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ORIENTATIONAL ANISOTROPY INDUCED BY THE INTERACTION OF A LASER WITH A PERMANENT ELECTRIC DIPOLE : AN FMD SIMULATION.

by

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ABSTRACT

Field applied molecular dynamics (FMD) computer simulation is used to show the presence of a novel orientational anisotropy generated by the first order interaction of a permanent molecular electric dipole moment with the electric field of a circularly polarised laser at visible (terahertz) frequencies. The anisotropy appears in orientational second order rise transients and laser-applied time correlation function components, despite the fact that the laser frequency is far higher than the characteristic reorientational frequencies of the molecule and despite the fact that Langevin-Kielich functions for this process cannot be defined.

INTRODUCTION

Recently, the powerful numerical technique known as "field applied molecular dynamics (FMD)" computer simulation has been successfully applied to several different nonlinear optical phenomena by Evans et al. {1-8} and Robinson et al. {9-12} using independent programs and methods. Examples of application include the following higher order (optically nonlinear) processes: 1) time dependent (or dynamic) electric polarisation {1,2}; 2) the inverse Faraday effect {3}; 3) inverse magnetochiral birefringence {4}; 4) the optical Kerr effect {5}; 5) laser modulated NMR (or "LENS") spectroscopy {6}; 6) the optical Stark effect with torque frequency doubling {7}; 7) orientational anisotropy due to the Rosenfeld tensor {8}. Additionally, Robinson et al. {9-12} have extended the method to include molecular flexibility and instantaneous electronic polarisation, which may be of importance in determining, for example, the effect of the external field on the potential energy of a molecular ensemble {9}. Both groups have found that a strong external field

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fundamentally changes the molecular dynamical and structural characteristics of an ensemble in many interesting and useful ways. It appears that the FMD method is, furthermore, potentially applicable to any nonlinear optical phenomenon in a variety of interesting materials, and describes fundamentally the way in which an advanced material responds to a strong laser field.

In this paper we describe using FMD a novel orientational anisotropy induced by a visible frequency circularly polarised laser's electric field strength (E) as it propagates through a molecular ensemble and forms a torque at first order with the permanent electric dipole moment (μ) of a molecule. Despite the fact that the time average of the laser field disappears, and no Langevin Kielich functions {13,14} can be defined, and despite the fact that the frequency of the laser is far higher than the characteristic reorientational frequencies of the molecular ensemble (far infra red range), a hitherto uncharacterised orientational anisotropy develops in the sample. The anisotropy can be identified through second order orientational averages (rise transients) and through the components of time correlation functions in the laser-applied steady state.

Section 1 describes the essentials of the FMD method, section 2 presents some characteristic results, and section 3 is a discussion of how this effect could be identified and measured experimentally.

1. SUMMARY OF FMD METHODS.

The essence of the FMD method is to code into any standard molecular dynamics simulation algorithm {15,16} an extra torque originating from the interaction of a molecule of the ensemble and an applied field. The FMD technique is therefore simple to code and perfectly general in applicability, because the intermolecular torque in a simulation is usually computed directly from intermolecular forces, and other molecular dynamical variables such as angular momentum are obtained by integration at a later stage. This means, essentially, that all the variables and trajectories can be generated from a knowledge of the external and internal torques on a given molecule. FMD was originally developed for strong time independent electric fields {17}, and was extended to electromagnetic and other types of fields {18-22} such as shear or vortex flow.

In this paper we use a torque which is made up of the vector cross product between the permanent molecular electric dipole moment and the electric field component of the laser

$$\boldsymbol{T} = \boldsymbol{\mu} \times \boldsymbol{E} \qquad (1)$$

where E is given for left and right circular polarisation according to whether the sign in the following equation is positive or negative

$$\boldsymbol{E} = E_0 (\boldsymbol{i} \pm i\boldsymbol{j}) \exp(-i\phi_{R,L}) \qquad (2)$$

Here, the subscripts L and R denote respectively right and left circular polarisation and the phase of the laser is approximated by

$$\phi_{L,R} \doteq \omega t \qquad (3)$$

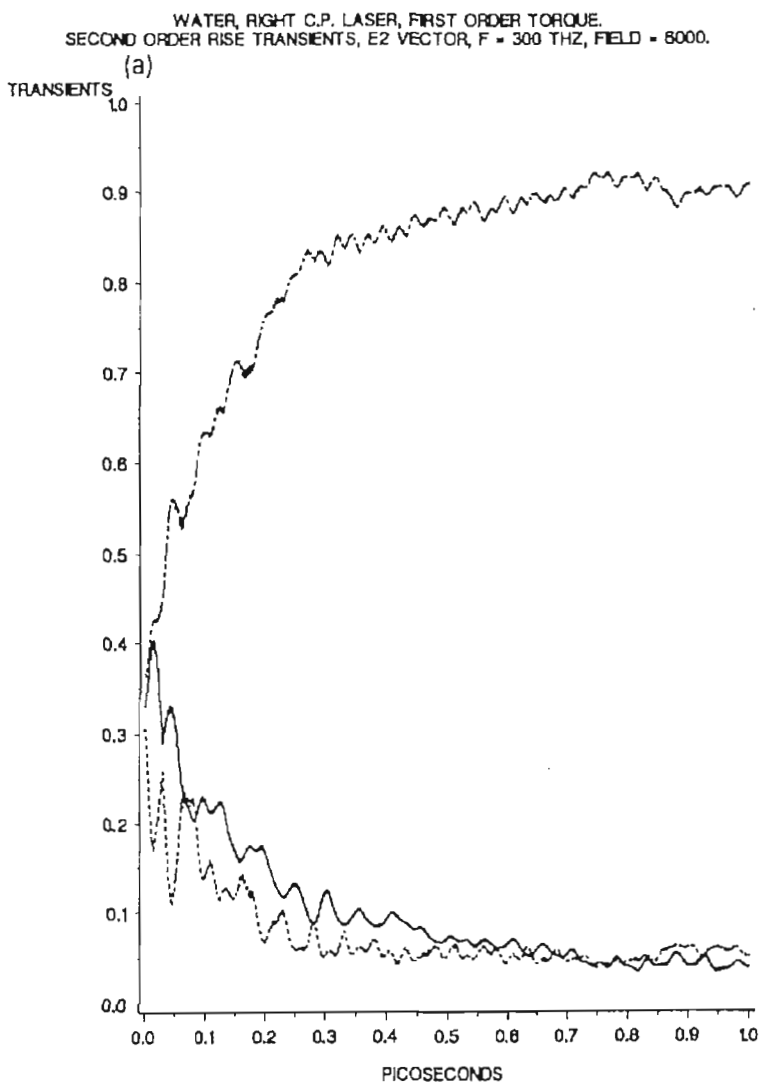
where ω is the laser's angular frequency in radians per second and t the time. The simulation proceeds by setting ω to the hundred terahertz (visible frequency) range in order to gauge the effect of the first order torque on 108 molecules of liquid water.

The effect is evaluated by FMD through second order orientational rise transients, which are generated over 2,000 time steps of 0.5 fs each immediately after the torque is switched on, and through a variety of time correlation functions computed in the laser-applied steady state over 6,000 time steps after rise transient saturation. The intermolecular potential and FMD methods are described fully in the recent literature {1-8}.

2. RESULTS

The torque (1) is clearly time dependent, and the equivalent interaction energy averages to zero. In consequence it is not possible to define, thermodynamically, orientational averages of the Langevin Kielich type {1-8}. Despite this the sequence of rise transients in Fig (1) at different frequencies of the pump laser shows the presence of clearly defined differences from the laser-off condition, where all such averages take a value of 1/3. This type of behaviour has also been observed by FMD in the inverse Faraday effect {3}. The present simulation has been carried out with rigid site-site potentials with no instantaneous electronic polarisation, and it will be interesting in future to repeat the work with molecular flexibility as in the work of Robinson et al. {9-12} to determine whether such an ensemble continues to support these second order averages.

The sequence of results in Figs. (2) to (4) illustrates orientational anisotropy in response to several visible frequencies of the pump laser, anisotropy which is measured through autocorrelation function components in the presence of the laser in the steady state after transient saturation. This is evidence for the ability of a visible frequency laser to impart


WATER, RIGHT C.P. LASER, FIRST ORDER TORQUE.
SECOND ORDER RISE TRANSIENTS, E2 VECTOR, F = 300 THZ, FIELD = 6000.
(a)
TRANSIENTS
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
PICOSECONDS

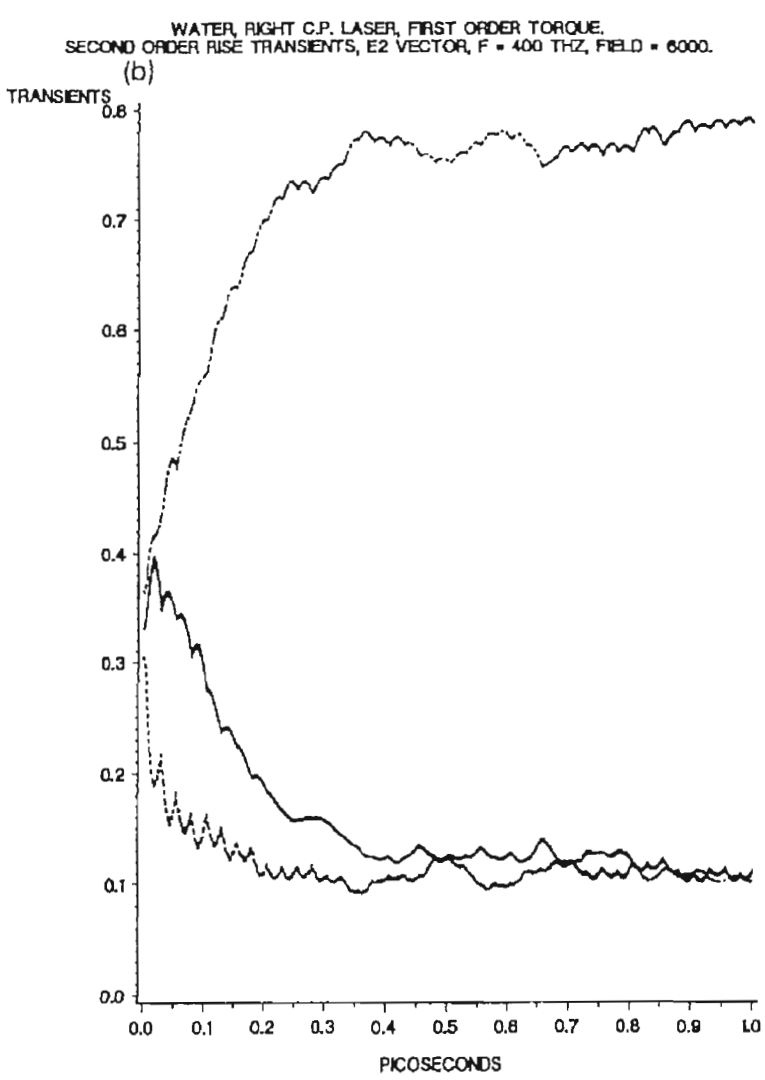

WATER, RIGHT C.P. LASER, FIRST ORDER TORQUE.
SECOND ORDER RISE TRANSIENTS, E2 VECTOR, F = 400 THZ, FIELD = 6000.
(b)
TRANSIENTS
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
PICOSECONDS

Figure 1.

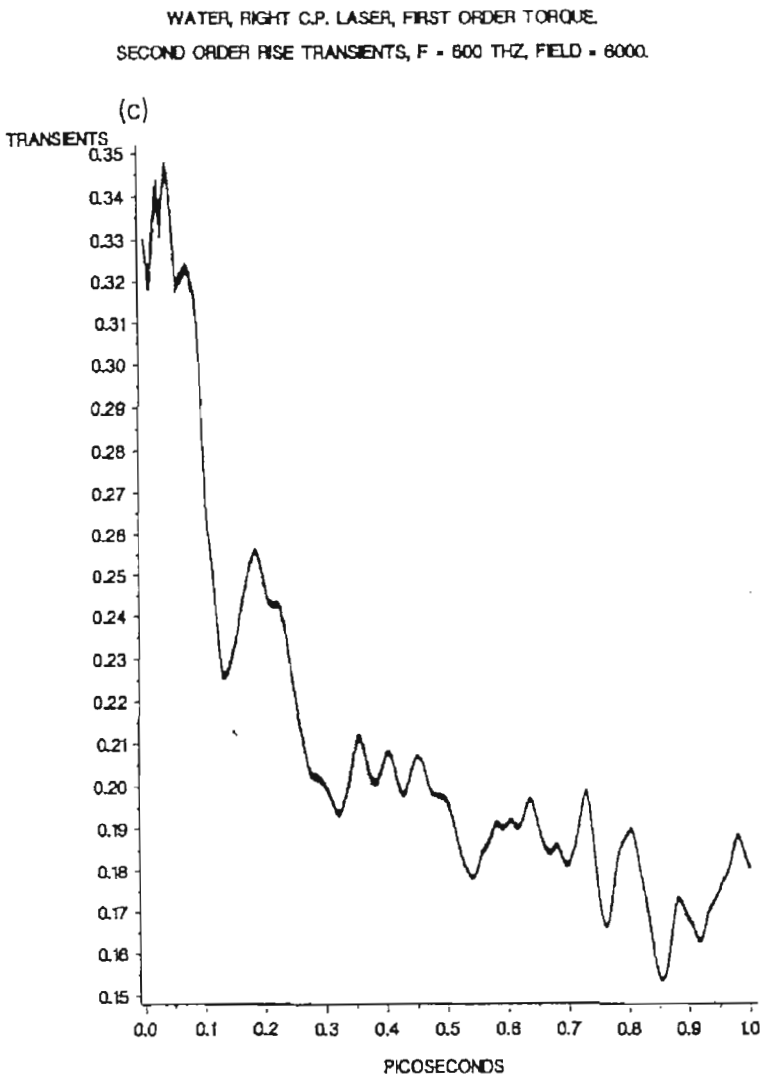


Figure 1.

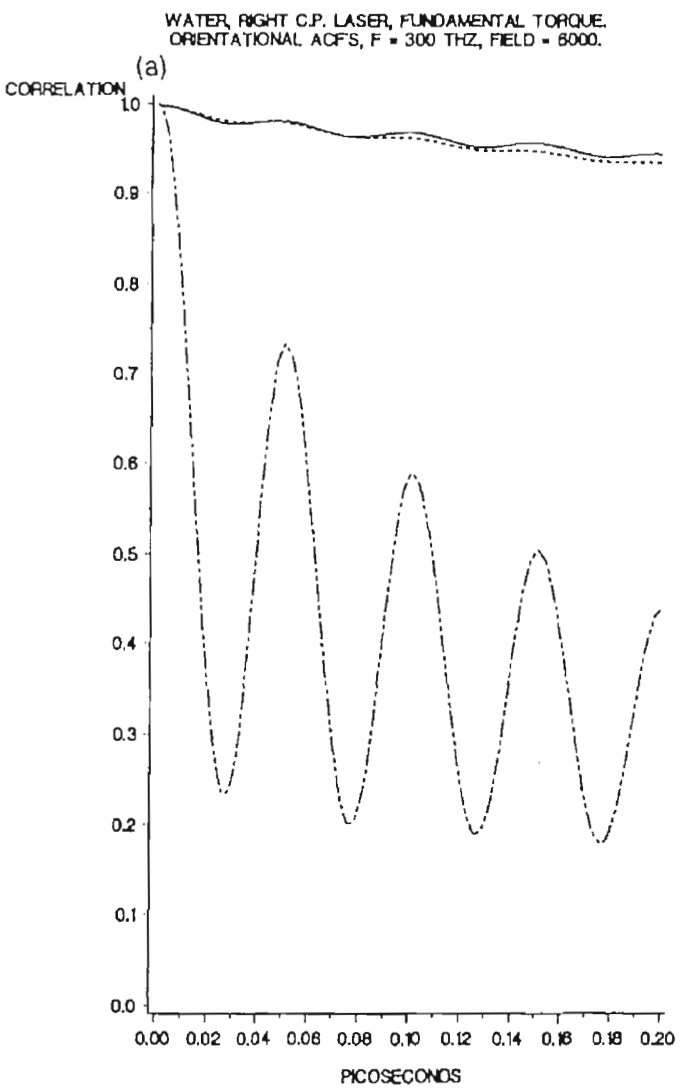
Second order rise transients $<e_{2i}^2>$. a) 300 THz, b) 400 THz, c) 600 THz.

_____ $<e_{2X}^2>$; ---------- $<e_{2Y}^2>$; -..-..- $<e_{2Z}^2>$.

bi-axial birefringence to an ensemble of structurally rigid water molecules, even though the characteristic orientational frequencies of the molecules are in the much lower far infra red / microwave / megahertz range of frequencies.

DISCUSSION

We regard these results as a first inroad to the understanding of the effect under study, because our model of the water molecule consists of a rigid site site potential with no


WATER, RIGHT C.P. LASER, FUNDAMENTAL TORQUE.
ORIENTATIONAL ACF'S, F = 300 THZ, FIELD = 6000.
(a)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS

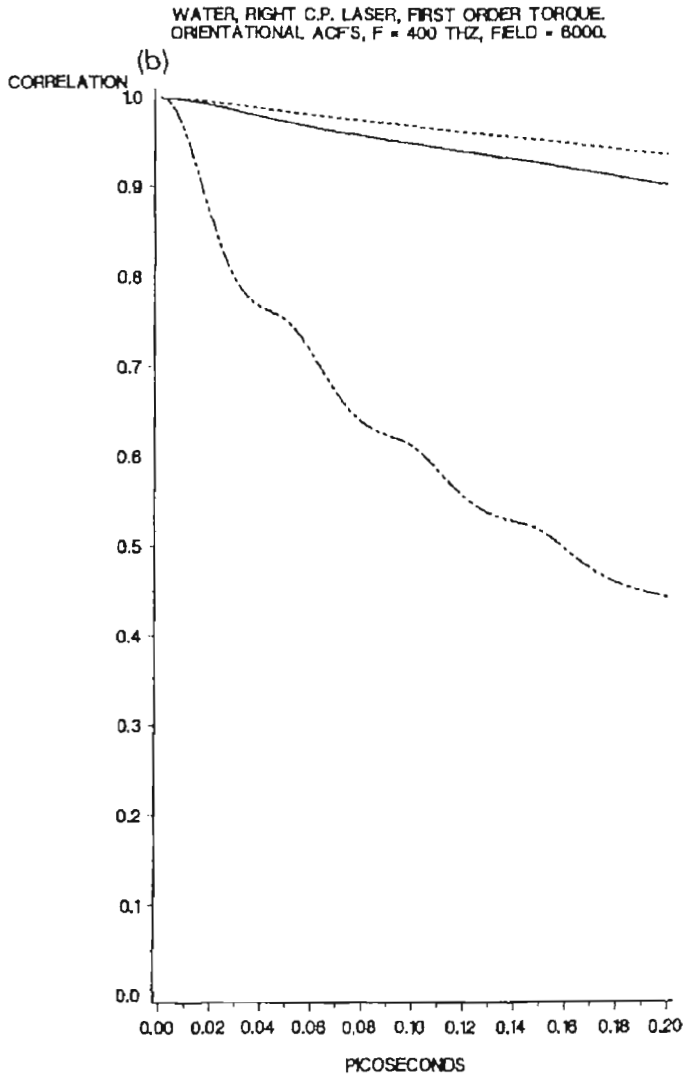

WATER, RIGHT C.P. LASER, FIRST ORDER TORQUE.
ORIENTATIONAL ACF'S, F = 400 THZ, FIELD = 6000.
(b)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS

Figure 2.

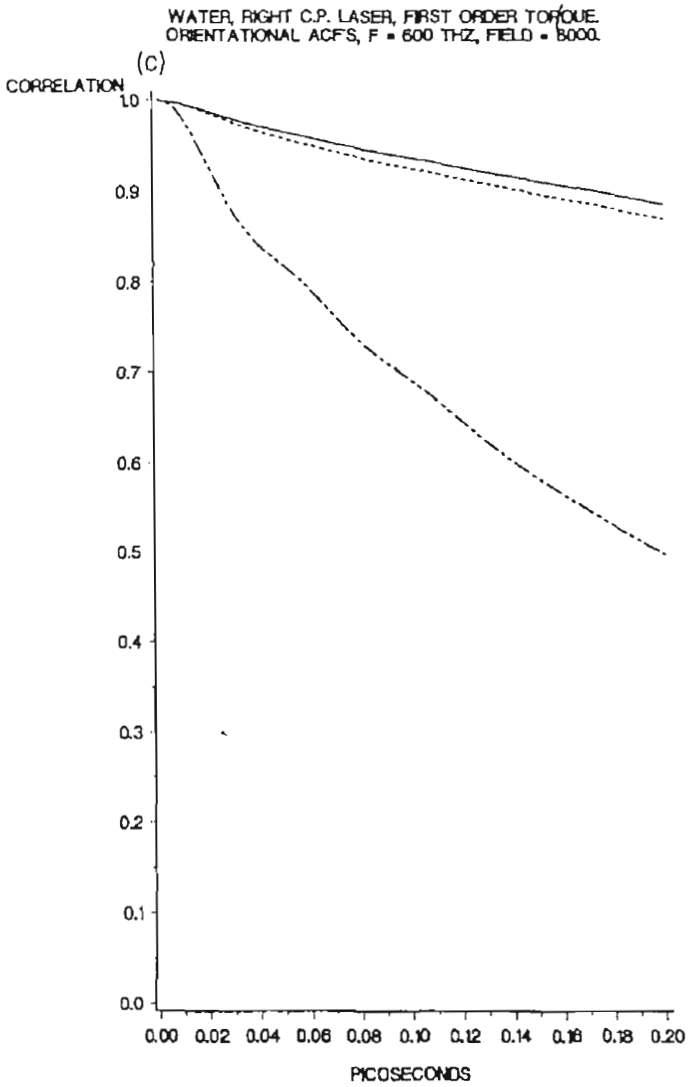


Figure 2.

As for Fig 1, orientational autocorrelation functions of the e_1 (dipole) orientational vector.

instantaneous electronic polarisation. This model has been extended recently by Robinson et al. {9-12}, who have reported the effects of an intense laser field on liquid water using an intermolecular potential model which for the first time includes both flexible intramolecular bonds and instantaneous electronic polarisation effects. Under the influence of the strong external torque, both the liquid structure and the intramolecular geometry are distorted, effects which significantly change {9} the dynamical behaviour of the liquid compared with the field-off system. Robinson et al. have found, furthermore {9}, that an intense external electric field give rise to a nonlinear response of the medium, and these workers have

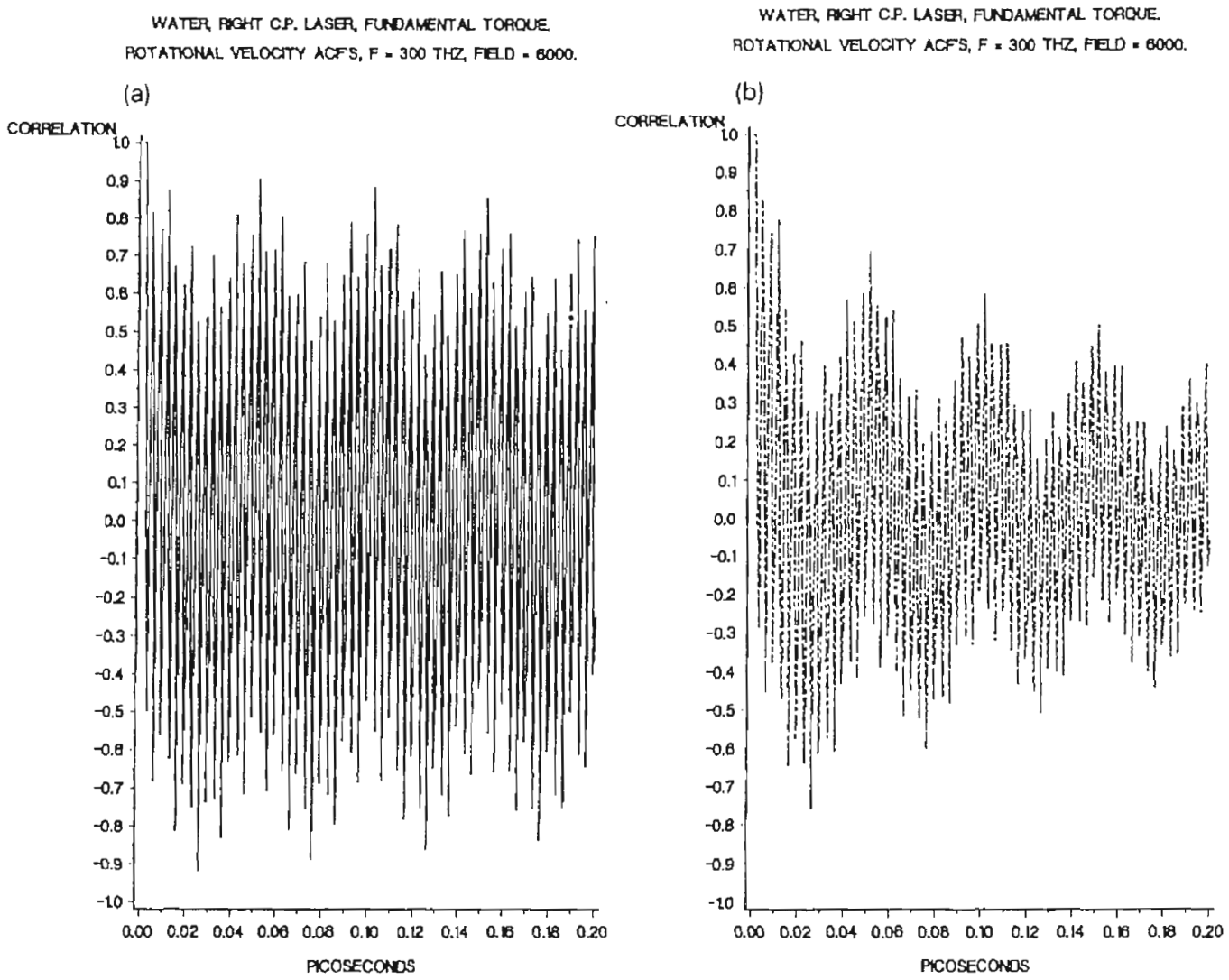
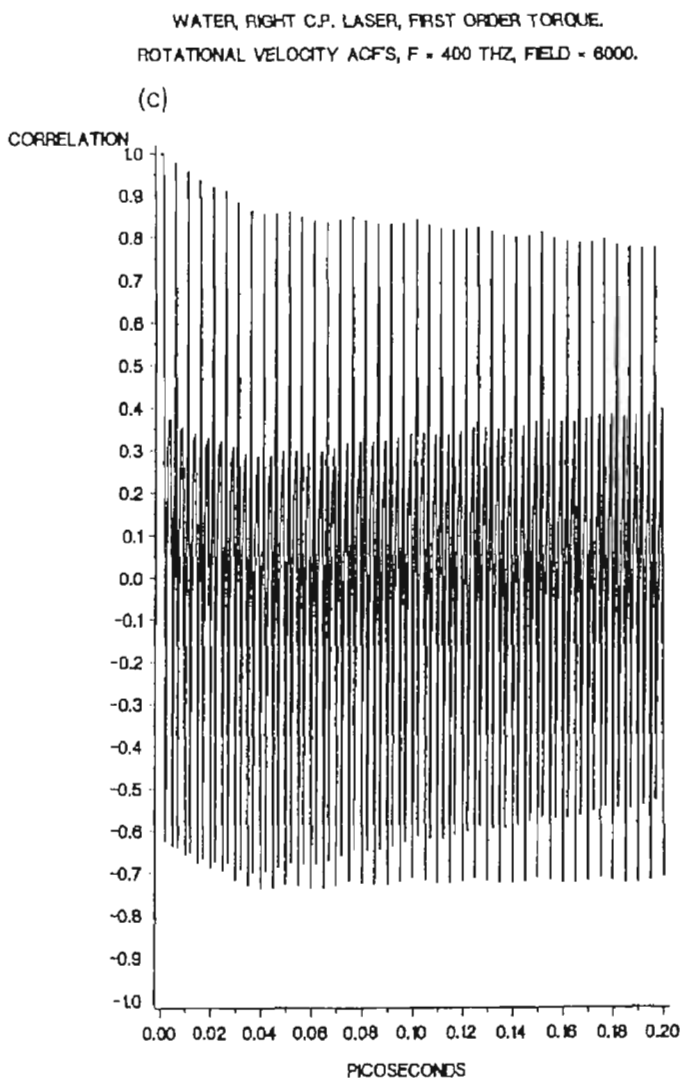

WATER, RIGHT C.P. LASER, FUNDAMENTAL TORQUE.
ROTATIONAL VELOCITY ACF'S, F = 300 THZ, FIELD = 6000.
(a)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS
WATER, RIGHT C.P. LASER, FUNDAMENTAL TORQUE.
ROTATIONAL VELOCITY ACF'S, F = 300 THZ, FIELD = 6000.
(b)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS

Figure 3.


WATER, RIGHT C.P. LASER, FIRST ORDER TORQUE.
ROTATIONAL VELOCITY ACF'S, F = 400 THZ, FIELD = 6000.
(c)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS

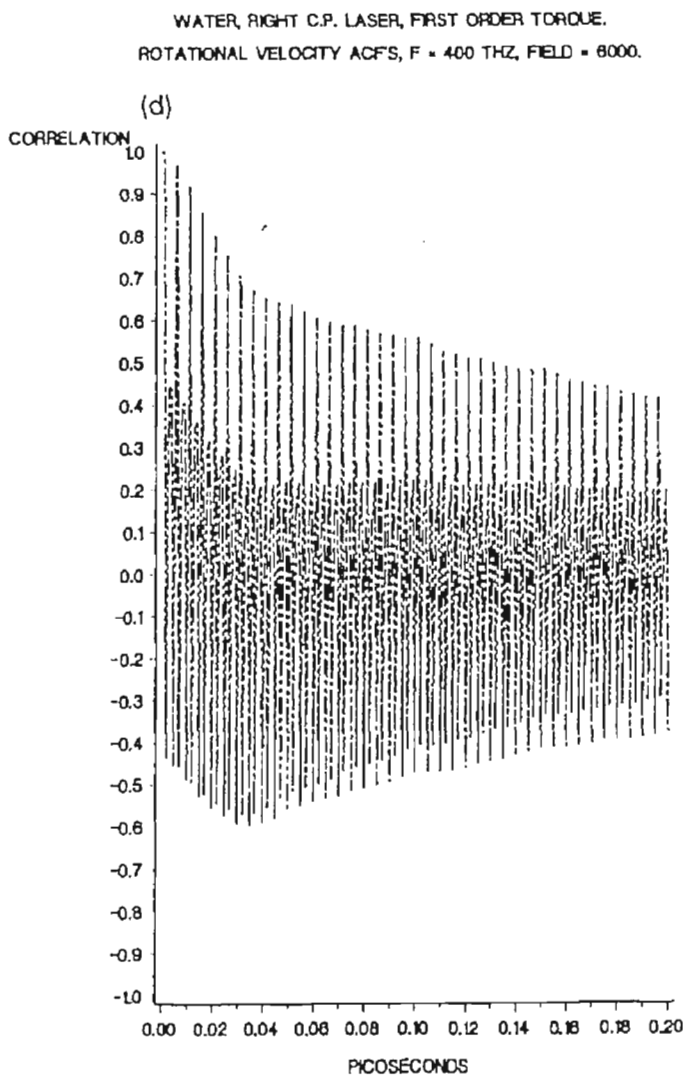

WATER, RIGHT C.P. LASER, FIRST ORDER TORQUE.
ROTATIONAL VELOCITY ACF'S, F = 400 THZ, FIELD = 6000.
(d)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS

Figure 3.

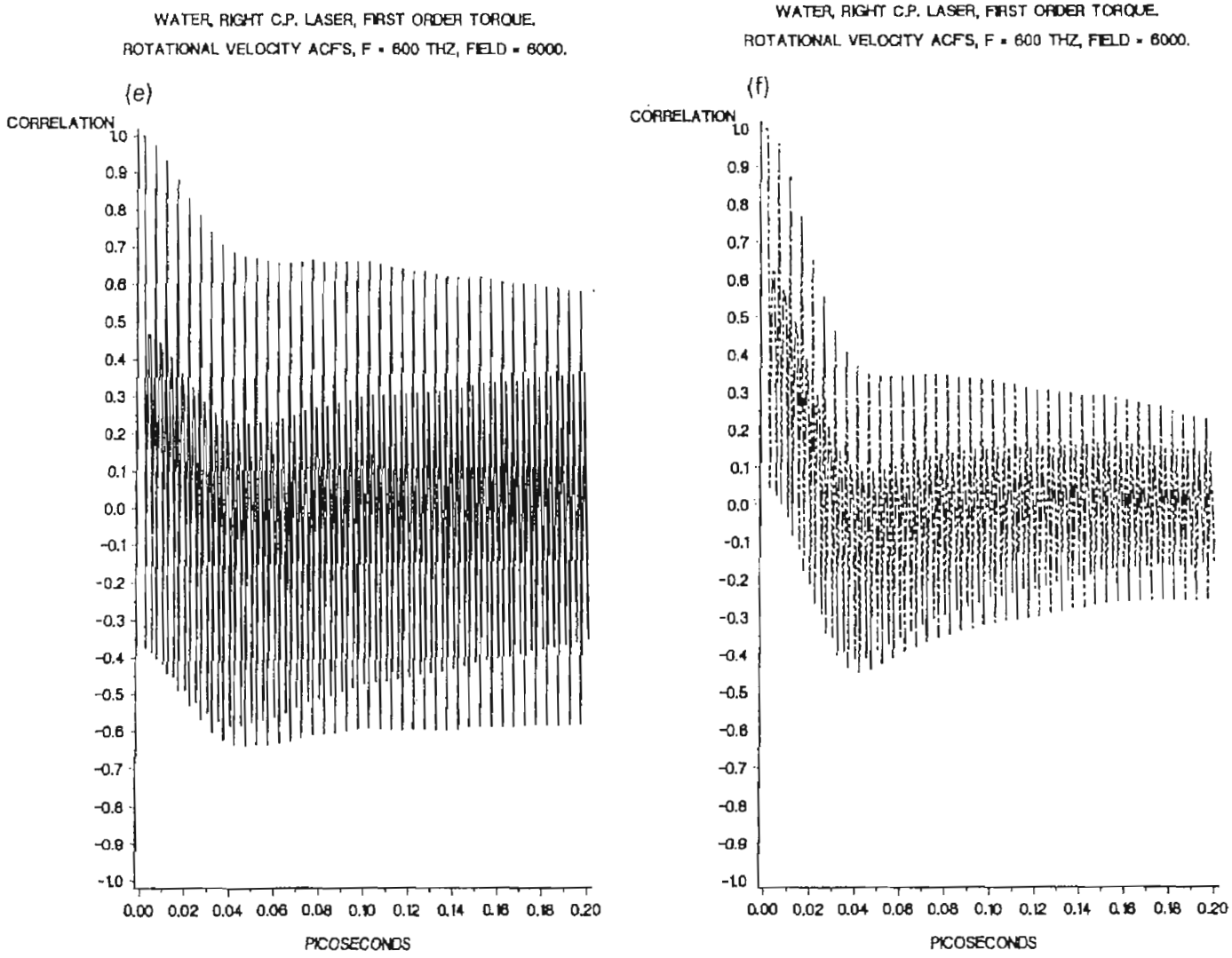


Figure 3.

As for Fig. 2, rotational velocity autocorrelation functions.

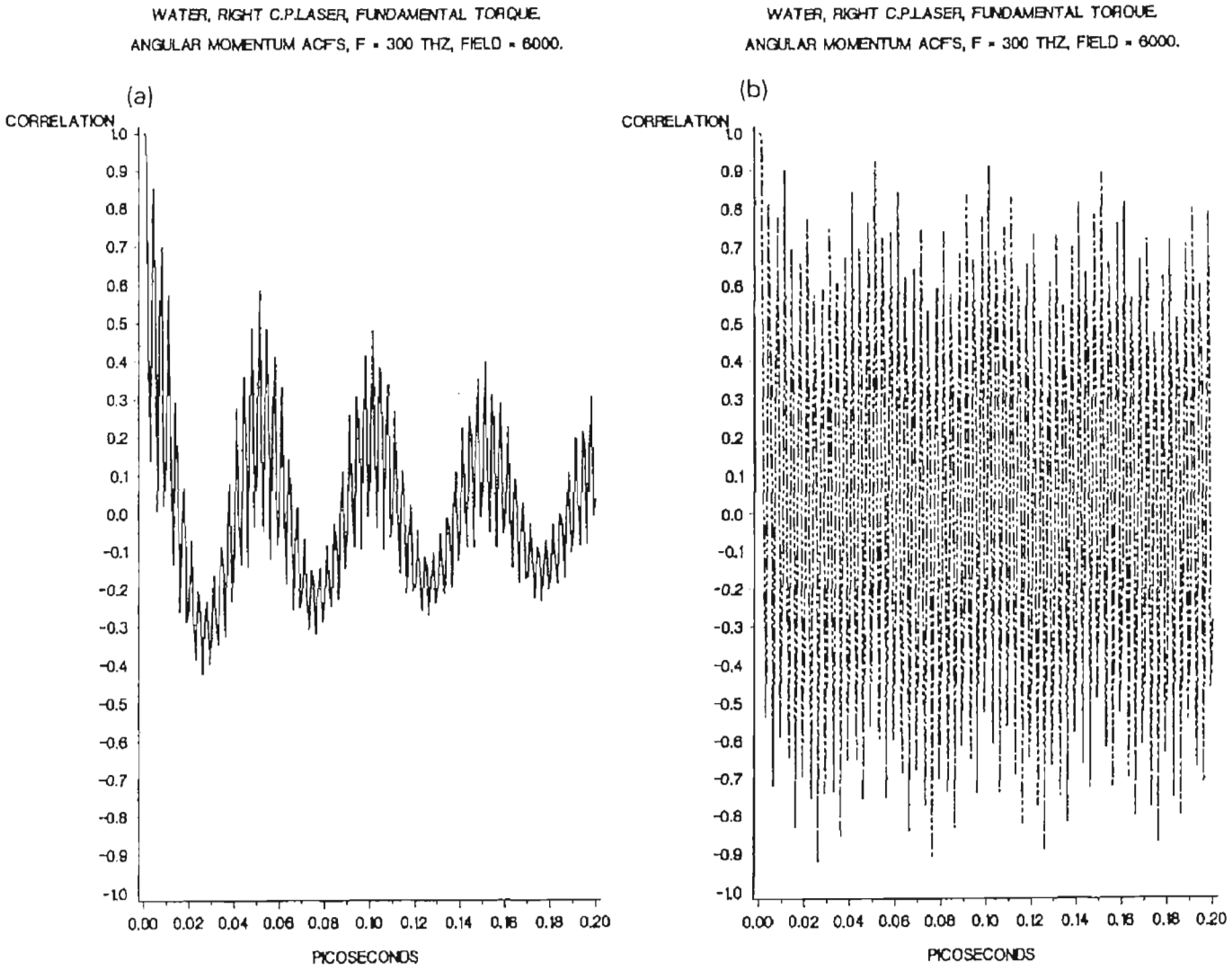

WATER, RIGHT C.P.LASER, FUNDAMENTAL TORQUE.
ANGULAR MOMENTUM ACF'S, F = 300 THZ, FIELD = 6000.
(a)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS
WATER, RIGHT C.P.LASER, FUNDAMENTAL TORQUE.
ANGULAR MOMENTUM ACF'S, F = 300 THZ, FIELD = 6000.
(b)
CORRELATION
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20
PICOSECONDS

Figure 4.

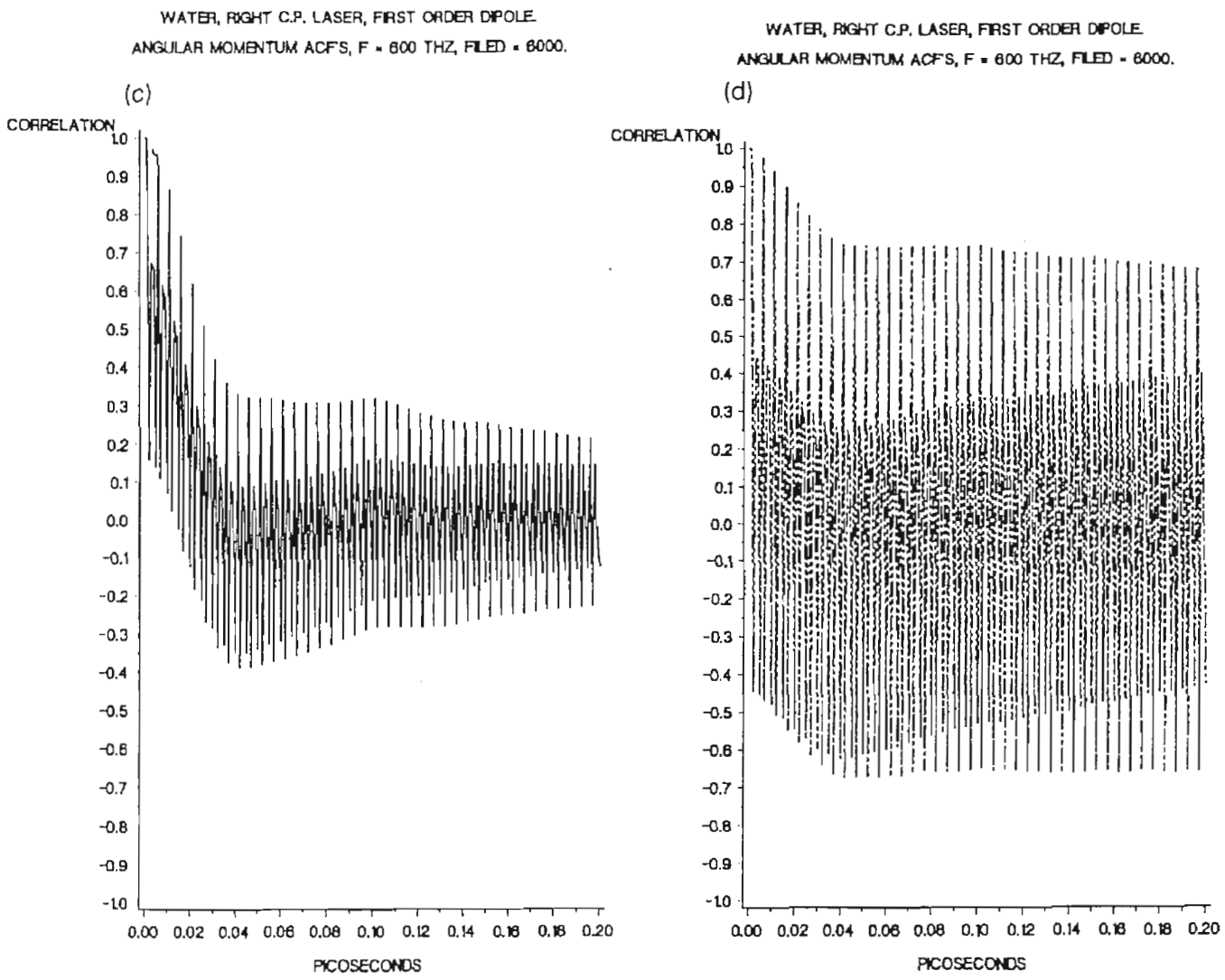


Figure 4.

As for Fig. 2, angular momentum autocorrelation functions.

measured and characterised using their FMD method the field induced nonlinear refractive index, self focussing, and supercontinuum phenomena.

Returning to our simple rigid model, Figs (1) to (4) show a variety of interesting dynamical phenomena introduced by a simple first order torque.

1) The circularly polarised laser produces through the torque (1) well defined second order rise transients such as

$$\langle e_{1i}^2 \rangle ; \langle e_{2i}^2 \rangle ; \langle e_{3i}^2 \rangle ; \; i = X, Y, Z ;$$

illustrated in Figure (1). The X, Y, and Z components of these transients clearly become separated from the initial value of 1/3 (isotropic liquid) and gradually evolve to saturation.

2) In the post-saturation condition the anisotropy induced by right circularly polarised pump lasers at visible frequencies of 300, 400 and 600 THz is illustrated in Figures (2) to (4) through autocorrelation functions of a) the orientational vector e_1 , b) its time derivative, the rotational velocity vector $\dot{e}_1$, and c) the angular momentum vector J. In the sequence of Fig. (2) it is clear that the component autocorrelation function in the Z direction, the propagation axis of the laser, evolves quite differently from orthogonal components, indicating bi axial anisotropy and birefringence which is measurable experimentally with a probe laser or with broad band radiation. The details of the birefringence depend markedly in this simulation on laser frequency, as illustrated at 300, 400 and 600 THz. Similar trends are illustrated in Figs. (3) and (4).

The anisotropy illustrated in these figures is not a transient phenomenon, but persists indefinitely in the laser-on steady state, implying that under the action of the first order torque (1) the liquid becomes permanently birefringent. The interaction energy responsible for this is proportional to the electric field strength of the pump laser in volts per meter, and therefore to the square root of the laser intensity in watts per square metre, multiplied by the permanent electric dipole moment of the molecule. Clearly, if the molecule is non-dipolar, there should be no effect of this type. The birefringence should be measurable through these characteristics, and through the fact that the refractive index of the sample is different parallel and perpendicular to the pump laser. The birefringence from the computer simulation appears to be very sensitive to the (visible) frequency of the pump laser, a result which should be discernible using a probe laser parallel and perpendicular to the pump laser, or broad band radiation in the same configuration.

We note finally that this phenomenon is not one of instantaneous electronic polarisation {9}, but of whole molecule reorientation, its physical origins appear to reside in the ability of a rapidly rotating electric field (that of the laser) to gradually cause permanent orientational anisotropy by interaction with the permanent molecular electric dipole moment. An analogy would be a gradually evolving vortex motion set up by a thin, rapidly rotating, low friction rod situated at the eye of the vortex. Figures (1) and (2) show that this occurs over a much longer time scale than that of the high frequency oscillations apparent in Figures (3) and (4), oscillations which occur at the frequency of the applied laser field, and which are superimposed on much lower frequency oscillations characteristic of the orientational correlation times of the molecular ensemble.

This is a phenomenon which is well defined, to first order in the externally applied rotating electric field, but which is not easily seen with contemporary diffusion theory, because the simple time average of the applied field disappears, and Langevin functions cannot be defined. Despite this, the FMD method shows clearly the presence of anisotropy. In those situations where Langevin functions are defined, the FMD method produces excellent agreement {1-8} with the analytical theory. Figures (1) to (4) therefore indicate the presence of a hitherto uncharacterised mechanism that produces permanent anisotropy through a first order torque of type (1).

ACKNOWLEDGEMENTS

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