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ORIENTATIONAL ANISOTROPY IN THE OPTICAL STARK EFFECT: AN FMD COMPUTER SIMULATION

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ABSTRACT

Field applied molecular dynamics (FMD) computer simulation is used to investigate the optical Stark effect in a liquid ensemble of chiral molecules, using left and right circularly polarised laser radiation, interacting with each molecule through the appropriate torque. A novel orientational anisotropy develops under the influence of this torque, an anisotropy which indicates bi-axial birefringence. The latter is the same for right and left circularly polarised laser components, even when a contribution is included from the imaginary part of molecular polarisability. The torque used in the FMD simulation is independent of the phase of the laser implying that the orientational birefringence persists at all frequencies.

INTRODUCTION

The optical Stark effect is well known from gas phase quantum spectroscopy to cause a shift in absorption lines [1–4]. Much less is known experimentally and theoretically about the nature of the effect in the liquid state of matter, much less still in chiral ensembles. In this paper we find and report a novel orientational anisotropy which accompanies the optical Stark effect in chiral liquids at all frequencies of the pump laser, and which is the same for right and left circularly polarised laser components. The anisotropy has been found numerically, using a technique called “field applied molecular dynamics (FMD) computer simulation”. FMD was originated for static electric fields of arbitrary field strength (volts per metre), [5], and gradually extended [6–10] for use with electromagnetic fields applied through the appropriate field/molecule torque. Very recently [11–15] it has been extended for more realistic models of water and carbon disulphide by Robinson and co-workers, using improved simulation techniques. The same overall conclusions were

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reached by Evans and co-workers and Robinson and co-workers, that an arbitrarily strong external field markedly, sometimes profoundly, changes the nature of the molecular dynamics in a liquid or gaseous ensemble. The FMD technique has been extended, furthermore, to various nonlinear optical effects by Evans, Wozniak and Wagnière [16–28] in a series of papers. Among the effects studied so far are: (1) dynamic electric polarisation due to the antisymmetric conjugate product of a circularly polarised pump laser [16,17]; (2) the inverse Faraday effect [18–20], which is magnetisation by a circularly polarised laser; (3) the optical Kerr effect [21,22]; (4) the optical Stark effect with frequency doubled torque [23]; (5) optical NMR [24]; (6) bi-axial anisotropy due to the electric dipole/magnetic dipole property tensor [25,26]; (7) effect 6 accompanied by torque frequency doubling; (8) inverse magnetochiral birefringence [27,28]. In each of cases (1) to (8) the appropriate interaction between pump laser and ensemble was coded in through a torque generated between the appropriate molecular property and the electric and magnetic components of the electromagnetic plane wave. Some of these effects have been animated [29] for direct viewing, and have been studied in chiral and achiral ensembles. Good agreement with Langevin Kielich orientational functions has been found where the latter can be defined analytically, and FMD has revealed a variety of novel orientational effects which do not rely on instantaneous electronic polarisation. It will be of interest to extend FMD to nonlinear materials of technological importance, for example those in which the second hyperpolarisability is relatively pronounced in the solid state. This would help in the design of optical wave guide devices of the future. The next step in the development of FMD appears to be the incorporation of molecular flexibility and instantaneous electronic polarisation into the rigid site–site potentials of (1) to (8) above.

It has also been pointed out by Lakhtakia and co-workers [30] that the nature of the electromagnetic plane wave itself changes profoundly in bi-anisotropic media, and this is a region of electrodynamics which needs exploration with techniques based on contemporary FMD.

In this paper, FMD is used with a rigid site–site model of (S)-CHBrClF, a C_1 symmetry chiral molecule, to show the existence of a novel orientational anisotropy accompanying the optical Stark effect in liquid (and gaseous) chiral ensembles. Section 1 describes the torque used in the simulation; Section 2 summarises the FMD methods, and Section 3 is a summary of results and a discussion in the context of other nonlinear effects.

1. THE TORQUE BETWEEN MOLECULE AND PUMP LASER

The torque coded into the FMD algorithm is defined as

$$\boldsymbol{T} = \mu^{(\text{ind})} \times \boldsymbol{E}^* \tag{1}$$

where $\mu^{(\text{ind})}$ is an electric dipole moment induced in the molecule through

$$\mu_i^{(\text{ind})} = .{}^{e}\alpha_{ij}^{e} \boldsymbol{E}_j \tag{2}$$

Here ${}^{e}\alpha_{ij}^{e}$ is the complex molecular polarisability tensor and $\boldsymbol{E}_j$ is the electric field strength in volts per metre of an electromagnetic plane wave propagating in the molecular ensemble, in this case 108 (S)-CHBrClF molecules. Note that in eqn. (2), the standard tensor notation has been used, with summation over repeated indices. In eqn. (1) the standard vector cross product notation is more transparent. Here $\boldsymbol{E}^*$ denotes the complex conjugate of $\boldsymbol{E}$, so that the torque does not involve the phase of the laser, the latter having been removed in the conjugate product of electric field components. The torque of the optical Stark effect is therefore independent of the frequency of the pump laser for finite scalar amplitude of the electric field strength, and is finite after time averaging. At zero laser frequency the $\boldsymbol{E}$ component of the laser reduces to a simple, static, electric field, and the birefringence is still, therefore, independent of any electromagnetic frequency. It can therefore be used to construct Langevin Kielich functions [2,21,22] by standard thermodynamic averaging. The electric component of the laser is assumed to have the following characteristics as it propagates through the ensemble

$$\boldsymbol{E}_L = \boldsymbol{E}_0(\boldsymbol{i} - i\boldsymbol{j})e^{i\phi_L}; \tag{3a}$$

$$\boldsymbol{E}_R = \boldsymbol{E}_0\,(\boldsymbol{i} + i\boldsymbol{j})e^{i\phi_R} \tag{3b}$$

Here $\boldsymbol{E}_0$ is a scalar amplitude in volts per metre, $\boldsymbol{i}$ and $\boldsymbol{j}$ are unit vectors in axes X and Y respectively, ϕ_L and ϕ_R are the phases of left (L) and right (R) circularly polarised components. The laser is propagating, therefore, in axis Z of the laboratory frame (X, Y, Z). We note in passing that other representations [30] of the plane wave may be used in FMD simulation, provided a torque can be defined between laser and molecule. We have left out of consideration entirely details of the internal field, instantaneous polarisation, and molecular flexibility, issues which have begun to be tackled by Robinson and co-workers [11–15] in liquid water and carbon disulphide. It would be interesting to incorporate these effects in future FMD simulations in nonlinear optics.

The first step in constructing the molecule/field torque is to transform the electric field to a frame (1, 2, 3) fixed in each molecule. Each molecule's (1, 2, 3) is oriented differently in general with respect to (X, Y, Z), so the frame transformation is done for all 108 molecules. We define (1, 2, 3) conveniently as that of the principal molecular moments of inertia, and assume that the frame is also that of the principal molecular polarisability components. In a low symmetry C_1 molecule such as (S)-CHBrClF this is an approximation in general, but one which does not reduce the generality of our conclusion. Defining unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$ in the axes 1, 2, and 3 respectively the frame transformation proceeds through a rotation matrix

$$\begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} = \begin{bmatrix} e_{1X}\, e_{1Y}\, e_{1Z} \\ e_{2X}\, e_{2Y}\, e_{2Z} \\ e_{3X}\, e_{3Y}\, e_{3Z} \end{bmatrix} \begin{bmatrix} E_X \\ E_Y \\ E_Z \end{bmatrix} \tag{4}$$

giving

$$\begin{aligned} E_{1L} &= E_0(e_{1X} - ie_{1Y})\,\exp(i\phi_L) \\ E_{2L} &= E_0(e_{2X} - ie_{2Y})\,\exp(i\phi_L) \\ E_{3L} &= E_0(e_{3X} - ie_{3Y})\,\exp(i\phi_L) \end{aligned} \tag{5}$$

for a left circularly polarised laser and

$$\begin{aligned} E_{1R} &= E_0(e_{1X} + ie_{1Y})\,\exp(i\phi_R) \\ E_{2R} &= E_0(e_{2X} + ie_{2Y})\,\exp(i\phi_R) \\ E_{3R} &= E_0(e_{3X} + ie_{3Y})\,\exp(i\phi_R) \end{aligned} \tag{6}$$

for a right circularly polarised laser. A linearly polarised laser is made up of equal parts of left and right. In general the field/molecule torque of the optical Stark effect therefore depends on the polarisation of the pump laser.

The second step is to work out the induced electric dipole moment in frame (1, 2, 3), which in general is

$$\begin{bmatrix} \mu_1^{(\mathrm{ind})} \\ \mu_2^{(\mathrm{ind})} \\ \mu_3^{(\mathrm{ind})} \end{bmatrix} = \begin{bmatrix} .^{e}\alpha^{e}_{11} & .^{e}\alpha^{e}_{12} & .^{e}\alpha^{e}_{13} \\ .^{e}\alpha^{e}_{21} & .^{e}\alpha^{e}_{22} & .^{e}\alpha^{e}_{23} \\ .^{e}\alpha^{e}_{31} & .^{e}\alpha^{e}_{32} & .^{e}\alpha^{e}_{33} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{7}$$

where the alpha components are complex. From semi-classical theory [31] each has a real and imaginary part. The real part is positive to motion reversal T and to parity inversion P, and the imaginary part is negative to T and positive to P. Furthermore, the real part is symmetric in its indices, and the imaginary part is antisymmetric. For any second rank symmetric cartesian tensor [31] it is always possible to choose a set of axes, which we label (1, 2, 3), called the principal axes, such that only the diagonal components are non-zero. This implies that in (1, 2, 3), there are only three components of the real part of the polarisability, components which are denoted α_{11}', α_{22}', and α_{33}'. In (1, 2, 3), furthermore, the diagonal components of the imaginary part of the molecular polarisability must vanish, because this cartesian tensor is antisymmetric in its indices. The off diagonal components are non-zero and denoted by

$$\begin{aligned} \alpha_{12}'' &= -\alpha_{21}''; \\ \alpha_{23}'' &= -\alpha_{32}''; \\ \alpha_{13}'' &= -\alpha_{31}''. \end{aligned} \tag{8}$$

With these considerations of fundamental semiclassical theory [31] we arrive at the following expressions for the torque components in frame (1, 2, 3)

$$\begin{aligned} Real(T_{1L_R}) &= (e_{2X}e_{3X} + e_{2Y}e_{3Y})\,(.^{e}\alpha^{e}_{22}{}' - .^{e}\alpha^{e}_{33}{}')E_0^2 \\ &\pm\left[.^{e}\alpha^{e}_{31}{}''(e_{1X}e_{2Y} - e_{1Y}e_{2X}) - .^{e}\alpha^{e}_{21}{}''(e_{1X}e_{3Y} - e_{1Y}e_{3X})\right]E_0^2 \\ Real(T_{2L_R}) &= (e_{3X}e_{1X} + e_{3Y}e_{1Y})\,(.^{e}\alpha^{e}_{33}{}' - .^{e}\alpha^{e}_{11}{}')E_0^2 \\ &\pm\left[.^{e}\alpha^{e}_{12}{}''(e_{2X}e_{3Y} - e_{2Y}e_{3X}) - .^{e}\alpha^{e}_{32}{}''(e_{2X}e_{1Y} - e_{2Y}e_{1X})\right]E_0^2 \\ Real(T_{3L_R}) &= (e_{1X}e_{2X} + e_{1Y}e_{2Y})\,(.^{e}\alpha^{e}_{11}{}' - .^{e}\alpha^{e}_{22}{}')E_0^2 \\ &\pm\left[.^{e}\alpha^{e}_{23}{}''(e_{3X}e_{1Y} - e_{3Y}e_{1X}) - .^{e}\alpha^{e}_{13}{}''(e_{3X}e_{2Y} - e_{3Y}e_{2X})\right]E_0^2 \end{aligned} \tag{9}$$

We note that the parts involving the imaginary (T negative) polarisability components change sign between right and left circular polarisation of the pump laser. The parts involving real polarisability components vanish if there is no anisotropy of polarisability, i.e. if the diagonal components are all equal, as in high symmetry molecules and atoms. The optical Stark effect in this case must therefore rely on imaginary components of the polarisability. However, the latter are T negative, and vanish if there is no net electronic angular momentum. In diamagnetic molecules, therefore, only the real part of the polarisability can contribute to the optical Stark effect as described in eqns. (9), because there is no net electronic angular momentum. In high symmetry diamagnetic molecules, therefore, there is no optical Stark effect of this type if the molecule does not possess some other source of net electronic angular momentum. In atoms with net electronic angular momentum there is always a contribution from the imaginary components in eqn. (9).

For the molecule under consideration, (S)-CHBrClF, the contribution in (9) from imaginary components vanishes if there is no net electronic angular momentum. However, this "paramagnetic" contribution may be present if in a quantum state of (S)-CHBrClF there happens to be some source of net electronic angular momentum. To maximise generality we have assumed for the sake of demonstration by FMD that the imaginary, as well as real, parts of the polarisability are non-zero. In the apparent absence of data on the scalar components of electronic electric polarisability in the test molecule, we have simply chosen

$$.^{e}\alpha^{e}_{11} : .^{e}\alpha^{e}_{22}{}' : .^{e}\alpha^{e}_{33}{}' = 1 : 2 : 3;$$

$$(.^{e}\alpha^{e}_{12}{}'' = -\, .^{e}\alpha^{e}_{21}{}'') : (.^{e}\alpha^{e}_{13}{}'' = -\, .^{e}\alpha^{e}_{31}{}'') : (.^{e}\alpha^{e}_{23}{}'' = -\, .^{e}\alpha^{e}_{32}{}'') = 7 : 8 : 9$$

This is an extremum where the paramagnetic terms dominate the diamagnetic terms. We have checked that changing these numbers does not affect our overall conclusions given later in this paper.

The final step is to back-transform the torque into the laboratory frame using the inverse rotation matrix

$$\begin{bmatrix} T_X \\ T_Y \\ T_Z \end{bmatrix} = \begin{bmatrix} e_{1X} & e_{2X} & e_{3X} \\ e_{1Y} & e_{2Y} & e_{3Y} \\ e_{1Z} & e_{2Z} & e_{3Z} \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \end{bmatrix} \tag{10}$$

Note that we have assumed that the torque is a purely real quantity. It appears to be unphysical to assume that the torque has an imaginary component, but this is mathematically possible. Similarly, it appears to be unphysical to assume that the interaction energy is anything but a real scalar (in the absence of parity non-conservation, a small P negative effect that does not concern us here).

2. BRIEF SUMMARY OF FMD METHODS

The torque (10) is coded into the FMD program at the point in the forces loop where the intermolecular torques are worked out from atom–atom forces [32]. The external torque between field and molecule supplements the internal torque and this gradually affects the trajectories and dynamical properties of each molecule in the ensemble. This process occurs over a rise transient interval [16–28]. The rise transient eventually saturates, i.e. reaches a plateau. In this condition, the field-on steady state, time correlation functions of many different varieties can be computed by running time averaging, because the field-on state is statistically stationary [33]. For this work we evaluated second order orientational rise transients defined by averages at each time step of the type

$$\langle e_{1X}^2\rangle, \langle e_{1Y}^2\rangle, \langle e_{1Z}^2\rangle, \ldots, \langle e_{3X}^2\rangle, \langle e_{3Y}^2\rangle, \langle e_{3Z}^2\rangle \tag{11}$$

Correlation functions of three different types were evaluated at field-on equilibrium

$$C_{1ij}^{(t)} = \frac{\langle e_{1i}(t)\, e_{1j}(o)\rangle}{\langle e_{1i}^2\rangle^{1/2}\langle e_{1j}^2\rangle^{1/2}} \tag{12}$$

$$C_{2ij}^{(t)} = \frac{\langle J_i(t)\, J_j(o)\rangle}{\langle J_i^2\rangle^{1/2}\langle J_j^2\rangle^{1/2}} \tag{13}$$

and

$$C_{3ij}^{(t)} = \frac{\langle \dot{e}_{1i}(t)\, \dot{e}_{1j}(o)\rangle}{\langle \dot{e}_{1i}^2\rangle^{1/2}\langle \dot{e}_{1j}^2\rangle^{1/2}} \tag{14}$$

Here all quantities are defined in the laboratory frame and $\langle\ \rangle$ denote running time averaging [33]. The vectors used were $\mathbf{J}$, $\boldsymbol{e}_1$, and $\dot{\boldsymbol{e}}_1$, where

$\mathbf{J}$ is the net molecular angular momentum and $\dot{\boldsymbol{e}}_1$, the rotational velocity [34], signifies the time derivative of $\boldsymbol{e}_1$. In these expressions i and j denote cartesian components in (X, Y, Z), so when $i = j = X$, for example, we are constructing the X component of the time autocorrelation function. For rise transients, $\boldsymbol{e}_{1X}$ for example denotes the X component of $\boldsymbol{e}_1$ with respect to the laboratory frame.

Rise transients were evaluated over 2,000 time steps of 5.0 fs each, and correlation functions over 6,000 time steps.

Further details of the FMD technique have been given elsewhere in the recent literature [16–28], including full details of temperature rescaling and intermolecular potential. The complete FORTRAN code is published in ref. [32]. Essentially, the temperature rescaling routine allows the temperature to fluctuate freely for N time steps, and when this is value of N is exceeded resets the translational and rotational kinetic energies of each molecule to the input value. N can vary from 1 to 50, and the effect of doing so on rise transients has been demonstrated in detail in ref. [27]. The temperature rescaling routine was shown in that reference to have no effect on the final value attained by the rise transient, a value which is used to construct the Langevin Kielich function by computer simulation.

3. RESULTS AND DISCUSSION

We present results which provide numerical evidence for orientational anisotropy accompanying the optical Stark effect, an anisotropy which implies that the refractive index and power absorption coefficient of the ensemble become measurably different in the propagation and orthogonal axes through this whole (i.e. rigid) molecule mechanism of reorientation. Figure 1 illustrates the development of orientational anisotropy through the second order rise transients, whose initial value in the isotropic (laser-free) ensemble is 1/3 for all components. The final values in this figure clearly differ from 1/3 at the respective plateau levels that signify rise transient saturation. Furthermore, within the noise of the simulation, the final levels are identical for right and left circular polarisation of the pump laser, despite the fact that the paramagnetic part of the torque changes sign when the laser is switched from right to left.

This result is corroborated in the laser-on steady state by the computation of the X, Y, and Z components of autocorrelation functions (12) to (14), illustrated respectively in Figs. 2–4. The anisotropy in the orientational autocorrelation function is the greatest in this particular set of results. In all figures there is no difference within the noise between right

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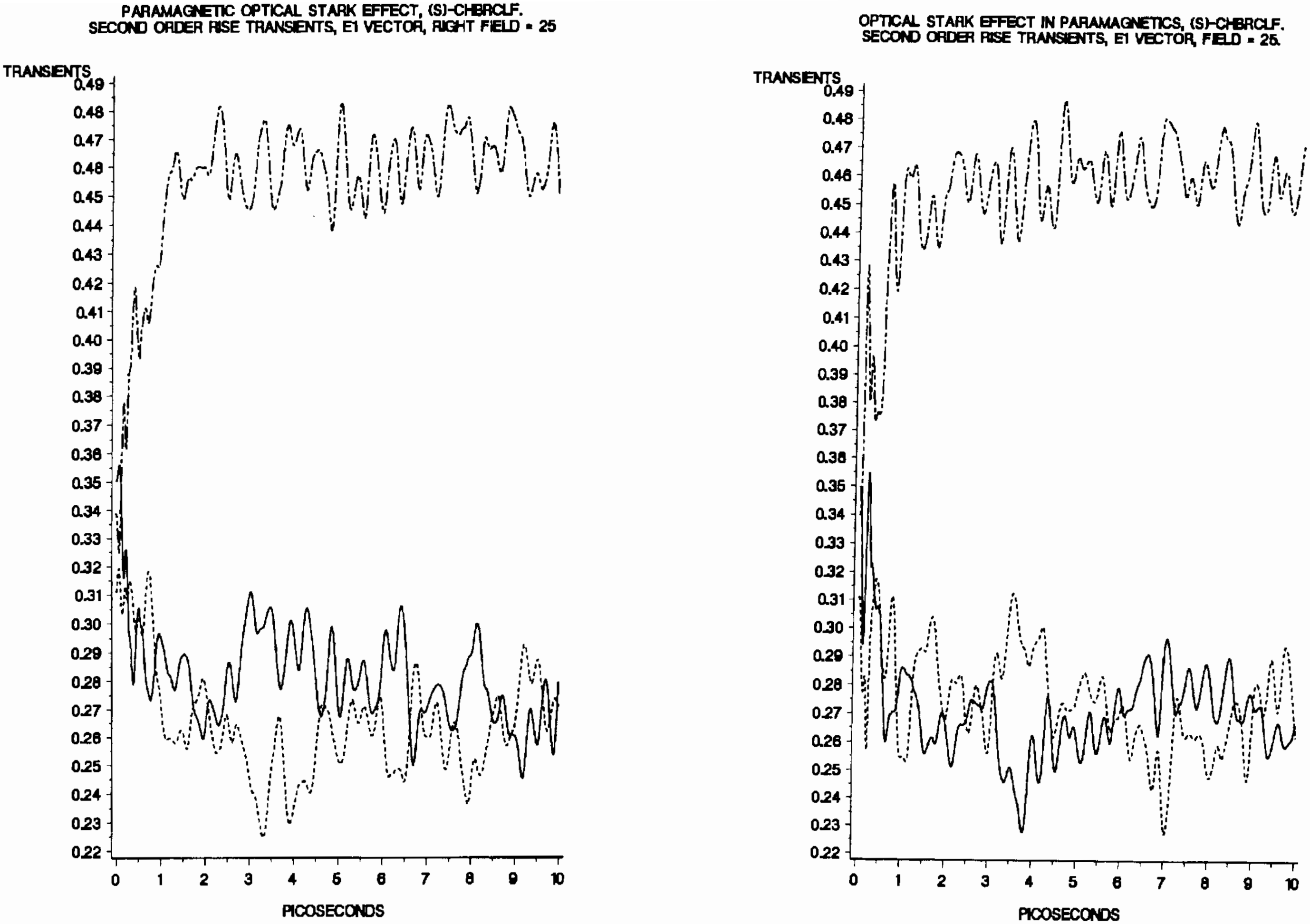


Fig. 1. Second order rise transients, exemplified by $\langle e_{1i}^2 \rangle$ with _____ $i = X$, ----- $i = Y$, _ .. _ .. $i = Z$. (a) Left, (b) right pump laser circular polarisation.

and left laser components.

It is well known that the orientational autocorrelation function is related through a Fourier transform to the complex dielectric permittivity, which is the complex refractive index squared. Figure 2 therefore implies the existence of *orientational birefringence* accompanying the optical Stark effect, a birefringence which is independent of the phase of the pump laser and therefore of its frequency. Figures 3 and 4 for the angular momentum and rotational velocity autocorrelation functions, corroborate this result. The Fourier transform of the rotational velocity autocorrelation function is related [33] to the far infra red power absorption coefficient, another experimental observable. The optical Stark effect therefore produces a far infra red power absorption coefficient which is different in the propagation and orthogonal axes of the pump laser.

Experimentally this type of birefringence must be isolated from other types of nonlinear phenomena [1–4]. It is characterised by the following:

(1) The birefringence is independent of the circular polarisation of the pump laser and of the laser frequency, and is proportional to the square of the electric field strength of the laser in volts per metre, i.e. is proportional to the laser intensity in watts per square metre.

(2) In diamagnetic molecules with no anisotropy of polarisability there is no birefringence because the torque vanishes.

(3) In molecules with no net electronic angular momentum the effect depends on the anisotropy of the real electronic electric polarisability.

(4) In atoms with net electronic angular momentum the effect depends entirely on the imaginary part of the electronic polarisability.

(5) It is accompanied by the development of a Langevin Kielich function, because the torque is independent of the laser frequency and survives time and ensemble averaging [16–28].

(6) The effect is orientational in nature, involving whole molecule reorientation, and does not depend on instantaneous electronic polarisation [11–15], which is not coded into the program in this work.

These characteristics should be enough to isolate the effect experimentally. A suggested method is to use a pump laser pulse to produce the birefringence, which is measured by an unpolarised probe laser directed parallel and perpendicular to the pump laser. The probe measures the refractive index of the ensemble induced by the pump and this should be different in the two orthogonal measurement directions and satisfy criteria one to five. Another suggestion is to use a Fourier transform interferometer with a Rollin or similar helium cooled detector [33] fast enough to record a far infra red spectrum as the pump pulse or pulse train passes through the sample. The spectrum should be different in Z and

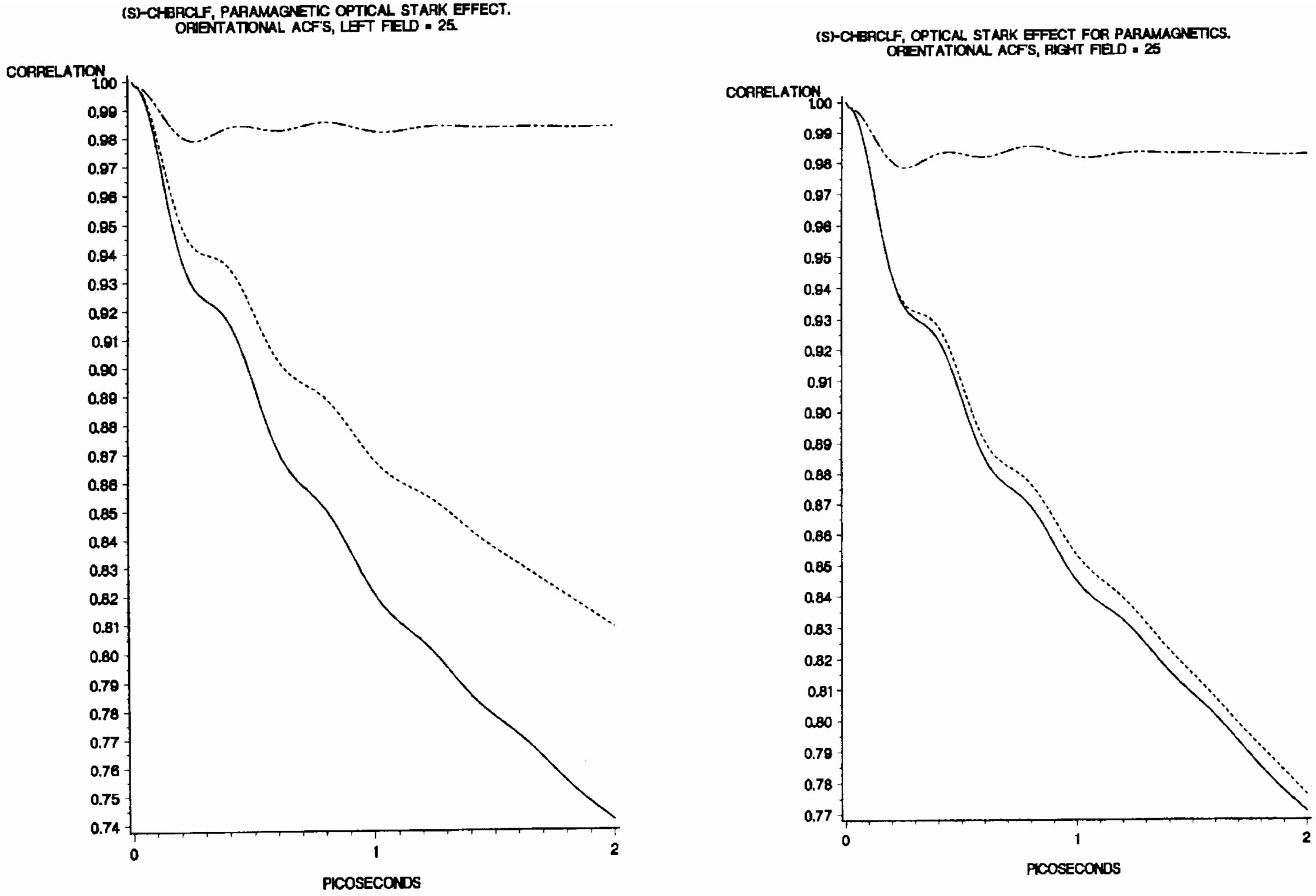
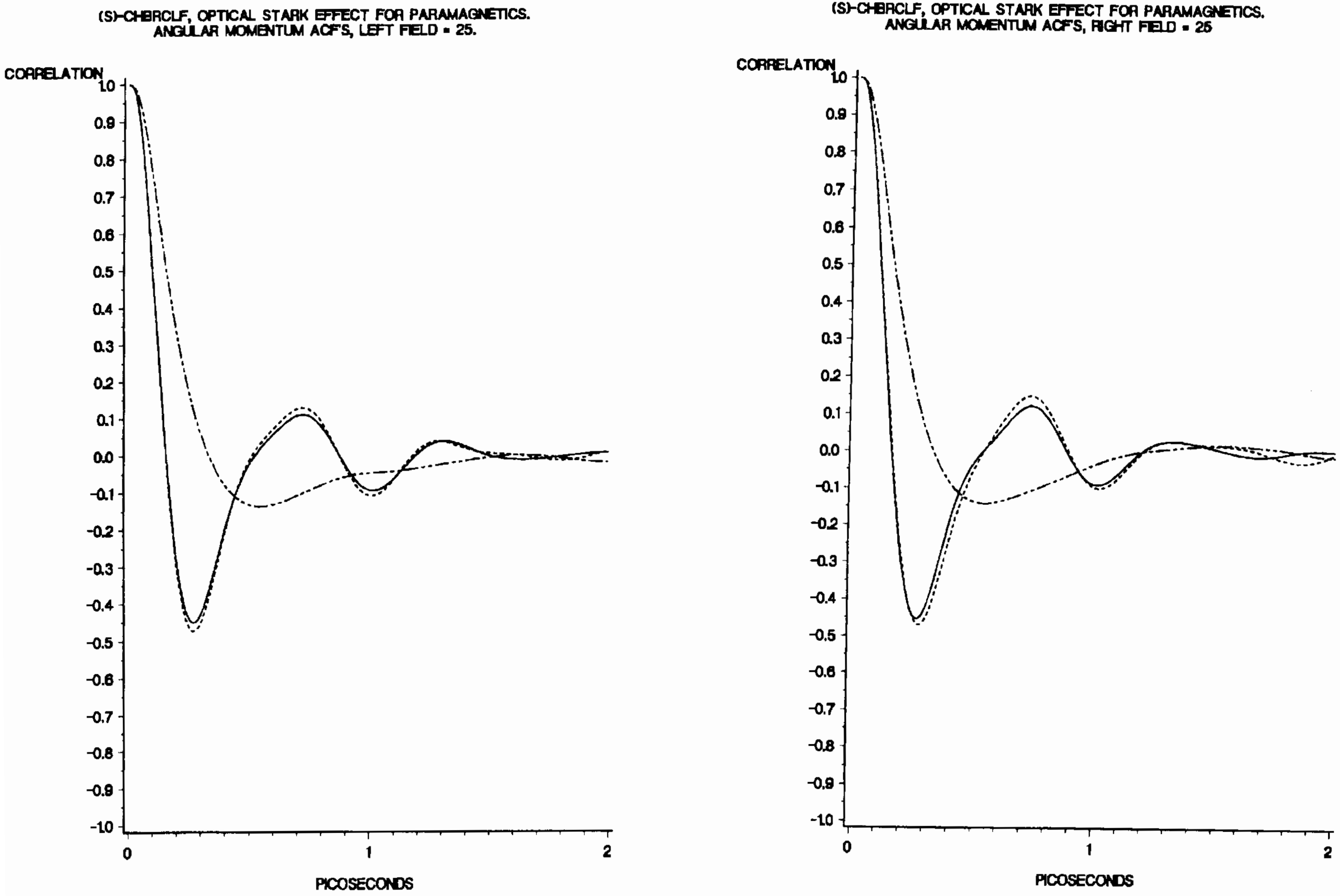


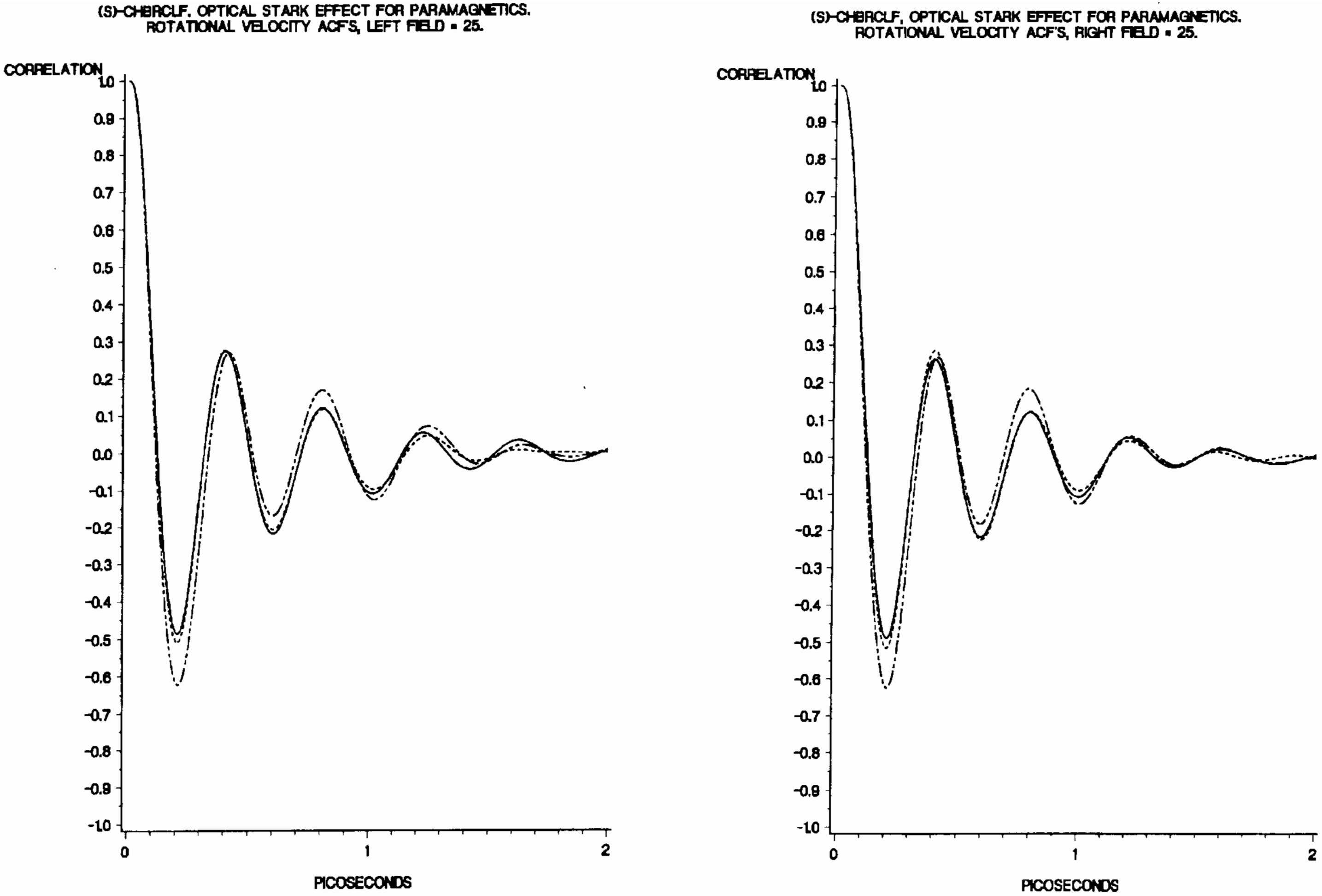
Fig. 2. Orientational autocorrelation functions (eqn. (12)), with _____ $i = j = X$, ----- $i = j = Y$, _ .. _ .. $i = j = Z$. (a) Left, (b) right pump laser circular polarisation.



(S)-CHBRCLF, OPTICAL STARK EFFECT FOR PARAMAGNETICS.
ANGULAR MOMENTUM ACFS, LEFT FIELD = 25.

(S)-CHBRCLF, OPTICAL STARK EFFECT FOR PARAMAGNETICS.
ANGULAR MOMENTUM ACFS, RIGHT FIELD = 25

Fig. 3. As for Fig. 2, angular momentum autocorrelation functions (13).


(S)-CHBRCLF. OPTICAL STARK EFFECT FOR PARAMAGNETICS. ROTATIONAL VELOCITY ACF'S, LEFT FIELD = 25.

(S)-CHBRCLF, OPTICAL STARK EFFECT FOR PARAMAGNETICS. ROTATIONAL VELOCITY ACF'S, RIGHT FIELD = 25.

Fig. 4. As for Fig. 2, rotational velocity autocorrelation functions (14).

orthogonal axes, but should show no difference if the circular polarisation of the pump is switched from left to right.

The effect found and reported here has several characteristics which distinguish it from others reported recently with FMD of rigid molecules [16–28], for example effect six of the introduction to this paper and the optical Kerr effect [21,22]. Effect six, which is orientational anisotropy caused by the Rosenfeld tensor (electric dipole/magnetic dipole molecular property tensor) is different by FMD for right and left circular polarisation [25,26] and is proportional to the electric field strength multiplied by the magnetic flux density of the pump laser. It is therefore a much smaller effect which is different for circular and linear polarisation of the pump laser. The effect in this paper is the same for right, left, and linear polarisations of the pump laser. Effect six exists in achiral molecules only when their point group symmetry sustains the appropriate [25,26] off-diagonal elements of the Rosenfeld tensor. It is easily distinguishable therefore from the effect reported here.

Similarly the optical Kerr effect depends on a different torque, due to the instantaneous modification of the charge distribution in the molecule through the hyperpolarisability, and is measured experimentally [34] by the rotation of the plane of polarisation of a linearly polarised probe. The probe for the effect of this paper need not be polarised and need not be directed in the same axis as that of the pump laser.

4. SOLVING THE MAXWELL EQUATIONS FOR THE NEW STARK BIREFRINGENCE

In this section the Maxwell equations are solved approximately for the bi-axial birefringence induced by the torque (eqn. (1)). The electric polarisation P

$$P_i = N\,\alpha_{ij}\,E_j \tag{15}$$

where N is the number of molecules per unit volume in the sample, is used in the Maxwell equation

$$\frac{1}{\mu_0}\nabla\times\boldsymbol{B} = \varepsilon_0\frac{\mathrm{d}\boldsymbol{E}}{\mathrm{d}t} + \frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} \tag{16}$$

to provide a very simple first approximation to the refractive index change in the propagation direction of the laser. In equation (16) ε_0 is the permittivity *in vacuo* and μ_0 is the permeability *in vacuo*. It is straightforward to show from eqn. (16) that

$$n_{\mathrm{avZ}} \approx 1 + \frac{N\alpha_0'}{\varepsilon_0} \equiv 1 + \frac{1}{3}\frac{N\alpha_{\mathrm{XX}}'}{\varepsilon_0} \tag{17}$$

Here, n_{avZ} is the refractive index of the sample in the Z axis, a quantity which can be measured with an unpolarised probe. Equation (17) shows that the refractive index changes by an amount ($\varepsilon_0 = 8.854\times10^{-12}$ J^{-1} C^2 m^{-1}):

$$n_{\mathrm{avZ}} - 1 \approx \frac{N\alpha_0'}{\varepsilon_0} \tag{18}$$

which in this approximation is independent of the intensity of the laser, and is determined by the trace of the polarisability tensor multiplied by the number of molecules per unit volume, N.

More realistically, the polarisation P used in eqn. (15) depends on a Langevin Kielich function, i.e. upon a thermodynamic average involving the energy $\alpha_0' E_0^2$. The Langevin Kielich function can be expanded for $\alpha_0' E_0^2 << kT$ by [2]:

$$L(q) \equiv L\left(\frac{\alpha_0' E_0^2}{kT}\right) = \frac{1}{3} \pm \frac{4q}{45} + \frac{8q^2}{945} \pm \frac{16q^3}{14175} + \ \ldots \tag{19}$$

so that incorporating it into the Maxwell equation (16) produces finally the result

$$n_{\mathrm{avZ}} - 1 \approx \frac{N\alpha'_{\mathrm{XX}}}{\varepsilon_0} - L(q) \tag{20}$$

which shows that the refractive index change is dependent, in this better approximation, on the energy ratio

$$q = \frac{\alpha_0' E_0^2}{kT} \tag{21}$$

Using the relation

$$I_0 = \frac{1}{2}\,\varepsilon_0\, C\, E_0^2 \tag{22}$$

between laser intensity, I_0, in watts per unit area, and E_0, gives an expression for the refractive index in terms of I_0. For an intensity I_0 of 100 watts per square centimetre, for a polarisability trace of about 10^{-40} $C^2\,m^2\,J^{-1}$; and for N of the order 10^{26} (Avogadro number per m^3) we obtain a refractive index change of about 0.001 easily measurable by a probe. This is a rough analytical estimate of the indications obtained by computer simulation earlier in this paper.

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