Computer Simulation and Group Theoretical Statistical Mechanics of Liquid Water and Methyl Chloride: Part 2, Field Effects.

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Abstract

The new methods of group theoretical statistical mechanics (g.t.s.m.) are used to determine field effects on cross correlation functions (c.c.f.'s) in molecular liquids, on the basis that the ensemble average reduces as the totally symmetric irreducible representation (t.s.r.) in the laboratory frame (X, Y, Z) and the molecule fixed frame (x, y, z) of the point group character tables. It is shown that a Z axis electric field promotes the existence of two symmetric elements of the cross correlation function (c.c.f.) between molecular linear and angular velocity in frame (X, Y, Z) as predicted by g.t.s.m. These results are fully in agreement with computer simulations of water and liquid methyl chloride. The methods of g.t.s.m. are extended to predict the possible effects of electric and magnetic fields on c.c.f.'s in both frames.

Introduction

Many of the basic theories of molecular diffusion[1-20] do not attempt to consider the statistical correlation between the fundamental dynamical variables, translation and rotation. This leads to incomplete and incorrect results, as shown by computer simulation[21]. This is a serious flaw in fluctuation-dissipation theory[22] the theory of dynamical birefringence[23], and the Kerr effect, that of dielectric relaxation[24], including off-shoots such as the rotational itinerant oscillator[25-29]. The whole of molecular spectroscopy is based on the observation of molecular material with fields, and a method os needed with which to codify the effect of the field on that which is being observed. In the methods of dielectric relaxation, an external electric field breaks the $R_{(h)}$ symmetry of the laboratory frame (X, Y, Z) and promotes new time cross correlation functions (c.c.f.'s) in this frame. This has been shown clearly by computer simulation[30-40], and invalidates the traditional approach based on computer simulation. A large set of c.c.f.'s is now known to exist from detailed and systematic computer simulation, and through the recent emergence[41-46] of group theoretical statistical mechanics (g.t.s.m.). In this paper, symmetry arguments and computer simulation are used to characterise the electric and magnetic field induced changes in the diffusional dynamics of molecular liquids, changes which are left unconsidered in the traditional theoretical approach[25-29]. The group theoretical arguments used in frame (X, Y, Z) and also in the molecule fixed frame (x, y, z) of the point group character tables[41, 47-51]. In either frame a thermodynamic average survives if it contains the appropriate totally symmetric irreducible representation (t.s.r.) of the point group. Extra averages induced by field alignment must have at least one occurrence[41] of the t.s.r. The correctness of this axiom is tested in this paper with computer simulation of liquid water and methyl chloride in both frames and subjected to a Z axis electric field. It is found that this changes the time dependence but not the symmetry of the time c.c.f. between molecular linear velocity and angular velocity in frame (x, y, z). In frame (X, Y, Z) extra ensemble averages appear with the symmetry of the electric field. On this basis field effects are discussed for several point groups in both frames.

Birefringence Effects in the Laboratory Frame

The relevant point group is the three dimensional rotation-reflection group $R_h(3)$, whose irreducible representations are $D_g^{(0)}, \ldots, D_g^{(n)}$ and $D_u^{(0)}, \ldots, D_u^{(n)}$. respectively. These are even (gerade) and odd (ungerade) to the parity reversal (X, Y, Z) → (-X, -Y, -Z). A scalar in this notation has symmetry $D_g^{(0)}$; a pseudoscalar is $D_u^{(0)}$; a polar vector is $D_u^{(1)}$; and an axial vector such as angular velocity is $D_g^{(1)}$. In isotropic environments such as a molecular liquid the symmetry of the ensemble average $<A>$ will be that of A itself. The symmetry of $<AB>$ will be $\Gamma(A)\Gamma(B)$ where Γ denotes the property's symmetry representation in $R_h(3)$. Thus the average $<AB>$ over the product of molecular physical properties AB will exist in an isotropic molecular liquid if the product of symmetry representations contains the totally symmetric representation (t.s.r.) at least once.

In $R_h(3)$ the t.s.r. is $D_g^{(0)}$. Thus all ensemble averages over scalars will exist in field-free isotropic equilibrium. Ensemble averages over scalars will exist in field free isotropic equilibrium. Ensemble averages over both polar and axial vectors will vanish. Being of $D_u^{(1)}$ and $D_g^{(1)}$ symmetry respectively, they do not contain $D_g^{(0)}$. Similarly, the time c.c.f. $<v(t)\omega^T(0)>$ vanishes in frame (X, Y, Z) because the product

$$\Gamma(v)\Gamma(\omega) = D_u^{(1)}D_g^{(1)} = D_u^{(0)} + D_u^{(1)} + D_u^{(2)} \tag{1}$$

does not contain the t.s.r. In contrast, the time c.c.f.'s $<v(t)\mu^T(0)>$, $<v(t)\dot{\mu}^T(0)>$, and $<v(t)Q^T(0)>$ have non-vanishing elements in frame (X, Y, Z) in the isotropic liquid because the symmetries of the molecular dipole moment, μ, its time derivative, $\dot{\mu}$, and the normal molecular vibrational coordinates Q_i are all $D_u^{(1)}$. The appropriate product of representations is therefore

$$D_u^{(1)}D_u^{(1)} = D_g^{(2)} + D_g^{(1)} + D_g^{(0)} \tag{2}$$

which contains the t.s.r., $D_g^{(0)}$ once. This implies that the reequisite non-vanishing elements are the three diagonal elements, which are equal in magnitude and time dependence for each time c.c.f. in the isotropic liquid. Equations (1) and (2) are both examples of the Clebsch Gordan theorem[48]

$$D^{(n)}D^{(m)} = D^{(n+m)} + \ldots\ldots\ldots + D^{(|n-m|)} \tag{3}$$

The Effect of an Electric Field E in Frame (X, Y, Z)

The electric field vector itself has symmetry $D_u^{(1)}$. Its effect can be to break the isotropy of the (X, Y, Z) frame, so that

$$A_Z \neq A_X = A_Y \tag{4}$$

In terms of symmetry, this means that the ensemble average $< \; > \neq 0$ if its symmetry representation contains $D_u^{(1)}$ or $D_g^{(0)}$ or a combination of both. In electrically dipolar molecules, for example, the field E can generate the torque $-\mu \times E$ for each molecule in the liquid. The symmetry effect of an electric field in frame (X, Y, Z) is therefore to make possible the existence of ensemble averages with symmetry $D_g^{(0)}$ and $D_u^{(1)}$. For time autocorrelation functions (a.c.f.'s), $D_g^{(0)}$ signifies that the trace of the correlation tensor exists, although in the presence of the field the three components of the trace will no longer be equal. The electric field also allows the existence of $D_u^{(1)}$ quantities for ensemble averages over any physical property of the liquid in the presence of the field. However, the symmetry of any time a.c.f. is always gerade, and $D_u^{(1)}$ can never occur in the symmetry representation of any time a.c.f. For a time c.c.f. such as $<v(t)\omega^T(o)>$ however, the field induced $D_u^{(1)}$ quantity represents the (X, Y) = - (Y, X) off-diagonal elements which therefore become visible[52-54] in an electric field directed along the Z axis of the lab. frame. The symmetry of the electric field induced matrix is

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + E_Z \rightarrow \begin{bmatrix} 0 & A & 0 \\ -A & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{5}$$

This is exactly what is found by computer simulation[52-54] of diffusing dipolar molecules. The electric field also takes effect in the molecule fixed frame, where the resultant matrix symmetries are described by molecular point group theory.

General Effect of the Magnetic Field, H

The magnetic field, H is an axial vector of $D_g^{(1)}$ symmetry, and in frame (X, Y, Z) it allows the existence of ensemble averages of $D_g^{(1)}$ symmetry in addition to the t.s.r. The symmetry of a simple time a.c.f. in frame

(X, Y, Z) is

$$D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$$

so that the magnetic field produces changes in the trace of the time a.c.f. and also makes possible the existence of one pair of off-diagonal elements. If H is directed along the Z axis this element is $(X, Y) = -(Y, X)$. The effect of a magnetic field on the symmetry of any time a.c.f. is therefore

$$\begin{bmatrix} B & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & B \end{bmatrix} + H_Z \rightarrow \begin{bmatrix} B_1 & A_1 & 0 \\ -A_1 & B_1 & 0 \\ 0 & 0 & C \end{bmatrix} \tag{6}$$

On the other hand, the symmetry of an ungerade time c.c.f. such as $< v(t)\omega^T(0) >$ is

$$D_u^{(0)} + D_u^{(1)} + D_u^{(2)}$$

and consequently a magnetic field produces no new elements of this c.c.f. in frame (X, Y, Z). However, in the molecule fixed frame (x, y, z) the symmetry effect of the magnetic field may be different for each molecular point group. The effect of the magnetic field on a parity-even cross correlation function, such as that between linear and angular velocity, is tha same as its effect on an autocorrelation function. In both cases extra off-diagonal elements appear in frame (X, Y, Z).

Second Order Electric Field, E^2

The general effect of a field E^2 on ensemble averages is to make possible the existence in frame (X, Y, Z) of the symmetry signature

$$\Gamma(E)\Gamma(E) = D_u^{(1)}D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \tag{7}$$

implying that averages of all three symmetry types on the right hand side may appear in principle in the laboratory frame by suitable interaction of the second order field with a property such as the molecular polarisability. Averages of the first type, (superscript 0) signify changes in the trace of the generic even parity a.c.f. matrix; the second type (superscript 1) denotes the appearance of off diagonal elements antisymmetric to exchange of lab. frame orthogonal components

$$< A_X(t)A_Y(0) > = - < A_Y(t)A_X(0) > \tag{8}$$

and the third type (superscript 2) denotes the appearance of off diagonal elements symmetric in the interchange of subscripts

$$< A_X(t)A_Y(0) > = < A_Y(t)A_X(0) > \tag{9}$$

Time c.c.f.'s that are ungerade, such as that between linear and angular velocity, do not become observable in frame (X, Y, Z) as a result of treatment with a second order electric field.

Second Order Magnetic Field

The overall symmetry effect is the same as E^2, and its signature is the right hand side of eqn. (9).

Third Order Electric Field

The overall symmetry signature of the third order electric field is in general

$$\Gamma(E)\Gamma(E)\Gamma(E) = D_u^{(1)}D_u^{(1)}D_u^{(1)} = D_u^{(0)} + 3D_u^{(1)} + 2D_u^{(2)} + D_u^{(3)} \tag{10}$$

This means that the interaction between E^3 and a molecular property such as the first hyperpolarisability tensor leads to birefringence (superscript zero D signature) and many other possible effects allowed by the overall symmetry signature (10). Only some of these seem to have been realised[55] in the literature, which seems to have been largely confined to powers of a strong uniaxial electric field. The signature (10) is equally applicable to three separate electric fields applied in combination. In third order fields we expect ensemble averages which are overall ungerade in nature, such as off-diagonal elements of $<v(t)\omega^T(0)>$, and also of time correlation functions whose overall symmetry signature is the same as that on the right hand side of eqn. (10), e.g.

$$<v(t)\omega(t)\omega(0)> ; \quad | \quad <v(t)v(t)v(0)> ;$$

direct in the laboratory frame (X, Y, Z). This type of induction would be particularly important in liquid crystals.

Third Order Magnetic Field

The symmetry signature of a third order magnetic field, or a combination of three magnetic fields, is the same as the right hand side of eqn (10) but with subscript u replaced by subscript g.

Effect of Fields on Transport Processes in Frame (X, Y, Z)

There are many measurable diffusion coefficients or Green Kubo functions which can be constructed in the laboratory frame by the integration of time c.c.f.'s or a.c.f.'s. A time c.c.f. between transport processes exists in isotropic $R_h(3)$ if the product of representations of each component of the correlation function contains $D_g^{(0)}$ at least once. If the latter appears more than once there are more than one independent elements of the correlation function. In the presence of external fields new cross transport coefficients become visible in frame (X, Y, Z). To illustrate this we consider the following examples.

1) Symmetry of Some Bulk and Molecular Properties

Elasticity, for example, is a symmetric fourth rank tensor of symmetry

$$2D_g^{(0)} + 2D_g^{(2)} + D_g^{(4)}$$

The symmetry of the time a.c.f. of this tensor is given by the product of representations

$$(2D_g^{(0)} + 2D_g^{(2)} + 2D_g^{(4)})(2D_g^{(0)} + 2D_g^{(2)} + D_g^{(4)})$$
$$= D_g^{(8)} + D_g^{(7)} + 5D_g^{(5)} + 13D_g^{(4)} + 9D_g^{(3)} + 17D_g^{(2)} + 5D_g^{(1)} + 9D_g^{(0)} \tag{11}$$

which is developed from an application of the Clebsch Gordan theorem. In isotropic three dimensional space ((X, Y, Z)), nine independent elements (9 $D_g^{(0)}$) of the time a.c.f. of elasticity exist in the laboratory frame. In a magnetic field, these would be supplemented by five independent elements of $D_g^{(1)}$ symmetry, and in higher order fields by the appropriate higher order elements of the complete symmetry signature. There is therefore an intricate field effect, depending on the interaction of the signature of the applied field with that of the time correlation function (11).

Cross Transport Coefficients

Some cross transport coefficients, which are Green Kubo integrals over cross correlation functions, become visible in the electric field because the laboratory frame then supports the symmetry $D_u^{(1)}$. Electric field induced time c.c.f.'s in frame (X, Y, Z) are generated whenever a product of representations of any two physical properties contains the representation $D_u^{(1)}$. The electric field can therefore promote finite time cross correlation between a pseudo vector $D_g^{(1)}$ and a pseudo scalar $D_u^{(0)}$, or between any symmetric second rank tensor ($D_g^{(0)}$ $D_g^{(2)}$) and a polar (true) vector $D_u^{(1)}$ and so on. An applied electric field also makes possible time cross correlation between the molecular quadrupole moment ($D_g^{(2)}$) and dipole moment ($D_u^{(1)}$) which would otherwise vanish in isotropic $R_{(h)}(3)$. A full appreciation of the field- induced possibilities is available from the table of symmetries of physical properties in ref. (51), p. 63.

Molecule Fixed Frame (x, y, z)

The symmetry effect of an external field in the molecule fixed frame (x, y, z) may be found by mapping the appropriate D representations from $R_h(3)$ to the molecular point group. For each of the molecular point groups the symmetry of $D_u^{(1)}$ is different in frame (x, y, z) and is found by the mapping rules of group theory[47-51]. Similarly, $D_g^{(1)}$ induced by the magnetic field B has its equivalent representation in each molecular point group. In this section the effect of electric and magnetic fields in frame (x, y, z) is investigated.

Rotation and Translation

(A) The Electrically Dipolar Point Groups

The C_{2v} Point Group (the Asymmetric Top)

In this point group the true (polar) and pseudo (axial) vectors map as follows

$$\Gamma(v) = D_u^{(1)} \to A_1 + B_1 + B_2 \tag{12}$$

$$\Gamma(\omega) = D_g^{(1)} \to A_2 + B_1 + B_2 \tag{13}$$

(a) Electric Field

The symmetry representation in this case contains the totally symmetric representation A_1 once. The molecular dipole moment is in axis z of frame (x, y, z) and reduces as A_1 within the C_{2v} point group. The symmetry

effect of the electric field on the time c.c.f. $<v(t)\omega^T(0)>$ is therefore found by considering the product of representations

$$\Gamma(v)\Gamma(\omega) = (A_1 + B_1 + B_2)(A_2 + B_1 + B_2) \tag{14}$$

of which B_1B_1 and B_2B_2 produce A_1. The overall effect of the electric field is to change the time dependence of the elements corresponding to these symmetry products, which are the (x, y) and (y, x) elements, those which exist at field free equilibrium. This result is illustrated in liquid water in Fig. (1) from a computer simulation.
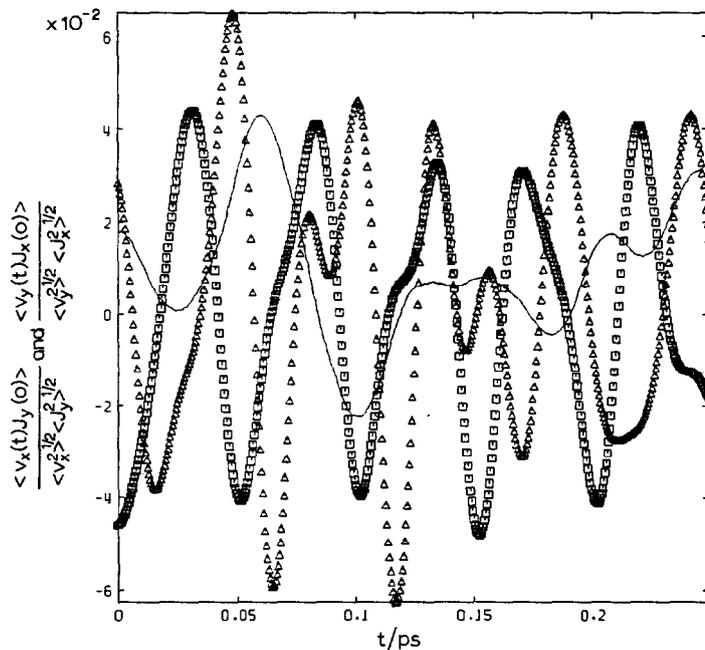
Figure 1

(a) Computer simulation of $< v_\chi(t)\omega_\gamma(0) > = - < v_y(t)\omega_\chi(0) >$ for a Z axis electric field applied in liquid water. Solid line, field free equilibrium.

Electric Field Effect for Some Point Groups

This result can be generalised for the dipolar molecular point groups by noting that those elements that exist in the absence of the field appear in the field-on steady state but with a different time dependence. This is in agreement with available computer simulations[34, 52-61] and with those of this paper, exemplified by water (Fig. (1)), and dichloromethane (Fig. (2)). In achiral non-dipolar point groups E does not include the totally sym-

(a) $\times 10^{-2}$

$\frac{<v_y(t)J_x(o)>}{<v_y^2>^{1/2}<J_x^2>^{1/2}}$ and $\frac{<v_x(t)J_y(o)>}{<v_x^2>^{1/2}<J_y^2>^{1/2}}$

t/ps

(b)

$\frac{<v_y(t)J_x(o)>}{<v_y^2>^{1/2}<J_x^2>^{1/2}}$ and $\frac{<v_x(t)J_y(o)>}{<v_x^2>^{1/2}<J_y^2>^{1/2}}$

t/ps
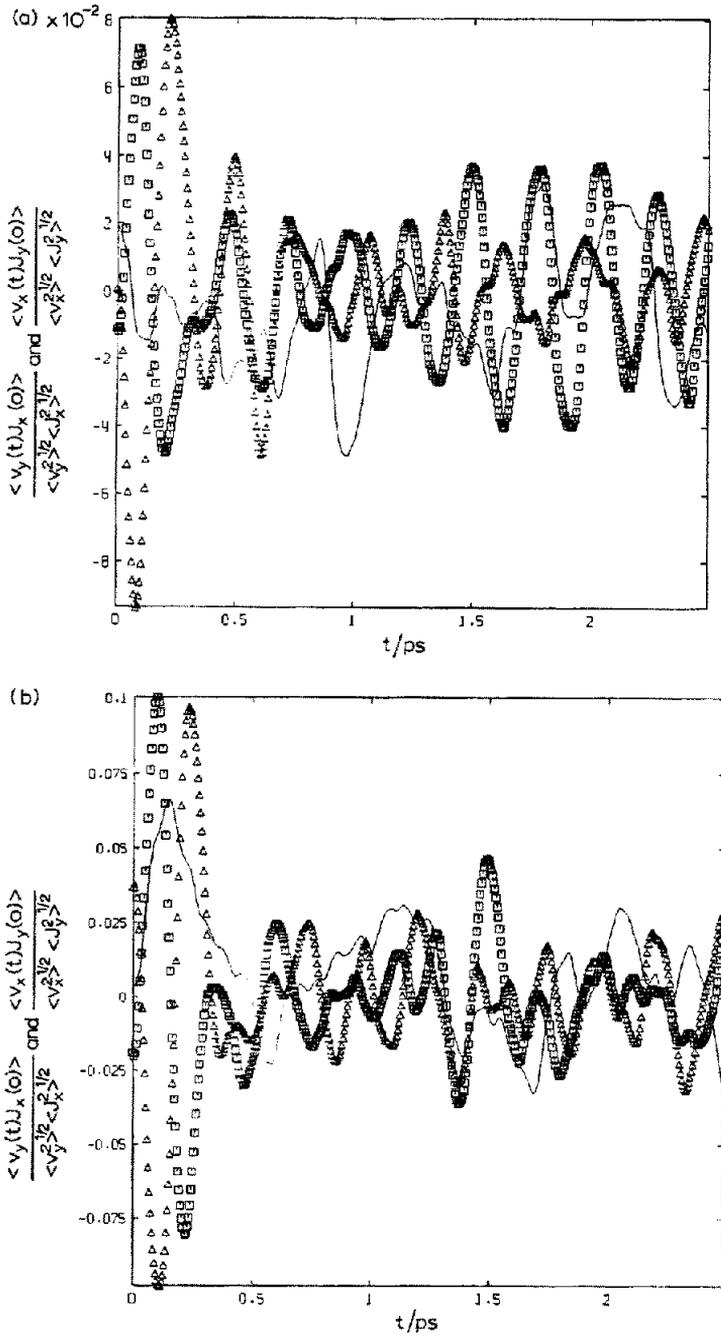
Figure 2

As for Fig. (1), (a) liquid methyl chloride. In this case the (x, y, z) elements are mirror images and are not independent. (b) Equivalent elements in frame (x, y, z).

metric representation and neither does the velocity / angular velocity c.c.f., signifying the absence of electric dipole interaction.

The "Uncertainty Principle".

The application of an electric field affects the symmetry of this c.c.f. in frame (X, Y, Z), making possible the existence of

$$< v_X(0)\omega_Y(t) > = - < v_Y(0)\omega_X(t) > \tag{15}$$

and affects the time dependence of the two independent elements (x, y) and (y, x) in frame (x, y, z). This profoundly changes the nature of the molecular diffusion process and introduces uncertainty to the customary theory of diffusion processes in the presence of a strong electric field, such as the Kerr effect. Standard dielectric relaxation theories[58] such as those of the itinerant oscillator ignore all cross correlation effects of the type considered here and are incomplete. The probe electric field in the theory of dielectric relaxation changes the observed molecular dynamics to produce new cross correlation functions which are incompletely described in contemporary diffusion theory.

(b) Magnetic Field

The interaction of the magnetic field with the molecular ensemble produces averages of $D_g^{(1)}$ type in frame (X, Y, Z). Such orientation can only apply to $D_g^{(1)}$ which have non-zero ensemble averages in frame (x, y, z), whose signature is the totally symmetric representation of the molecular point group. In C_{2v}, $D_g^{(1)}$ reduces as

$$A_2 + B_1 + B_2$$

and does not contain A_1. We conclude that the field induced average in frame (X, Y, Z) does not affect the symmetry of c.c.f.'s in frame (x, y, z). However, certain point groups such as the chiral C_n and D_n for example have $D_g^{(1)}$ representations in frame (X, Y, Z) which include t.s.r.'s of the appropriate point group in frame (x, y, z) and in this case the effect, as usual, depends on the number of occurrences of the t.s.r.

(B) Electrically Non-Dipolar Point Groups

In this type of molecule the electric dipole moment vanishes for all point groups. If the molecule contains a magnetic dipole moment or is polarisable or magnetisable then averages of the type $D_g^{(1)}$ or $D_g^{(0)} D_g^{(2)}$ can exist in frame (X, Y, Z) provided that such orientations have occurrences of the appropriate t.s.r. in the molecular point group.

(C) Higher Order Magnetic and Electric Field Effects

When strong electric fields are applied to a molecular liquid, interactions can occur between E^2 and the molecular polarisability, allowing non-zero thermodynamic ensemble averages of the type $D_g^{(0)} + D_g^{(2)}$ to exist in frame (X, Y, Z), provided that this sum includes the t.s.r. of the point group at least once in frame (x, y, z). Similarly averages of this type are also generated by the interaction of the magnetisability tensor with H^2. In C^{2v} for example, this sum maps on to

$$3A_1 + A_2 + B_1 + B_2$$

which contains the t.s.r. three times, implying the existence of three independent diagonal elements. In C_{3v} there are two independent diagonal elements, and none in O_h.

Computer Simulations

These are described in part 1[59] of this series and elsewhere in the literature[60-62]. The results illustrated in Fig. (1) show over two segments the existence of electric field induced off-diagonal elements in liquid water. Alignment of the water dipoles with an electric field is always accompanied by the emergence of two elements of the linear / angular velocity cross-correlation function in the laboratory frame of reference.

Fig. (2) illustrates the field induced elements for methyl chloride in both frames of reference, (X, Y, Z) and (x, y, z). These results were produced with two contiguous elements of at least 4,000 time steps each, and are in agreement with group theoretical predictions. The elements in the molecule fixed frame are mirror image pairs of the one independent A_1 element that survives for C_{3v} symmetry in frame (x, y, z).

Acknowledgements

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