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THE ELECTRIC FIELD EQUIVALENT OF THE FARADAY EFFECT: A COMPUTER SIMULATION.

by

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Abstract

First order electric field induced optical rotatory dispersion, the analogue of the Faraday effect, is investigated in liquid bromochlorofluoromethane with molecular dynamics computer simulation, using a time varying electric field to conserve reversality. Frequency dependent features are identified which are the spectral signatures of electric circular dichroism and birefringence. These results indicate clearly, and for the first time, that there exists, under the right conditions, an electric analogue of the Faraday effect, mediated by the molecular electric hyperpolarisability tensor.

Introduction

A simple, first order, analogue of the well known Faraday effect has never been observed with a static electric field. The reasons for this have been discussed by Barron, for example {1}, who has discounted by symmetry the possibility of first order electric circular dichroism (ECD) due to a static electric field. According to Barron, ECD violates reversality (T) both in chiral and achiral ensembles, and also violates parity (P) in achiral ensembles. In chiral ensembles, however, ECD would not violate P {2,3}. The symmetry objections {1} are removed completely in a chiral ensemble by using a time varying electric field $\dot{E}_Z(t)$, which is negative to T. (The time independent static magnetic field is also negative to T.) Thus, there is no argument based on P and T conservation which prohibits the existence of ECD in a chiral ensemble when the effect is mediated by $\dot{E}_Z(t)$.

Here, we report briefly on the first molecular dynamics computer simulation of such a phenomenon, and discuss the results in terms of time correlation functions of the chiral molecular ensemble (Fourier transforms of spectra, some of which are directly observable). The nature of the simulation confines discussion to the picosecond time window (far infra red frequency range), but the results indicate clearly that the effect is present at all appropriate electromagnetic frequencies, up to and including the visible, the usual frequency window for the Faraday effect.

2. The Interaction of $\dot{E}_Z(t)$ and Molecular Hyperpolarisability.

Electric circular dichroism is treated here through the standard Voigt/Born expansions of the molecular electric dipole moments (in tensor notation)

$$\mu_{iR} = \mu_{oi} + \left(\alpha_{1ij} \pm \alpha_{1ijz}\dot{E}_Z(t)\right)E_j^R + \ldots \quad - (1)$$

$$\mu_{iL} = \mu_{oi} + \left(\alpha_{1ij} \pm \alpha_{1ijz}\dot{E}_Z(t)\right)E_j^L + \ldots \quad - (2)$$

induced respectively by a right (R) and left (L) circularly polarised (c.p.) electromagnetic field propagating in Z. Here μ_{oi} is the permanent moment, α_{1ij} is the molecular electric polarisability, α_{1ijk} the electric hyperpolarisability, and E_j^R and E_j^L the electric field strengths of the right and left c.p. electromagnetic field. Note that the induced moments are linear in the electric field $\dot{E}_Z(t)$. The simulation method relies on the evaluation of the torque difference between left and right components

$$\Delta \underset{\sim}{Tq} = -\left(\underset{\sim}{\mu}_R \times \underset{\sim}{E}^R - \underset{\sim}{\mu}_L \times \underset{\sim}{E}^L\right) \quad - (3)$$

and specifically on the difference of torque differences

$$\Delta\Delta \underset{\sim}{Tq} = \left(\Delta \underset{\sim}{Tq}\right)_{\uparrow\uparrow} - \left(\Delta \underset{\sim}{Tq}\right)_{\uparrow\downarrow} \quad - (4)$$

with $\dot{E}_Z(t)$ parallel ($\uparrow\uparrow$) and antiparallel ($\uparrow\downarrow$) respectively with the propagation vector $\underset{\sim}{K}$ of the electromagnetic radiation. If $\dot{E}_Z(t)$ is parallel or antiparallel with $\underset{\sim}{K}$, the total molecular polarisability is respectively

$$\alpha_{1ij} \pm \alpha_{1ijZ}\dot{E}_Z(t).$$

With these definitions, we arrive after some calculation at the expression

$$\Delta\Delta \underset{\sim}{T_q} = 4E_0^2\dot{E}_Z(t)\left(\alpha'_{1XYZ} - 2\cos\omega t\sin\omega t\,\alpha''_{1XYZ}\right)\underset{\sim}{k} \quad -\ (5)$$

which is LINEAR in the time varying electric field $\dot{E}_Z(t)$ and quadratic in the electric field component E_0 of the electromagnetic field. Here $\underset{\sim}{k}$ is a unit vector in Z, ωt the phase of the electromagnetic field, α'_{1XYZ} the real and α''_{1XYZ} the imaginary part of the complex tensor component α_{1XYZ}. Finally these components are written in terms of the molecule fixed, (1,2,3), hyperpolarisabilities, as usually defined, through the tensor relation

$$[\alpha_{ik\ell}]_{(X,Y,Z)} = R_{ij}\,[\alpha_{jk\ell}]_{(1,2,3)} \quad -\ (6)$$

where R_{ij} is the rank two rotation matrix {4}. This gives

$$\alpha_{1XYZ} = e_{1X}\alpha_{1,123} + e_{1Y}\alpha_{1,223} \quad -\ (7)$$

where e_{1X}, e_{1Y} are laboratory frame components of the unit vector $\underset{\sim}{e}_1$ in axis 1 of the frame of the principal molecular moments of inertia, which is, to a good approximation, the axis of the permanent electric dipole moment.

It can be shown from the Maxwell equations {4,5} that the experimentally observable circular birefringence due to this difference of torque differences is

$$\langle n_L' - n_R'\rangle_{\uparrow\uparrow} - \langle n_L' - n_R'\rangle_{\uparrow\downarrow} = 4\mu_0 N c^2\dot{E}_Z(t)\langle\alpha''_{1XYZ}\rangle \quad -\ (8)$$

where μ_0 is the magnetic permeability, N the number of molecules per metre cubed, c the velocity of light. This is again linear in

$\dot{E}_Z(t)$, in analogy with the well known Faraday effect. The difference of torque differences (5) is coded in to the molecular dynamics program TETRA using a method first developed for static electric fields (8-10), and used extensively for different types of external field (11-15).

3. Molecular Dynamics Simulation Methods and Conditions.

In the apparent absence of ab initio and experimental data on the hyperpolarisability of (S) CHBrClF, and indeed chiral molecules in general, the relative magnitudes

$$\alpha'_{1,123} : \alpha'_{1,223} : \alpha''_{1,123} : \alpha''_{1,223} = 1:2:3:4 \quad -(9)$$

were used in order to illustrate the effect. The electric field was coded cosinusoidally at 60 kHz, with a time step of 0.05 ps (5.0×10^{-14} s) with a sample of 108 molecules at a molar volume corresponding to 293 K, 1.0 bar in the liquid state. Eqn. (8) shows that for an order of magnitude (16) of $\sim 10^{-50}$ for $\langle \alpha''_{1XYZ} \rangle$, an electric field strength of $\sim 10^{5}$ volts per metre is sufficent to induce an observable circular birefringence. For a dipole moment of $\mu_{0i} \doteq 10^{-28}$ C m this is about 6.0 kJ per mole. In order to see the effect clearly above the statistical noise of the simulation, this energy was raised to ~ 7.0 kJ per mole, this being the difference between the total energy of the ensemble with and without the applied electric field. Under these conditions, the orientational (C_2) and rotational velocity (C_1) time correlation functions of the ensemble were computed over two or more contiguous segments of up to 6,000 time steps each. These are defined respectively as

$$C_{2ij} = \langle \mu_i(t)\mu_j(0)\rangle / \langle \mu_i^2(0)\rangle^{1/2} \quad -(10)$$

and

$$C_{1ij} = \langle \dot{\mu}_i(t)\dot{\mu}_j(0)\rangle / \langle \dot{\mu}_i^2(0)\rangle^{1/2} \quad -(11)$$

The former is the Fourier transform of the dichroism in the dielectric spectrum, and the latter of the dichroism in the far infra red power absorption coefficient (17). The latter is now almost accessible experimentally with Fourier transform

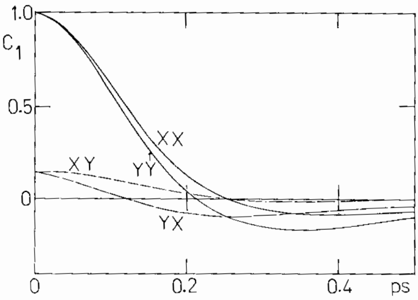

Figure (1)

Diagonal (auto) and two off-diagonal (cross) elements of the rotational velocity correlation function under the applied torque (5). The Fourier transform of the auto correlation function is the far infra red dichroism.

vibrational circular dichroism (18). The time cross correlation function (c.c.f.) between molecular linear and angular velocity (15-18) was also monitored in the simulation.

Simulations were carried out using parallel and sequential code on an I.B.M. 3090-6S processor of the Cornell National Supercomputer Facility in segments of up to 6,000 time steps. Some runs were also made on the IBM 6000 / 530 workstation.

4. Results and Discussion.

Figure (1) illustrates the far infra red circular dichroism due to the difference of torque differences in eqn (1) for an electric field energy of 7.0 kJ / mole in terms of its Fourier transform, $C_1(t)$. It is seen that the XX and YY components of the tensor $C_1(t)$ have become markedly anisotropic. Asymmetric cross correlation functions (XY and YX elements) also develop direct in frame (X, Y, Z) (Figure (1)). Electric field induced birefringence and dichroism is therefore accompanied by the appearance of asymmetric cross correlation functions and of anisotropy in the diagonal elements of the rotational velocity correlation function, which is the Fourier transform of the far infra red power absorption coefficient. In principle, this difference is observable with a modified Fourier transform spectrometer (17) with electrodes with central apertures to allow alternating left and right circularly polarised probe radiation from a piezzo-optic modulator (18 - 20) to pass through the chiral sample in the Z axis of the laboratory frame. The electrodes are used to apply the A.C. electric field.

The orientational autocorrelation function exhibits the same type of behaviour (Figure (2)). However, in this case the cross correlation functions (XY and YX elements of the tensor $C_2(t)$) are symmetric in time dependence.

This type of asymmetry is accompanied by interesting non-vanishing diagonal elements of the cross correlation tensor between the linear and angular velocities. These are much smaller in magnitude than the XY and YX c.c.f.'s in the orientational and rotational velocity correlation functions shown in Figs. (1) and (2), but nevertheless exist above the noise of the simulation. The ZZ element has a different time dependence from the XX and YY elements, which are approximately equal.

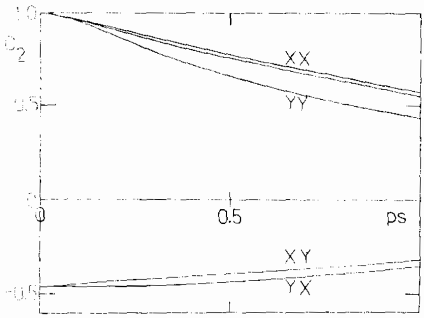

Figure (2)

As for Figure (1), orientational correlation functions

Elements of the rotational velocity correlation function

Conclusions

Using a time varying electric field applied to a chiral ensemble, the electric field equivalent of the Faraday effect has been observed for the first time, using a technique based on molecular dynamics computer simulation.

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