effect when an electric field is applied in the z direction.

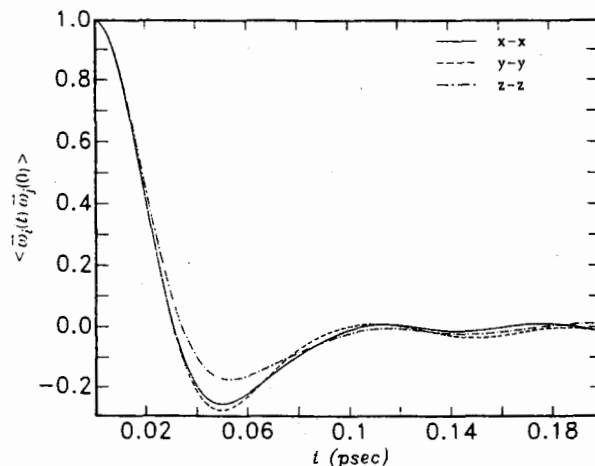


FIG. 9. Normalized x , y , and z components of the molecular angular velocity autocorrelation functions in the laboratory frame when an electric field is applied in the z direction.

able in favorable instances.

Figure 8 illustrates for self-consistency the Kerr effect in the orientational autocorrelation function (ACF's) obtained with precisely the same configurations as Fig. 7. It is clear from Fig. 8 that the orientational ACF in the z axis decays much more slowly than those in the x and y axes, as expected from an applied z -axis electric field, which causes the dipole axes of the molecules to be aligned on average in this direction.

Finally in Fig. 9 the anisotropy of the angular velocity ACF in the laboratory frame is illustrated in the x , y , and z axes. In this case the effect of the electric field is to render the ACF less oscillatory in the z axis; the negative overshoot is diminished, implying that the molecular libration in the z axis sweeps through smaller angles on the average than that in the x and y axes. This is because the torque imposed by the external z -axis electric field tends to lock the molecular "antennae," the dipole moments, onto the z axis of the laboratory frame. The field-induced anisotropy of the angular velocity ACF is part of the dynamics of the Kerr effect, and is expected from an applied external torque.

IV. CONCLUSION

The effect of an uniaxial electric field applied in the z axis of the laboratory frame to liquid water is to promote the existence of cross-correlation functions directly in the lab frame. These CCF's undermine the validity of response theory and conventional "rotational diffusion" theory. The external field causes anisotropy in the translational diffusion coefficients in the z and x axes of the laboratory frame. This appears to be a new phenomenon which we have named "electric-field-induced translational anisotropy." This is believed to be due to dipole alignments and fundamental cross mode correlations, and may be measurable experimentally.

ACKNOWLEDGMENT

One of us (M.W.E.) is grateful to IBM Kingston for support.

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