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SYMMETRY EFFECTS OF ELECTRIC AND MAGNETIC FIELDS IN LIQUID STATE MOLECULAR DYNAMICS

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ABSTRACT

It is shown that ensemble averages in molecular liquids may be investigated using group theoretical methods. These my be applied both in the laboratory frame (X,Y,Z) and the frame of the principal molecular moments of inertia (x,y,z). Using these methods the effect of an external electric field ($\underline{E}$) and external magnetic field ($\underline{H}$) may be considered in terms of second order ungerade quantities such as the single molecule cross correlation function $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ where $\underline{v}$ is the molecular centre of mass linear velocity and $\underline{\omega}$ the angular velocity of the same molecule. Group theory, applied in this way, confirms the recent discovery by computer simulation of non-vanishing elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ in frame (X,Y,Z) in the presence of an electric field. Group theory predicts, however, that these elements vanish in the presence of a magnetic field, even though this produces alignment and birefringence through the Langevin function. This leads to a straightforward experimental method for the direct observation of the non-vanishing elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$.

INTRODUCING

Computer simulation has recently revealed [1-10] a new set of non-vanishing cross correlation functions in molecular liquids. The members of this set can be measured both in frame (x,y,z) of the principal molecular moments of inertia [1-5] and frame (X,Y,Z) of the laboratory observer. [1-10] The use of external fields, including electric and electromagnetic fields, promotes the existence [8-12] of cross correlation functions (c.c.f.s) in frame (X,Y,Z) which vanish at field free equilibrium.

Recently Whiffen [13] has developed a group theory of liquid state ensemble averages, including c.c.f.'s of all orders, which may be used to deduce by symmetry whether such averages exist or vanish for all t in frames (X,Y,Z) and (x,y,z). This group theoretical approach has been tested by Evans for specific cases [9-12] by computer simulation. Both group theory and simulation are self consistent in their description of those c.c.f elements that exist for $t > 0$ in either frame of reference. Having thus established the validity of the group theoretical approach [13] to liquid state ensemble averages [14] this paper aims to extend the investigation of molecular dynamics in liquids to c.c.f.'s in the presence of magnetic fields. This has not been possible by computer simulation because the Lorentz forces set up by the external magnetic field affects the molecular velocity directly, and interfere with the Verlet integration routine.[15]

By considering by group theory the alignment of a liquid crystal, first with an electric field and then, in a separate experiment, with a magnetic field, this paper shows how a straightforward method can be developed to investigate directly the effect of elements of the non-vanishing c.c.f. $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ on microwave and far infra red spectra in liquid crystals. Here $\underline{v}$ is the linear centre of mass velocity of the liquid crystal molecule in the nematic phase and $\underline{\omega}$ its own angular velocity in the rigid molecule approximation Flexibility and internal bond vibration in the molecule requires separate consideration.

THEORY

In developing the theory the notation S, P, D, F, G is used for the spherical harmonics of order 0,. 1, 2, 3, and 4 respectively. An ensemble average such as the cross correlation function (c.c.f.) is termed a gerade quantity if it is symmetric to inversion of (X,Y,Z) axes of the laboratory frame, and ungerade if it is anti-symmetric to inversion. [13] A scalar quantity such as mass is taken to be order $n = 0$, a vector quantity $n = 1$, a 3x3 tensor quantity such as $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ to be $n = 2$ and so forth. The second rank tensor $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ is therefore an ungerade quantity for the purpose of group theory in frames (X,Y,Z) and (x,y,z).

Whiffen has shown [13] that the elements of the non-vanishing c.c.f.'s exist for $t > 0$ if the totally symmetric representations [13,16] (A, A_g, or A_1, for example) of the molecular point group occur in the appropriate symmetry reduction. In frame (X,Y,Z) at field-free equilibrium the appropriate reduction [13] for order $n = 0$ to $n = 4$ is under R(3) rotation symmetry. [13,16] In the frame (x,y,z) the S,P,D,...... gerade (g) and ungerade (u) tensors further reduce according to the appropriate molecular point group. [13,16] The occurrences of the totally symmetric representation after these symmetry reductions provide the indication [13] of whether or not elements of c.c.f.'s may exist in either frame of reference for $t > 0$. If the group theory shows that they <u>may</u> exist, then computer simulation is then used to obtain the exact time dependence. The necessary tabular detail and further information on how to apply the group theory in these contexts is given in the paper by Whiffem. [13] Taking for example the c.c.f., 3x3, $n = 2$ tensor $\langle \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)\rangle$ this reduces as the sum $S_u + P_u + D_u$ in frame (X,Y,Z) where the suffix u denotes that it is an ungerade tensor, i.e. anti-symmetric to (X,Y,Z) inversion. For this reason the nine elements of the tensor vanish in (X,Y,Z) for all t. In frame (x,y,z) however, the individual tensors of the sum $S_u + P_u + D_u$ further reduce according to the molecular point group. For C_{2v} symmetry the reduction [13] is

$$S_u + P_u + D_u = 2A_1 + 3A_2 + 2(B_1 + B_2) \tag{1}$$

and the totally symmetric representation occurs twice in the sum on the right hand side, i.e. $2A_1$. This means that two different elements of $\langle \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)\rangle$ exist in frame (x,y,z), and these are available from the work of Evans [3,4] and (z,y) elements, which have <u>different</u> time dependencies. Examples are available in the literature for dichloromethane [3] and water [4]. For C_{3v} symmetric top symmetry the reduction in frame (x,y,z) is

$$S_u + P_u + D_u = A_1 + 2A_2 + 3E \tag{2}$$

producing only one occurrence of the totally symmetric representation (i.e. A_1) on the r.h.s. of (2). This result is confirmed by several computer simulations by Evans and co-workers [3] for example in liquid chloroform and t butyl chloride, which show the existence of $(y,z) = -(z,y)$ for $t > 0$ in frame (x,y,z). For C_{2h} symmetry the result is

$$S_u + P_u + D_u = 5A_u + 4B_u \tag{3}$$

and all elements vanish in frame (x,y,z) because there is no surviving totally symmetric representation. Similarly in T_d spherical top symmetry (e.g. carbon tetrachloride) the result is

$$S_u + P_u + D_u = A_2 + T_1 + T_2 + E \tag{4}$$

which is again confirmed in the simulations [5] of Evans and co-workers in spherical tops diffusing in the liquid state. Similar predictions can be made for all point groups.

SYMMETRY EFFECT OF AN ELECTRIC FIELD

If the electric field ($\underline{E}$) is applied to the liquid in the Z axis of frame (X,Y,Z) computer simulation for C_{2v} symmetry has shown [6,7] the existence of the (X,Y) and (Y,X) elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ for $t > 0$. This is explained by group theory on the grounds that an electric field breaks R(3) symmetry for linear electric field terms such as E_Z and allows P_u terms to have non zero components. The relevant P_u terms in this context are $\langle v_X(t)\omega_Y(o)\rangle$ and $\langle v_Y(t)\omega_X(o)\rangle$ whose time dependence from computer simulation is symmetric: [6,7]

$$\langle v_X(t)\omega_Y(o) = - \langle v_Y(t)\omega_X(o)\rangle \tag{5}$$

for all dipolar molecules. Electric field alignment takes effect through the torque between $\underline{E}$ and the molecular dipole moment, $\underline{\mu}$, and this is possible only for P_u elements which have non-zero ensemble averages in frame (x,y,z), the set of dipolar molecules. The number of P_u elements with the fully symmetric representation (A, A_g, or A_1) are 1, 0, 1, 1, and 0 respectively for C_2, C_{2h}, C_{2v}, C_{3v}, and T_d point group symmetry. There can be no P_u terms in frame (X,Y,Z) for non-dipolar mlecules, and only one such occurrence for dipolar molecules. Computer simulation shows this occurrence to be, for E_Z:

$$(X,Y) = - (Y,X) \tag{6}$$

in for example water [8] and dichloromethane. [6,7] The time dependence of the non-vanishing elements is symmetric in frame (X,Y,Z), and there is direct statistical correlation between $v_X(t)$ and $\omega_Y(o)$ for a diffusing dipole molecule for $E > 0$. Again the group theory and computer simulation are consistent.

For E^2, for which no simulations are available yet, the new elements span $S_g + D_g$. In a strong electric field, whose E^2 is important, there is therefore alignment due to E^2, as measured through the second order Langevin function (or Kielich function) [17] and represented by the D_g terms. However this alignment is not accompanied by the appearance of P_u elements or elements of any ungerade quantity such as $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$. The quadratic electric field does not therefore produce non-vanishing elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ in frame (X,Y,Z). This result may be used to provide an experimental method for determining the effect of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ on spectra in the frequency range up to the far infra red (THz).

The cubic terms in the electric field, which interact with the molecular hyperpolarisability, result in the appearance of $P_u + F_u$ terms in frame (X,Y,Z). The reduction of this sum according to point group symmetry [13,16] produces 4, 0, 3, 3, and 1 occurrence(s) respectively of the totally symmetric representation (A_1, A) for the point groups C_2, C_{2h}, C_{2v}, C_{3v} and T_d respectively. For C_{2v} symmetry, for example, this means that E^3 promotes the existence of the (X,Y) and (Y,X) elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$, which are symmetric; and also the existence of higher order c.c.f. elements of the third order tensor representation F_u, i.e. elements of the type $\langle v_X^3(t)\omega_Y^3(o)\rangle$ (Similarly E^2 produces elements of the type $\langle v_X^2(t)\omega_Y^2(o)\rangle$, but these already exist after treatment by E_Z. Upon treatment of C_{2v} molecules by E^3 the F_u elements in frame (X,Y,Z) reduce as $2A_1 + A_2 + 2B_1 + 2B_2$ and there are four elements of the type $\langle v_i^3(t)\omega_j^3(o)\rangle$ possible in frame (X,Y,Z), two symmetric pairs. For C_2 symmetry there are three symmetric pairs, for C_{2h} symmetry none, for C_{3v} symmetry two, and for T_d symmetry one. The interaction of molecular hyperpolarisability with E_Z^3 for T_d spherical tops this promotes the existence in frame (X,Y,Z) of elements such as $\langle v_i^3(t)\omega_j^3(o)\rangle$. Their time dependence by computer simulation is as yet unknown.

SYMMETRY EFFECT OF A MAGNETIC FIELD

The application of a magnetic field, $\underline{H}$, also breaks R(3) symmetry in a molecular liquid, but promotes the existence of P_g quantities rather than P_u quantities. This means that no elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ can exist in a molecular liquid at magnetic-field-on equilibrium. It is well known, however, that a magnetic field produces a Langevin function, first shown by Langevin himself in the first decade of this century. In liquid crystals the alignment of the nematic phase near room temperature by magnetic fields is well known, [18] and produces a large and easily measurable change in the dielectric loss and permittivity and far infra red power absorption. Similar nematic phase alignment is easily possible with electric fields. With electric field alignment, however, elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ must exist, and with magnetic field alignment they cannot by group symmetry considerations. Clearly this provides a straightforward experimental method of measuring directly the effect of such c.c.f. elements on spectra. The method is as follows.

1) Align a nematogen near room temperature with an electric field. Measure the refractive index parallel and perpendicular to the Z axis with an Abbé refractometer. [18] Take the dielectric and far infra red spectra (loss, dispersion, power absorption and frequency dependent refractive index).

2. In a separate experiment align the same nematogen with a magnetic field. Adjust the magnetic field strength to give the same refractive indices on the

Abbé refractometer, and remeasure the dielectric and far infra red spectra.
3) Comapre the spectral data. They should be different because the electric field data include the non-vanishing $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ elements and the magnetic data do not. The spectral differences reveal the effect of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ in frame (X,Y,Z) on the spectral bandshapes and time correlation functions [17] therefrom.

For H^2 the extra elements span $S_g + D_g$ as for the electric quadratic case. They appear from the interaction of H^2 with the molecular magnetisability tensor. Such terms as $\langle v_X^2(t)\omega_Y^2(o)\rangle$ are therefore produced by H^2.

For H^3 the extra elements span $P_g + F_g$ and no elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ are produced by H^3.

DISCUSSION

The above provides the first straightforward experimental method of measuring directly the effect of elements of $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ on spectra by a comparison of sepctral data in electrically and magnetically aligned room temperature nematogens. The application of group theory also removes the necessity of computer simulation in magnetically aligned liquid media in this context because, clearly, no elements of the tensor of interest $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ will exist. The details of why the tensor should exist with an electric field and vanish with a magnetic field need separate consideration. The Langevin alignment by a magnetic field results from the torque between the field and the magnetic dipole. For diamagnetic and paramagnetic molecules the nature of the torque is different, and different again for ferromagnetics. Additionally, if the molecule is seen as carrying effective net atomic partial charges, i.e. concentrations of electron density, there will be Lorentz forces set up by the magnetic field which act directly on the atomic linear velocities. The group theory predicts that only quantities of P_g symmetry can exist in a magnetic field $\underline{H}$ applied to an initially isotropic liquid. In this context this means ensemble averages of P_g symmetry. The laboratory frame ensemble average $\langle \underline{v}(t)\underline{\omega}^T(o)\rangle$ has P_u symmetry and therefore cannot exist in the magnetic field. For the same reason neither can it exist at field-off equilibrium, i.e. in the normally isotropic liquid or overall isotropic nematogen. Other liquid symmetries, such as the smectics and cholesterics, need special consideration. Therefore application of group theory applied to thermodynamic ensemble averages leads to considerable insight and removes the need for a difficult computer simulation of liquid crystals in a magnetic field. Note that computer simulation is needed to explain satisfactorily [3] the observed dielectric and far infra-red spectra of liquids, including electric field aligned nematogens.

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