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Computer simulation of the optical Kerr effect in liquid water

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A field applied molecular dynamics (FMD) computer simulation of the optical Kerr effect in liquid water has produced femtosecond rise transients which reproduce accurately the available analytical theory, based on generalised Langevin–Kielich functions. The transients and associated field applied correlation functions prove to be sensitive to the anisotropy of polarisability in water, showing that femtosecond transient spectroscopy is potentially a much more accurate method of measurement than hitherto available.

1. Introduction

We report the first computer simulation of the optical Kerr effect, using field applied molecular dynamics (FMD). FMD is a simple variation on standard molecular dynamics computer simulation in which the torque generated between the molecules of an ensemble and an external field is coded into the forces loop. FMD provides rise and fall transients, thermodynamic and structural data, and field-on or field-free statistical mechanical data, for example time correlation functions of many different kinds [1], some of which are Fourier transforms of directly observable spectra. FMD was devised originally for strong electric fields, and accurately reproduced known Langevin–Kielich functions [2–4] from the final levels of rise transients. Additionally, it gave details of the time resolution of the transients themselves on the femto/pico-second scale, information which is now becoming directly accessible experimentally [5] in the transient optical Kerr effect. FMD also gives a wealth of information from the same trajectories on the dynamics of the laser applied steady state in the optical Kerr effect, on fall transients [6–8], and on pair distribution functions [9]. The method was later extended for use with circularly polarised laser fields [10,11], and for non-linear optical phenomena where in general [12–14], a laser field or field gradient forms a torque with an induced electric or magnetic dipole or multipole. FMD also revealed basic statistical mechanical laws such as fall transient acceleration [15], field decoupling [15], and rise transient oscillations on the femtosecond scale [16,17]; its generality springing from the fact that the integral of the torque with respect to orientation is potential energy, a term which is added to the Hamiltonian as the starting point of analytical theory. The interaction of any type of field and any type of ensemble is therefore described at a fundamental level, as in semi-classical theory [18], but FMD provides additionally much more information from the *same* set of molecular trajectories.

The particular type of torque relevant to the optical Kerr effect is described in section 2. The essentials of FMD in this context are recounted briefly in section 3, followed in section 4 by a description of rise transients and a comparison with generalised Langevin–Kielich functions. The latter from both simulation and theory are shown in two cases to *change sign* with anisotropy of polarisability, thus providing a potentially accurate method of measurement of this quantity in water from the transient optical Kerr effect [5]. Detailed agreement

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is demonstrated between simulation and theory concerning this useful change of sign and other transient properties of the optical Kerr effect.

2. Torque of the optical Kerr effect

It is well known that the optical Kerr effect is observed [19,20] through the rotation of the plane of polarisation of a probe laser in response to a pulse from a pump laser. We consider a probe polarised linearly along the X axis of the laboratory frame (X, Y, Z). The pump pulse can be shown to set up the torque

$$T_1 = e_{2X}e_{3X}(\alpha_{33}-\alpha_{22})E_0^2\,, \qquad T_2 = e_{1X}e_{3X}(\alpha_{11}-\alpha_{33})E_0^2\,, \qquad T_3 = e_{1X}e_{2X}(\alpha_{22}-\alpha_{11})E_0^2 \tag{1}$$

in the frame (1,2,3) of the molecular principal moments of inertia of the water molecule. Here, axis 1 is the dipole, or C_{2v} axis, axis 2 is perpendicular to the molecular plane, and axis 3 is mutually perpendicular in a right handed set. In eq. (1), E_0^2 is the square of the scalar electric field strength amplitude (volts/metre) of the pump laser, and the quantities e_{1X}, e_{2X} and e_{3X} are X components of unit vectors in axes 1,2 and 3. It is assumed that the polarisability is diagonalised in the same frame (1,2,3), giving the diagonal components α_{11}, α_{22}, and α_{33} of the molecular polarisability of water. It is convenient in this context to define the two anisotropies of polarisability of the asymmetric top water molecule,

$$\gamma = \alpha_{11} - \tfrac{1}{2}(\alpha_{22}+\alpha_{33})\,, \tag{2}$$

$$\delta = \tfrac{1}{2}(\alpha_{22}-\alpha_{33})\,. \tag{3}$$

The torque components (1) are coded into the forces loop of any MD algorithm, and back transformed [12] into the laboratory frame (X, Y, Z) using a rotation matrix.

3. FMD method

The FMD method was implemented with a sample of 108 water molecules interacting through a modified ST2 potential using Lennard-Jones and partial charge interactions,

$$\text{(H–H):} \qquad \epsilon/k = 21.1\ \text{K}\,, \quad \sigma = 2.25\ \text{Å}\,,$$

$$\text{(O–O):} \qquad \epsilon/k = 58.4\ \text{K}\,, \quad \sigma = 2.80\ \text{Å}\,,$$

$$q_{\text{H}} = 0.23|e|\,, \qquad q(\text{lone pair}) = -0.23|e|\,, \qquad q_{\text{O}} = 0.00|e|\,. \tag{4}$$

This potential has been compared in the literature [21] with the ab initio MCYL, and with experimental data [22] over a very wide range of conditions. We stress that FMD can be used with any type of model or ab initio water potential, and any type of MD algorithm. With a time step of 0.5 fs, transients were evaluated for different E_0^2, over a number of time steps sufficient for attainment of the final level, which was measured and used to construct generalised Langevin–Kielich functions (section 4) by FMD. The latter were also evaluated analytically [23–25]. The transient generating stage was followed by FMD evaluation of statistical dynamical properties in the pump laser applied steady state, using running time averaging over a minimum of 6000 steps. A data band of many different examples was collected and used to characterise the field-on dynamics.

Simulations were carried out at 296 K, 1.0 bar in the liquid state of water.

4. Rise transients and anisotropy of polarisability

There have been numerous reports [26–32] of the anisotropy function γ of water. Khanarian and Kent [26] have made a tabular comparison of experimental and ab initio estimates from various sources, six of whose entries were positive, and four negative. In this section we use three literature estimates of the diagonalised polarisability components of water, and compare for each case generalised Langevin–Kielich functions and time resolved rise transients from FMD and the available theory. These are given in table 1. We note that the experimental data in table 1 give a negative anisotropy γ [26], and a conflicting positive anisotropy γ [27]. We also use one ab initio result [28].

For each of these three data sets transients and generalised Langevin–Kielich functions (GLKs) were simulated for $\langle e_{1X}^n \rangle$, $\langle e_{2X}^n \rangle$, and $\langle e_{3X}^n \rangle$, where $n=2,4,6$. GLKs were also evaluated analytically from [23–25]

$$\langle e_{1X}^n \rangle = \frac{\int_0^\pi \cos^n\theta \exp(q\cos^2\theta) \int_0^{2\pi} \exp[h\cos 2\phi\ (\cos^2\theta - 1)]\,\mathrm{d}\phi \sin\theta\,\mathrm{d}\theta}{\int_0^\pi \exp(q\cos^2\theta) \int_0^{2\pi} \exp[h\cos 2\phi\ (\cos^2\theta - 1)]\,\mathrm{d}\phi \sin\theta\,\mathrm{d}\theta}, \tag{5}$$

$$\langle e_{2X}^n \rangle = \frac{\int_0^\pi \sin^n\theta \cos^n\phi \exp(q\cos^2\theta) \int_0^{2\pi} \exp[h\cos 2\phi\ (\cos^2\theta - 1)]\,\mathrm{d}\phi \sin\theta\,\mathrm{d}\theta}{\int_0^\pi \exp(q\cos^2\theta) \int_0^{2\pi} \exp[h\cos 2\phi\ (\cos^2\theta - 1)]\,\mathrm{d}\phi \sin\theta\,\mathrm{d}\theta}, \tag{6}$$

$$\langle e_{3X}^n \rangle = \frac{\int_0^\pi \sin^n\theta \sin^n\phi \exp(q\cos^2\theta) \int_0^{2\pi} \exp[h\cos 2\phi\ (\cos^2\theta - 1)]\,\mathrm{d}\phi \sin\theta\,\mathrm{d}\theta}{\int_0^\pi \exp(q\cos^2\theta) \int_0^{2\pi} \exp[h\cos 2\phi\ (\cos^2\theta - 1)]\,\mathrm{d}\phi \sin\theta\,\mathrm{d}\theta}, \tag{7}$$

where

$$q = \gamma E_0^2/kT, \qquad h = \delta E_0^2/kT. \tag{8}$$

These integrals were evaluated numerically using IBM software [33] based on fine-grid double Gauss–Legendre quadrature.

Fig. 1 illustrates the fact that two of these GLK functions *change sign* with anisotropy of polarisability γ, in the sense that they increase or decrease from an initial value. Points on these analytical GLKs show simulated data from FMD under the same conditions, with potential energy corresponding to the torque (1) computed over a minimum of 6000 time steps at each point. The FMD method successfully simulates the change of sign in $\langle e_{2X}^n \rangle$ and $\langle e_{3X}^n \rangle$ given analytically from (6) and (7) as γ is changed from positive to negative. The function $\langle e_{1X}^n \rangle$ does *not* change sign analytically from eq. (5), and again this is reproduced successfully by FMD.

These results show that

(1) the sign of the anisotropy of polarisability of the water molecule can be determined from an experimental measurement of the three GLKs described already, possibly with contemporary femtosecond transient optical Kerr effect apparatus [5];

(2) FMD is in detailed agreement with the analytical theory on GLKs.

Table 1
Literature estimates of the polarisability tensor of water diagonalised in (1,2,3). (In figs. 1–3, (a), (b) and (c) refer to the data sets of refs. [26], [27], and [28] respectively.)

Ref.	α_{11}	α_{22}	α_{33}	
[26]	1.69	1.9	1.3	(S.I. units)
[27]	9.62	9.26	10.01	(a.u.)
[28]	8.15	7.12	9.03	(a.u.)

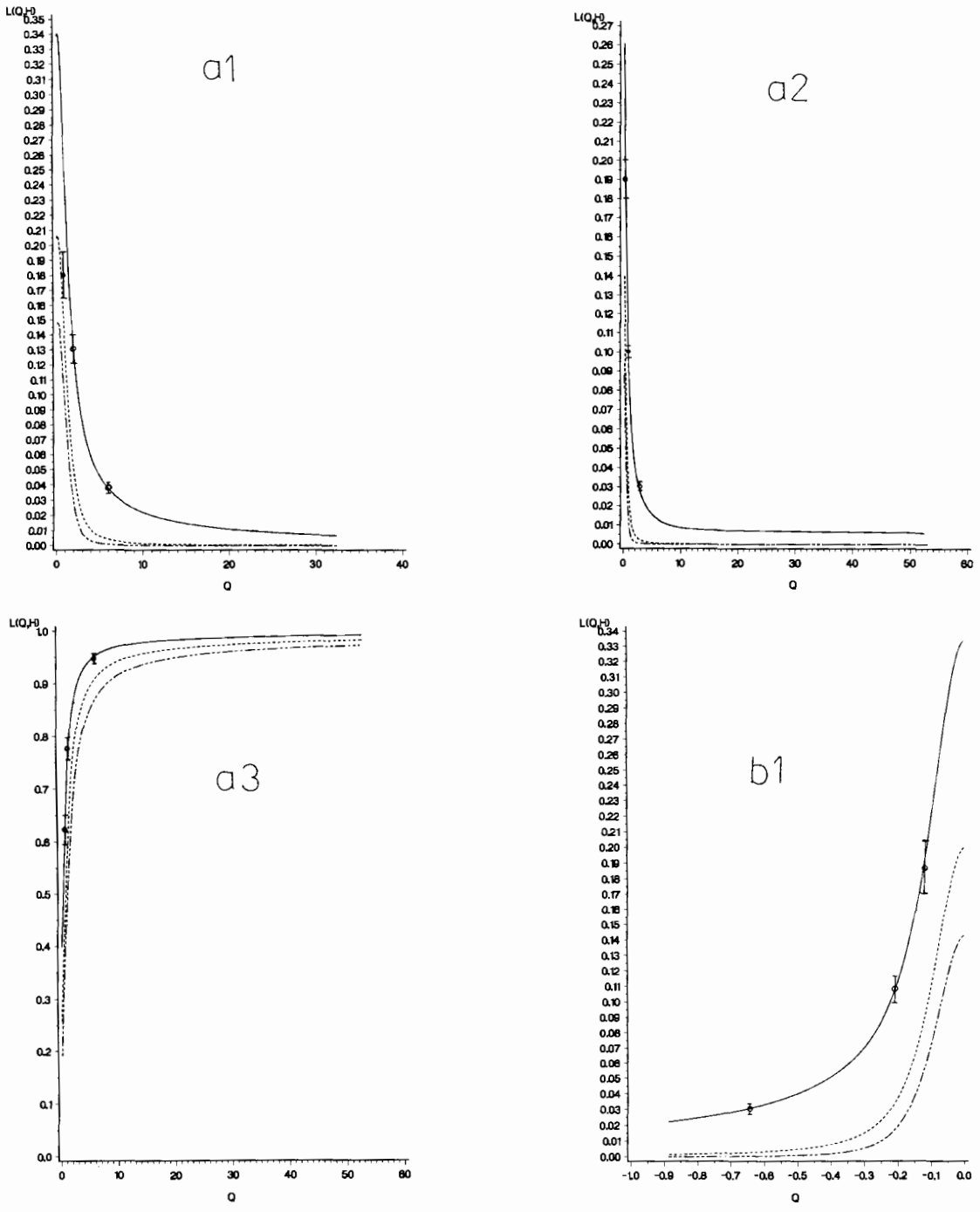


Fig. 1. Generalised Langevin–Kielich functions $L_1(q, h)$, $L_2(q, h)$, and $L_3(q, h)$ (labeled 1, 2, 3, respectively) from analytical theory (curves) and field applied computer simulation (points) for liquid water at 293 K, 1.0 bar: using the data (table 1) of (a) ref. [26], (b) ref. [27], and (c) ref. [28]. The functions initiate at 1/3 ($n=2$), 1/5 ($n=4$), and 1/7 ($n=6$). Note that in two cases the GLKs change sign between data sets (a) and (b), respectively representing negative and positive γ. (—) $n=2$, (- - -) $n=4$, (– · – · –) $n=6$. (⊙) FMD, $n=2$.

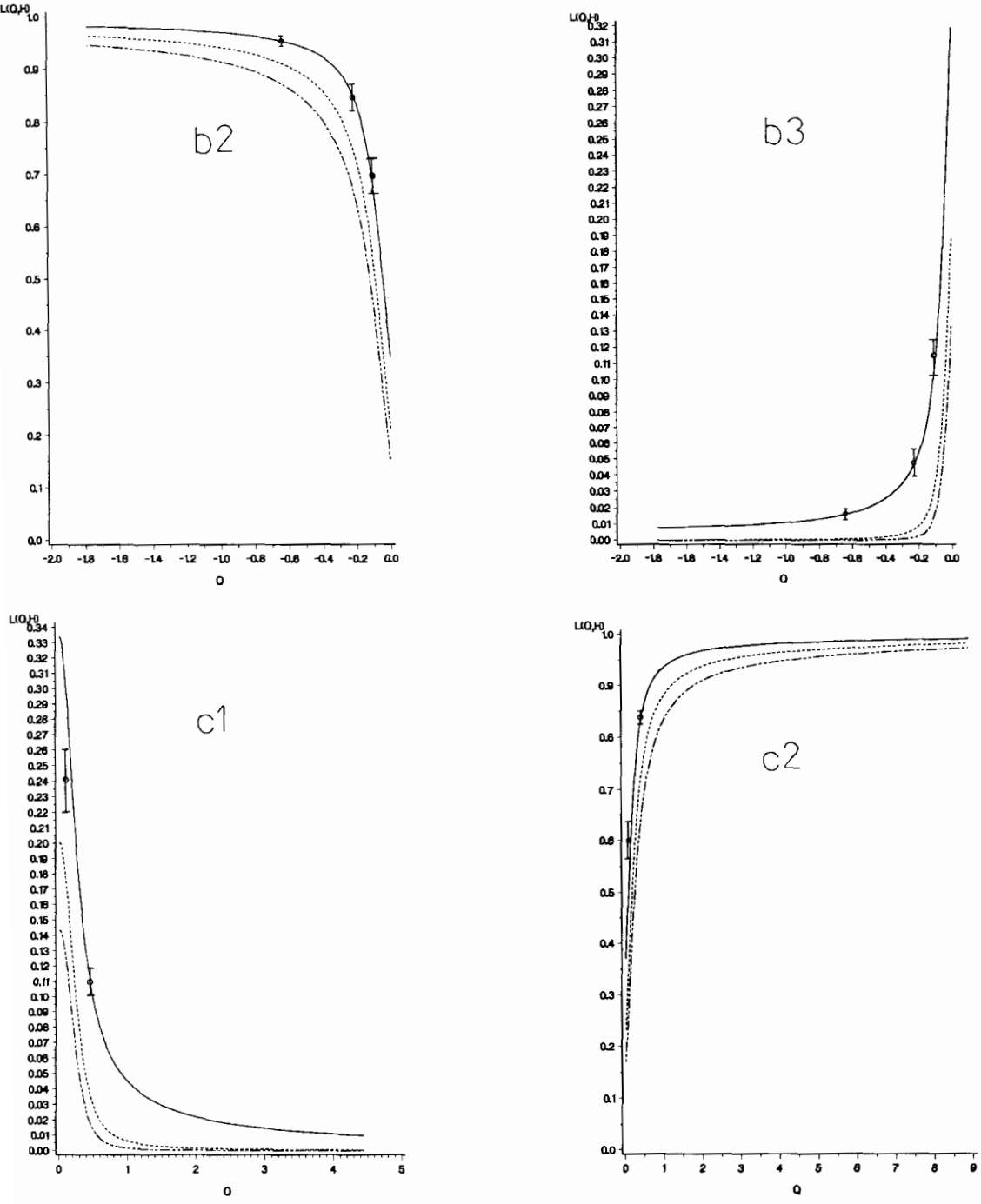


Fig. 1. Continued.

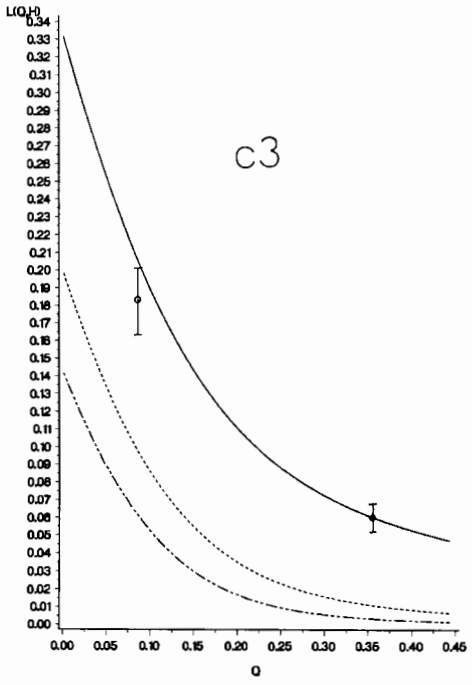


Fig. 1. Continued.

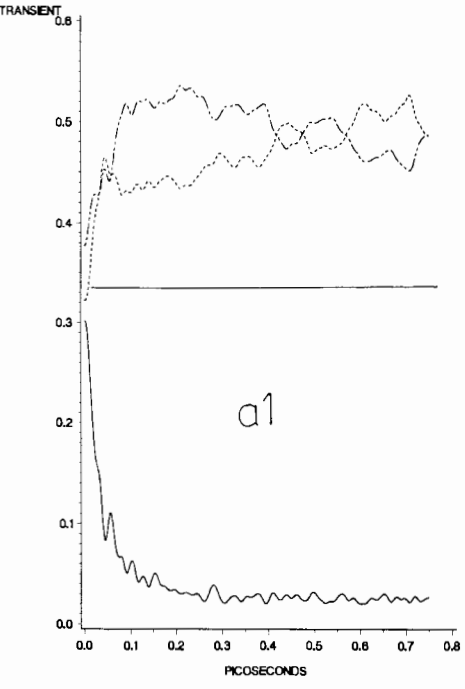
5. Time resolution of optical Kerr effect rise transients

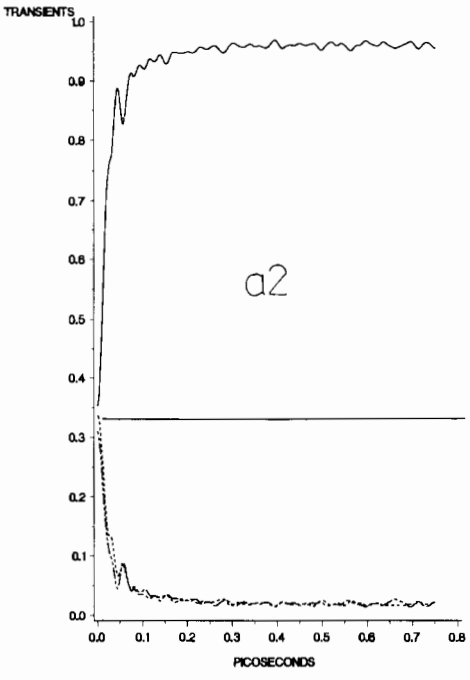
The time resolution on the femtosecond level of the optical Kerr effect has been achieved [5] by Kenney-Wallace and co-workers. The data are in the form of rise transients of probe optical absorption as a pump pulse is passed through the ensemble. These data can be related to our GLKs through the birefringence of the optical Kerr effect, which is in turn related to the observable changes in power absorption coefficient [5] through the Kramers–Kronig equations.

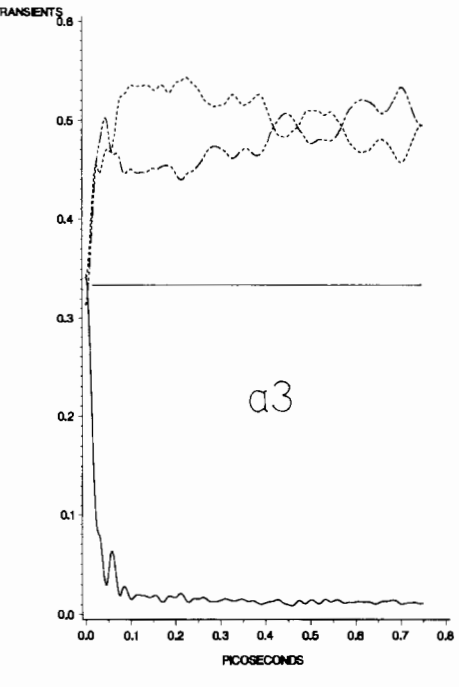
It is possible therefore, using a numerical iterative scheme, for example, to determine the anisotropy of polarisability from the rise transient experimental data [5]. Furthermore, FMD gives the time resolution of the rise transient as illustrated in fig. 2 using the conflicting literature data sets of table 1. Fig. 2 shows that the time resolved transients are markedly different for each data set at fixed pump laser equivalent potential energy, obtained by integrating the torque over configuration space in the FMD algorithm. For the Khanarian–Kent estimate [26] there are no rise transient oscillations [16,17] known from Kramers theory [17] to be due to specific non-linearities in the molecular dynamics. The presence of these oscillations is observed clearly (fig. 2), however, using the data given by Zeiss and Meath [27] and the ab initio computation of van Hemert and Blom [28].

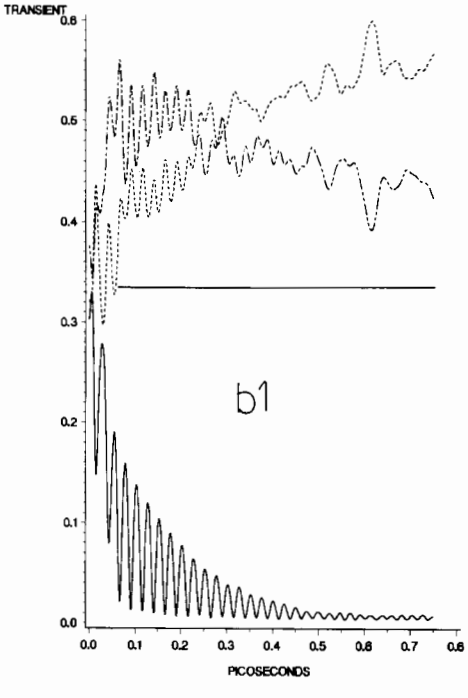
It is concluded that the details of the time dependence of the optical Kerr effect rise transient are intricate functions of the anisotropy of polarisability at a given pump laser intensity. It would be of interest to attempt to observe such oscillations experimentally [5].

Finally, we report that in the laser field applied steady state reached by the rise transient at a given pump laser intensity, a data bank of time correlation functions was accumulated to investigate in detail the field-on statistical dynamics by FMD. The correlation functions were observed also to be dependent markedly on which data set of table 1 was used, and this is illustrated in fig. 3 for the orientational autocorrelation functions

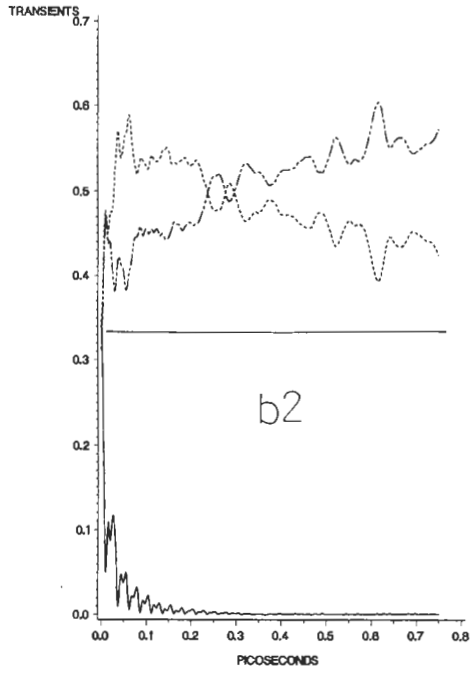


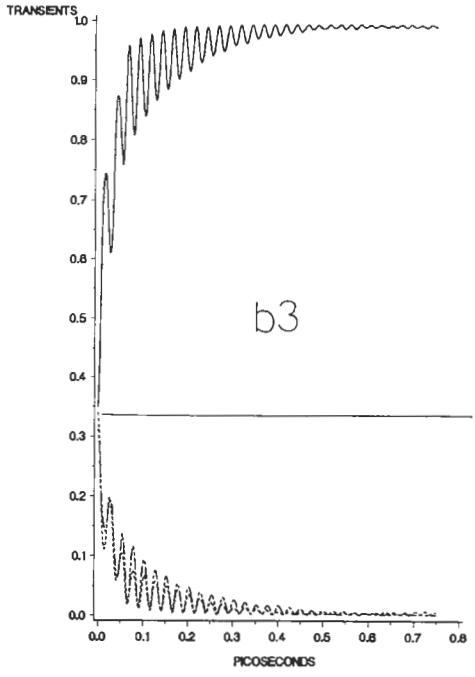


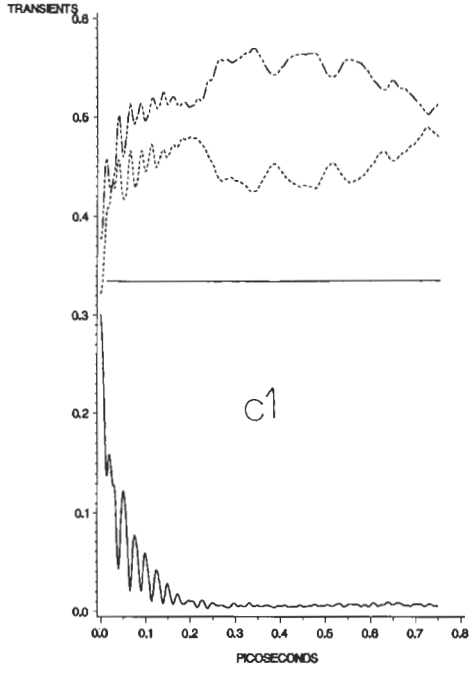


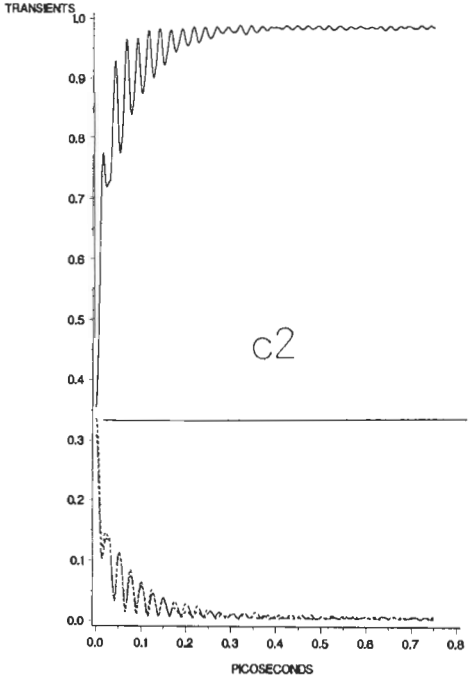


Time resolution of transients for data sets of (a) ref. [26], (b) ref. [27], and (c) ref. [28] (see table 1), simulated by FMD with alent laser potential energy of 2.0 kJ/mole. (—) $\langle e_{iX}^2 \rangle$, (- - -) $\langle e_{iY}^2 \rangle$, (– · – · –) $\langle e_{iZ}^2 \rangle$; $i = 1, 2, 3$ is the label added to a, b, c in ures.









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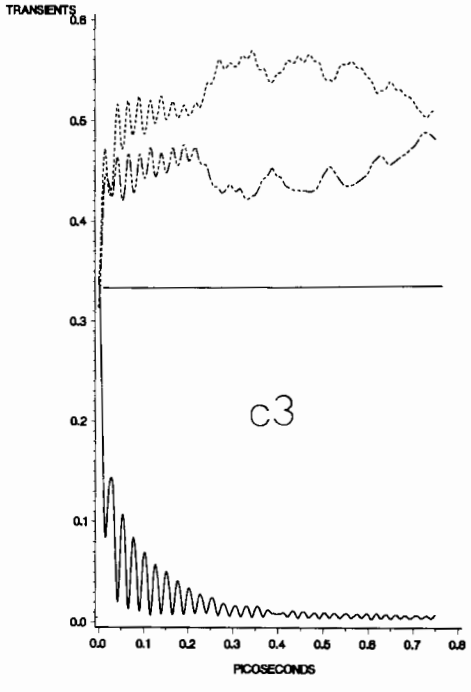

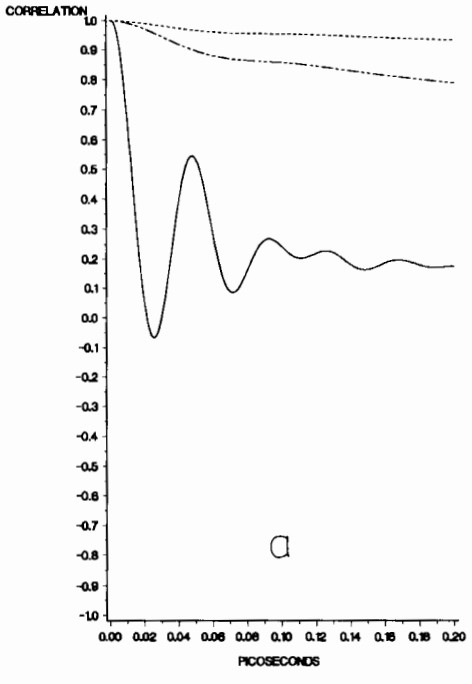

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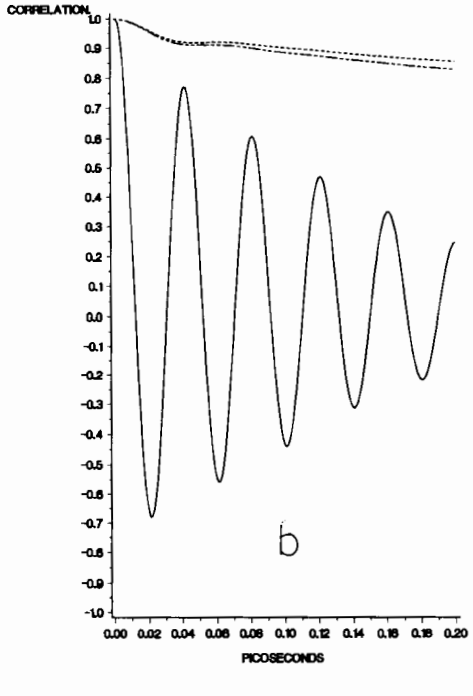

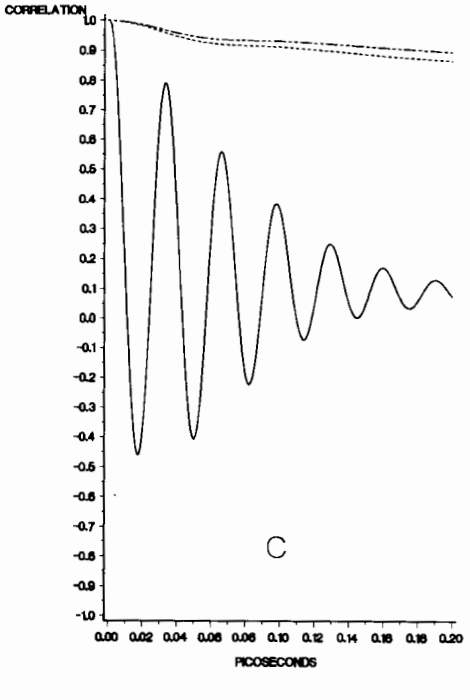

Fig. 3. As for fig. (2), orientational autocorrelation functions in the post transient steady state for data sets of (a) ref. [26], (b) ref. [27], and (c) ref. [28] (see table 1): (—) $i=j=X$; (- - -) $i=j=Y$; (- · - · -) $i=j=Z$.

$$C_{1ij}(t)=\frac{\langle e_{1i}(t)e_{1j}(0)\rangle}{\langle e_{1i}^2\rangle^{1/2}\langle e_{1j}^2\rangle^{1/2}}, \qquad i=j. \tag{9}$$

Such differences were also observed for the time correlation functions of molecular angular momentum

$$C_{2ij}(t)=\frac{\langle J_i(t)J_j(0)\rangle}{\langle J_i^2\rangle^{1/2}\langle J_j^2\rangle^{1/2}}, \tag{10}$$

and of rotational velocity

$$C_{3ij}(t)=\frac{\langle \dot{e}_{1i}(t)\dot{e}_{1j}(0)\rangle}{\langle \dot{e}_{1i}^2\rangle^{1/2}\langle \dot{e}_{1j}^2\rangle^{1/2}}. \tag{11}$$

Off diagonal components (cross correlation functions) were found to change sign with the anisotropy of polarisability γ. Further detailed discussion of these extensive data will be reported elsewhere.

The Fourier transform of the rotational velocity autocorrelation function [34] is the far infrared power absorption coefficient, and were it possible to observe this spectrum in the presence of a pump laser pulse, FMD as used in this paper shows that it would give information on the molecular dynamics of the optical Kerr effect in the laser on steady state, and specifically on the anisotropy of polarisability.

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