Field applied (FMD) computer simulation of the frequency doubled optical Stark effect

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It is shown by field applied molecular dynamics computer simulation (FMD) of liquid water that the frequency doubled optical Stark effect is accompanied by novel second order rise transients which have no known counterpart in orientational theory, based on Langevin/Kielich functions. In the statistically stationary, post transient, steady state, correlation function have been computed which are intrinsically dependent on the frequency of the pump laser. These transients can be obtained experimentally by modifications of optical Stark effect apparatus for measurement on a femtosecond time scale.

0. Introduction

The optical Stark effect is defined through the induction of an electric dipole moment by the following type of interaction between molecular polarisability and the electric field strength, \( \mathbf{E} \), of an electromagnetic plane wave

\[
\mu^{(\text{iso})} = \chi_0 (\omega \omega) \mathbf{E}_0.
\]

We consider at the outset the electric field defined as the plus conjugate of a left circularly polarised plane wave

\[
\mathbf{E}_1^+ = E_0 (i + j) \exp(-i\phi_1),
\]

Here \( j \) and \( i \) are unit vectors in the \( X \) and \( Y \) axes, respectively, of the laboratory frame \((X, Y, Z)\), and the phase factor is defined by

\[
\phi_1 = \omega t - \Delta 
\]

where \( \omega \) is the angular frequency in radians per second of the plane wave, \( t \) the time, \( \Delta \) the left handed propagation vector, and \( \mathbf{r} \) a position vector. For the purposes of computer simulation, we approximate the phase by

\[
\phi_1 = \omega t - \Delta \mathbf{r} \cdot \mathbf{t}.
\]

Note that the potential energy and torque generated by the interaction of \( E_1^+ \) with the induced electric dipole moment \( \mu^{(\text{iso})} \) are described respectively by the time independent expression

\[
\Delta H_{\text{L}} = -\mu^{(\text{iso})} \times E^* \tag{5}
\]

and

\[
T_k = -\mu^{(\text{iso})} \times E^* \tag{6}
\]

Here \( E_1^+ \) is the complex conjugate of \( E_1^+ \), i.e.

\[
E_1^{+\star} = E_0 (i + j) \exp(-i\phi_1).
\]

so that the phase factor, \( \phi_1 \), disappears in the vector dot and cross products (5) and (6) respectively. The time (i.e. phase) independent energy term (5) can then be applied straightforwardly [2,3] to the generation of Langevin-Kielich functions [4] which describe ensemble orientational averages of the optical Stark effect.

In this paper, we consider the thermodynamic and molecular dynamic characteristics of a torque of type

\[
T_k^{(\text{iso})} = -\mu^{(\text{iso})} \times E_k
\]

in which the optical Stark effect is accompanied by second harmonic generation. The energy corresponding to this torque is

\[
\Delta H_{\text{L}}^{(\text{iso})} = -\mu^{(\text{iso})} \times E_k
\]

and disappears when time averaged. In consequence, the Langevin description of orientational averages produced by the torque (8) cannot be implemented [5]. Use is made in this paper therefore of field applied molecular dynamics computer simulation (FMD) to investigate the orientational thermodynamics with rise transients and time correlation functions.
In Sec. 1, the torque \( \dot{\gamma} \) is worked out in the molecule fixed frame of water, assuming that the molecular polarisability is a pure real quantity of which can be diagonalised in the same frame \((1, 2, 3)\) as the principal molecular moments of inertia of water. Section 2 develops the theory with the use of FMD in an ensemble of 108 molecules interacting with a well-tested site-site potential. Section 3 presents results in terms of novel second order orientational transients of the type \( \langle \dot{\gamma}_1 \rangle, ..., \langle \dot{\gamma}_6 \rangle \), where \( \gamma \) is a unit vector in axes 1, 2, or 3. Transients were computed in this work for a number of pump laser frequencies corresponding with the frequencies of experimentally available pump lasers such as the various Nd:YAG systems and dye lasers, operating in the visible. The post transient steady state in the presence of the pump laser is described in Sec. 3 with appropriate time correlation functions. The discussion extends the argument to possible experimental verification of the theoretical and numerical indications obtained in this work.

1. The torque

In a diamagnetic molecule such as water, the polarisability \( \alpha \) is usually taken to be pure real [7, 8]. This is the approximation which holds in the transparent region of the water spectrum, but near optical resonance, the quantity \( \alpha \) becomes complex. Adopting a pure real alpha it is convenient to work out the torque \( \dot{\gamma} \) in the frame \((1, 2, 3)\) for the FMD computer simulation, which implements the torque [9-14] in the forces loop. The induced electric dipole moment \( \mu \) that worked out as a pure real quantity by multiplying the real polarisability tensor by the real part of \( E_d \), which frame \((1, 2, 3)\) becomes

\[
\begin{bmatrix}
\varepsilon_{1x} & \varepsilon_{1y} & \varepsilon_{1z} \\
\varepsilon_{2x} & \varepsilon_{2y} & \varepsilon_{2z} \\
\varepsilon_{3x} & \varepsilon_{3y} & \varepsilon_{3z}
\end{bmatrix}
\begin{bmatrix}
E_{1x}
E_{1y}
E_{1z}
\end{bmatrix}
\begin{bmatrix}
E_{2x}
E_{2y}
E_{2z}
\end{bmatrix}
= 0
\]

Here \( E_d \) is in frame \((X, Y, Z)\) has been multiplied by a rotation matrix of unit vectors, and the \((X, Y, Z)\) field components in frame \((X, Y, Z)\) are

\[
E_{1x}^X = E_{1x} \cos \theta - E_{1y} \sin \theta \\
E_{1y}^X = E_{1x} \sin \theta + E_{1y} \cos \theta \\
E_{1z}^X = 0
\]

The laser therefore propagates in axis \( Z \).

Consequently, the electric field components in frame \((1, 2, 3)\) are

\[
E_{1x}^1 = \varepsilon_{1x} E_d x + \varepsilon_{1y} E_d y + \varepsilon_{1z} E_d z \\
E_{1y}^1 = \varepsilon_{2x} E_d x + \varepsilon_{2y} E_d y + \varepsilon_{2z} E_d z \\
E_{1z}^1 = \varepsilon_{3x} E_d x + \varepsilon_{3y} E_d y + \varepsilon_{3z} E_d z
\]

Assuming that the real molecular polarisability is diagonal in frame \((1, 2, 3)\) the induced electric dipole moment in this frame is

\[
\mu_{1(\text{tot})} = \varepsilon_{1x} E_d x + \varepsilon_{1y} E_d y + \varepsilon_{1z} E_d z
\]

The torque components in axes 1, 2, and 3 are

\[
T_{11}^{(\text{tot})} = \varepsilon_{1y} E_d y - \varepsilon_{1z} E_d z \\
T_{12}^{(\text{tot})} = \varepsilon_{2y} E_d y - \varepsilon_{2z} E_d z \\
T_{13}^{(\text{tot})} = \varepsilon_{3y} E_d y - \varepsilon_{3z} E_d z
\]

These torque components are proportional to the square of the field electric component, resulting in second harmonic generation. The torque is therefore phase dependent. It is finally back-transformed into the laboratory frame through the rotation matrix

\[
\begin{bmatrix}
T_{x}^{(\text{tot})} \\
T_{y}^{(\text{tot})} \\
T_{z}^{(\text{tot})}
\end{bmatrix} =
\begin{bmatrix}
\varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz}
\\
\varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz}
\\
\varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{bmatrix}
\begin{bmatrix}
T_{x}^{(\text{rot})} \\
T_{y}^{(\text{rot})} \\
T_{z}^{(\text{rot})}
\end{bmatrix}
\]

and supplements the intermolecular torques computed in the forces loop of the algorithm Tera [9], whose code is given in the literature [14].

Note that the torque depends twice on the frequency of the applied pump laser, and its effect is superimposed in an intricate way upon the natural, or thermal, molecular dynamics of the ensemble.

2. FMD computer simulation

The FMD computer simulation was carried out in liquid water at 293 K, 1.0 bar, with 108 water molecules, using a time step of 0.5 fs. The site-site interaction potential was

\[
\phi_{ij} = \sum_{\alpha} \frac{46}{\varepsilon} \left( \frac{\sigma}{r_{\alpha}} \right)^6 - \left( \frac{\sigma}{r_{\alpha}} \right)^8
\]

\[
\varepsilon/k(\text{H-H}) = 21.1 \text{ K}; \quad \sigma(\text{H-H}) = 2.25 \text{ Å}; \\
\varepsilon/k(0-0) = 58.4 \text{ K}; \quad \sigma(0-0) = 2.80 \text{ Å},
\]

\[
q_{\text{water}} = 0.25 \text{ e}; \quad q_{\text{H}} = 0.00 \text{ e}; \quad q_{\text{O}} = -0.23 \text{ e},
\]

which was developed [15] from the ST2, and which has been compared with the MCYL water potential [16] and with water data over a considerable thermodynamic range [17]. An initial FCC water lattice was melted into the liquid over about 6,000 time steps, the attainment of a liquid like condition being monitored through various orientational averages such as

\[
\langle \dot{\gamma}_1 \rangle; \quad \langle \dot{\gamma}_2 \rangle; \quad \langle \dot{\gamma}_3 \rangle; \quad \langle \dot{\gamma}_4 \rangle; \quad \langle \dot{\gamma}_5 \rangle; \quad \langle \dot{\gamma}_6 \rangle
\]
over unit vectors in axes 1, 2, and 3 of frame (1, 2, 3). In the liquid condition first and higher odd order averages of this type fluctuate around zero, and second order averages fluctuate around the value $1/3$, fourth order around $1/5$, sixth order around $1/7$, and so on.

The torque (15) was applied in the liquid condition, and the levels of the transients measured at odd and even order. All odd order ensemble averages remained around zero after the torque was switched off, but the same trajectories produced easily discernible even order rise transients, which are illustrated in the results Sect. 3 of this paper. The time evolution of these transients depends on the square of the applied scalar electric field strength, $E_0^2$, of the laser, and also on the laser frequency. They eventually reach a saturation level, after which the sample is in a statistically stationary state suitable for the computation of time correlation functions [18] by running time averaging.

The $\text{FMM}$ simulation was carried out in four different laser frequencies corresponding with real pump lasers: 1) a $Q$ switched carbon dioxide laser, operating in the mid infra red at about 300.0 $\text{THz}$ (terahertz); 2) a mode locked neodymium phosphate glass laser at about 300.0 $\text{THz}$ in the visible; 3) a mode locked rhodamine 6G dye laser at about 500.0 $\text{THz};$ 4) a passively mode locked CW dye laser at about 600.0 $\text{THz}$. At each of these frequencies, rise transients at second order of the type

$$\langle \tilde{r}_x \tilde{r}_x \rangle; \quad \langle \tilde{r}_y \tilde{r}_x \rangle; \quad \langle \tilde{r}_y \tilde{r}_y \rangle; \quad \langle \tilde{r}_z \tilde{r}_z \rangle; \quad \langle \tilde{r}_x \tilde{r}_y \rangle; \quad \langle \tilde{r}_x \tilde{r}_z \rangle; \quad \langle \tilde{r}_y \tilde{r}_z \rangle$$

were computed as a function of $E_0$, building up a data bank available to the author. Now at odd and even order results are presented in Sect. 3 as plots of final level attained by the transient. It is precisely this kind of plot that would be analysed usually as a Langlevin/Kloeden function, but the latter is not accessible analytically because the energy (9) disappears over time, i.e. the average over many cycles of the phase of the pump laser disappears, in the same way that the $\text{aver}$ of $\text{cos}(x)$ and $\text{sin}(x)$ disappears.

The data bank also consists of time correlation functions worked out in the post transient state, with pump laser switched off. The examples used were

$$C_{ij}(t) = \langle \tilde{r}_i(t) \tilde{r}_j(0) \rangle \langle \tilde{r}_i(0) \tilde{r}_j(t) \rangle$$

the molecular angular momentum time correlation tensor;

$$C_{ij}(t) = \langle \tilde{r}_i(0) \tilde{r}_j(t) \rangle \langle \tilde{r}_i(t) \tilde{r}_j(0) \rangle$$

the orientational time correlation tensor of vector $\tilde{r}_i$ and

$$C_{ij}(t) = \langle \tilde{r}_i(t) \tilde{r}_j(t) \rangle \langle \tilde{r}_i(t) \tilde{r}_j(t) \rangle$$

the corresponding rotational velocity [18] time correlation tensor. These tensors are subcategorised into auto correlation functions (ACF's), with $i=j=\text{X}, \text{Y}, \text{O}, \text{Z}$; and cross correlation functions (CCF's) about the propagation axis, respectively $i=x, j=y$ and $i=x, j=y, z$. The running time average extended over 6,000 time steps, and ACF's and CCF's displayed to a maximum of 400 time steps, giving "good statistics". Component ACF's and CCF's are displayed to show that the sample is anisotropic in the presence of the laser, and also to illustrate in full detail the molecular dynamical characteristics of the second harmonic of the optical Stark effect. The details of transients and auto and cross correlation functions are markedly dependent on the diagonalised components $\tilde{x}_1, \tilde{x}_2, \tilde{x}_3$, of the real part of the polarisability of the water molecule. Unfortunately, the literature is inconclusive in this respect, even to the extent of knowing the signs of the anisotropies of polarisability. We have dealt with this question elsewhere, in the context of the optical Kerr effect [19]. For example, Khasanov and Kini [20] tabulate a number of estimates, roughly half of which give a positive anisotropy and the other half a negative anisotropy. This appears to be the state of the art for the water molecule, both experimentally and ab initio, and in this situation we have chosen to illustrate our methodology in this paper with one set of data, taken at random, from the careful experimental work [21] of Zeiss and Mathur. These authors propose

$$\tilde{x}_1 = 9.62; \quad \tilde{x}_2 = 9.26; \quad \tilde{x}_3 = 10.01$$

in atomic units. It should be noted carefully that the precise details of the time dependencies of our transients and correlation functions depend [19] on the values accepted for $\tilde{x}_1, \tilde{x}_2, \tilde{x}_3$. The values of time correlation functions in frame (1, 2, 3), the frame of the principal molecular moments of inertia.

Theoretical properties of water in the field free equilibrium state from our model potential are given in the literature [17] in terms of atom-atom pair distribution functions. Figure 1 is a distribution of the O-H, H-H, O-O of the water in the $\text{b}$ence and presence of a laser field at 600 THz. These were calculated over 8,000 steps. These pdf's give an impression of the (small) structural damage that the laser does to the H bond network and video animation [19] of the process shows that the main effect of the laser, approximately speaking, is to attempt to spin the molecules about the propagation axis, a process which occurs in competition with the background thermal dynamics. An extensive animation video of a similar process in reverse Zeeman effect [14] is available on request from the author. Clearly, disruption of the H bonding network is inevitable as the energetic laser radiation forces a torque with the appropriate proper tensor of each molecule in the ensemble. It has been shown [17] that H bonding in water can be described dynamically in terms of time correlation functions [18], and at each applied laser frequency in this work there are characteristic changes in these functions, implying that the H bonding network is indeed disrupted, both structurally (pdf's) and dynamically (time correlation functions).
The energy required to do this can be measured through the increase in the configurational part of the internal potential energy computed in the FMD simulation for the ensemble. This is defined by

$$\langle U \rangle \approx \left( \sum_{i<j} \phi_{ij} \right) + U_C$$

(21)

where the sum is over all atom-atom pairs for which the interatomic distance $r_{ij}$ is less than the cut-off distance $r_C$.

The correction $U_C$ is based on a uniform distribution of the molecules beyond this cut-off distance $r_C$. The configurational energy, calculated in the field-on steady state, was increased by about 20% by application of the laser.

When the laser is applied to the sample, there is an immediate increase in both rotational and translational temperature, so that there is a need for a thermostating subroutine. This is a temperature rescaling routine [14] whose effect is to drive down the temperature every $N$
time steps towards the input value. Since temperature is kinetic energy, temperature rescaling means that the linear and angular velocity vectors are scaled back digitally every N time steps. Our animations show this scaling back clearly as jumps in the absolute values of the vectors, jumps which maintain the molecular trajectories of velocity or angular velocity relative to each other. The 108 linear and angular velocity vectors were animated at equilibrium and through the rise transient. At the same time, animations of the orientational vectors show that there is little or no discernible effect of temperature rescaling on the relative orientation of each molecule, i.e. there are no sudden jumps in the 108 orientation vectors as the rescaling routine is applied. This is reflected in the second order averages of Fig. 2, where there are no discontinuities. At field applied equilibrium, the rescaling routine is maintained in action, because the laser is continuously pumping in energy to each molecule through each individual torque. We note that laser-on, steady state, time correlation functions and atom-atom pair distribution functions computed in this way show no discontinuities due to temperature rescaling.

Without this digital thermostat, the sample would heat up rapidly, the temperature would increase at each time step, and the pressure would increase, because we are using a constant volume simulation. It is highly recommended that the reader view our inverse Zeeman effect animation [14] (judged the best animation of the natural sciences category of the 1990 IBM Supercomputer Competition, and available from the author and IBM) to view directly the effect of temperature rescaling on the 108 velocity and angular velocity vectors. One animation in this context is worth a thousand words.

Digital rescaling can be applied every N time steps, and in Fig. 2 a comparison is given of the effect of rescaling every 50 time steps and every one time step for a 600 THz laser which has increased the configurational potential energy by 20%. There is little or no change in the correlation time of the rise transient, which attains the same field-on saturation level in both cases. Temperature rescaling every one time step is equivalent to maximizing the efficiency of the digital thermostat, so that the kinetic energy imparted by the external field is removed at its maximum rate. The latter may be defined as a maximum temperature dissipation rate. Clearly, however, the rise transient correlation time does not depend on temperature dissipation rate to any significant degree.

Finally, on the subject of temperature rescaling, it is noteworthy that where Langevin and Langevin-Kielich functions are definable, the saturation levels of the rise transients from FMD produce the analytical Langevin functions. This was first found in 1993 using a simple static electric field [9, 10], and has recently been verified for the optical Kerr effect [25], where the interaction energy is laser phase independent and forms generalised Langevin-Kielich (GLK) functions for the asymmetric top water molecule. These GLK functions check the FMD method independently.

The model used for water is a rigid molecule approximation, and we have not considered vibrational modes, which appear at 45 and 110 THz. It would be interesting to repeat the simulation with a flexible model of water. The literature contains a comparison [16] between the present model of water and the MCTY potential, in which a detailed evaluation was made of the (small) effect of vibration on the translational and rotational molecular time correlation functions.

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**Fig. 3a, b.** Comparison of rotational velocity autocorrelation functions at 600 THz with different time steps. --- i = j = X; --- i = j = Y; --- i = j = Z.  
(a) Time step = 0.5 fs.  
(b) Time step = 0.1 fs.
Finally, the runs at 600 THz were repeated with a time step of 0.1 fs, resulting in a better resolution of the details in the rise transients and time correlation functions. A comparison of runs at 0.5 fs and 0.1 fs at this frequency is given in Fig. 3.

3. Results. Rise transients and time correlation functions

The second harmonic of the optical Stark effect is accompanied by the development of even order rise transients, an example of which is shown in Fig. 2 at 650 THz using temperature raking every 50 time steps and every one time step. The transients at 100 THz and 500 THZ are similar in appearance to those at 600 THZ. These data show that an optical pump laser at any of these three visible frequencies would generate a frequency doubled optical Stark effect which could be measured as second order orientational rise transients, i.e. birefringence would be generated on a femtosecond time scale, now accessible experimentally in, for example, the optical Kerr effect [22, 23]. This provides a new experimental method for the measurement of the anisotropy of the polarisability, while at the same time probing the molecular dynamical and diffusion [10] nature of the ensemble under investigation. It can be seen clearly in Fig. 2 that the frequency (600 THZ) of the pump laser produces a well defined final level in the second order rise transients. A useful check on the FMD procedure is that the same trajectories produce vanishing first order averages, and there are no first order transients.

The second order transients clearly show oscillations at frequency corresponding so that of the laser. For example, at 30 THZ (i.e. g, the inverse of 0.033 ps. These 0.033 ps oscillations appear clearly in all nine second order transients, betraying the direct influence of the 30 THZ carbon dioxide pump laser. This is a second useful check on the FMD method.

Rise transient oscillations were first derived analytically [10] and their existence later confirmed computationally [24], however, this work appears to be the first evidence for transient oscillations generated in the frequency doubled optical Stark effect by intra red and visible frequency, intense, electromagnetric pump fields of a type accessible experimentally "off the shelf" (e.g. Nd:YAG systems and carbon dioxide lasers).

When the frequency of the pump laser is reduced to zero in the FMD simulation the second order rise transients show oscillations more typical of those known already from static electric fields [24]. At zero pump frequency the role of the X and Z components of the vectors $\epsilon_1, \epsilon_2$ and $\epsilon_3$, interchange, i.e. the ordering process results in anisotropy not about the Z axis, but about the X axis. This result was produced by changing nothing in the FMD source code except the input parameter for pump laser frequency, and appears to show that ordering in the conventional (frequency independent) optical Stark effect [1] is about an orthogonal laboratory frame axis to that of the frequency doubled optical Stark effect investigated in this paper. This particular result is confirmed in the analysis of the molecular dynamical properties of the water ensemble in the post-transient state in which second order orientational averages have reached their final levels. The sequence of results for the correlation functions is discussed in order of increasing pump laser frequency. There is space here for only a few illustrations from the complete data bank, available from the author. Each set of adi-
correlation functions (ACF's) is followed by one of the equivalent CCF's in order to illustrate the variety of behaviour observed in this work. A complete set of time correlation functions at the 30 THz infra red pump laser frequency is illustrated in Figs. 4-9, namely: the orientational, angular momentum and rotational velocity ACF's and CCF's at this frequency. The field off equivalents of the ACF's are available in the literature [16] and the field off CCF's vanish.

Orientational ACF components (see Sect. 2) were computed for the pump laser frequencies zero, 30, 300, 500, and 600THz. From 30 to 600THz applied laser frequency the Z component has a clearly different time dependence from those of the X and Y components, which evolve on closely similar lines. There is a variety of behaviour, markedly dependent on the pump laser frequency. It is interesting to note in Fig. 4 at 30.0 THz the presence of 0.03 ps oscillations, showing the influence

Fig. 6. As for Fig. 4, angular momentum c.c.'s

Fig. 7. As for Fig. 5, angular momentum c.f.'s

Fig. 8. As for Fig. 4, rotational velocity a.c.'s

Fig. 9. As for Fig. 5, rotational velocity c.f.'s
in the water molecule dynamics of a 28 THz pump laser. These are very short, inside a few ps, and the anisotropic velocity correlation in the frequency doubled optical Stark effect due to the unusual operation of a CCF is probably distinguishable from noise at 500, 600 and 800 THz. Now that the Fourier transform of the orientational ACF represents the anisotropic velocity correlation in water is related to the dielectric loss spectrum (18) and is therefore observable experimentally.

Similarly, the orientational ACF of $\hat{C}_\theta$ (the orientational velocity ACF) is related to the far infrared power absorption coefficient (18) and sequences of rotational velocity ACFs of CCF's were compared. At zero pump laser frequency the X component is completely independent of the other two in its time evolution, whereas for applied laser frequencies from 30 to 600 THz, the Z component is the one that is independent. The other, the same type of "anisotropy" seen in the rise of the Z component, the details of the excitations are clearly determined by the pump laser frequency, implying that the far infrared spectrum would also be determined by the characteristics of the pump laser: Very weak far infrared excitations appear in the inverse of the pump laser frequency spectrum superimposed on the X and Y components. The power 0.02 ps (versus 300 THz) near the limit of our time resolution, which for these data is two time-steps, or 0.06 ps, i.e., 0.01 ps. For this reason a run at 600 THz was repeated with a time step of 0.01 ps, with the result shown in Fig. 3. The accompanying rotational velocity CCF's of the data set display a variety of behavior and are clearly distinguishable from noise, with the possible exception of the Z component at zero pump laser frequency. It is notable that the CCF's are sometimes in a "mixed image pattern", as at 30 THz, and sometimes positive at $r = 0$ and negative at $r = t$ of the range of values at $r = t$ (600 THz). At 300, 400, and especially at 600 THz (time step of 0.01 ps), incoherently resolved excitations appear at 0.0356, 0.0369, and 0.0379 ps, which are the principal structure of the component CCF's. Reducing the time step to 0.01 ps at 600 THz resolves the 0.0369 ps incoherence

For both orientational and rotational velocity ACFs and CCF's it is clear that the complicated interaction of laser and ensemble dynamics (Orientational aliasing (18)) in the frequency doubled optical Stark effect results in the development of anisotropy, which can be measured through orientational functions, distinct from infrared and far infrared measurements. When dealing with the magnetic properties of ensembles it is useful to recall that the purity inversion (P) and time reversal (T) symmetries of the magnetic dipole moment are exchanged as those of angular momentum: (P positive, T negative). One is in general proportional to the other through a scalar quantity, whose presence reduces to a vector under center. In NMR, for example, it is the nuclear gyromagnetic ratio in ESR it is the electronic counterpart. It follows that the angular momentum time coordinate tensor $C_{\theta}$ is also a symmetric double - point vector. The sequence for $C_{\theta}$ corresponding to these for $C_{\theta}$ and $C_{\theta}$(ACF's and CCF's respectively of the tensor $C_{\theta}$) shows that there is a unitary transformation between the results for zero frequency pump laser and the other results, which range from 30 to 600 THz. The details of the time evolution of the components of $C_{\theta}$ depend on the applied laser frequency. As the pump laser frequency is increased via the frequency doubled optical Stark effect received excitations at 0.0369, 0.0379, and 0.0380 ps can be seen more in these correlation functions, but this visualization does not change the presence of the dipole moment, as for their orientational velocity counterparts. All components at 600 frequencies appear incoherently mixed into one vector, but the CCF's, which are the product of the pump laser (21) and the anisotropic, or vacuum, part of the molecular polarizability (28, 29). An interesting CCF's of $C_{\theta}$ was found in terms of the X and Y components, analogous to the Z components of the pump laser. The strongest cross correlation is at 30 THz (Fig. 3), which is an order of magnitude greater than the others, compared at zero frequency, and at 300 to 600 THz. The latter are weak but nevertheless direct, and characteristic of the frequency doubled optical Stark effect.

4. Discussion

In this paper we have carried out what appears to be the first direct measurement of the frequency doubled optical Stark effect, and have shown that even though the torque (13) is time dependent, second order time transients, with times in the 0.01 ps range, occur in response to the applied pump laser. These cannot be analyzed with Langmuir Klein functions (21), however, because the functions are only defined by the PDM (22) and PDM's, of which the early ones (PDM (22)) that determine Langmuir functions and Langmuir Klein functions exist, the PDM results are in good agreement. This finding has been confirmed recently (23) in an PDM simulation of the optical Stark effect, where the Langmuirian and torque are time independent. The existence of second and higher even order orientational rise transients has also been shown by PDM in a recent simulation of the infrared Faraday effect (23). In both the infrared Faraday effect and the frequency doubled optical Stark effect, the existence of transitions signals that of transient hysteresis. The latter is observable in principle by applications of complex theory to neutron scattering. The recycled laser excitation

In order to measure the effect of the torque (13) of the frequency doubled optical Stark effect on the far infrared and dielectric spectrum, an experimental configuration has been designed to measure for short high density pump laser pulses and the measurement rate of a spectrometer. The experimental Faraday spectra are required to measure a far infrared region in the milliwatt to microwatt range, as the contribution-
with a medium intensity pump laser pulse. It appears entirely possible, with ingenuity, to devise a design for the experimental investigation of the effect of pump laser pulses on a far infra red spectrum thus bringing together two major fields of investigation: far infra red and non-linear spectroscopy and optics. Interpretation of such spectra would rely, as in this paper, on FMD methods, which are applicable to any type of molecular dynamic source code in which a torque is computed in the forces loop. Such a procedure would form a point of contact between FMD and experimental data, the other point of contact, clearly, being femtosecond measurements of birefringence, or by Kramers Kronig transform, anisotropy in power absorption coefficient of a probe laser. The latter is implemented, as usual, in addition to pump laser pulses, and the two lasers are used to measure rise transients directly on a femtosecond time scale [23]. This type of methodology for the customary, frequency independent, optical Stark effect, is well developed experimentally [31–33], usually in the context of quantised optical Stark splitting in gases. This paper has shown that there is also a frequency doubled optical Stark effect, producing second order rise transients, birefringence and anisotropy in liquids as well as gases. Our treatment has necessarily been confined however to classical dynamics.

Finally, we note that the simulations have been performed with the equivalent of very intense lasers simply in order to isolate the existence of the effects reported in this paper from background noise. Experimentally, pump probe methods use a sub-picosecond pulse of intense laser radiation followed at an interval by a probe. These methods are used with efficient stimulants to remove any heating effects. The power of the pump laser pulse can reach the megawatt level, yet the liquid sample does not evaporate or heat because: 1) the pulse lasts for less than a picosecond; 2) the stimulants used experimentally are efficient dissipators of any heating effects. It is clear that the frequency doubled optical Stark type birefringence anticipated in this FMD simulation is a bi-axial birefringence, i.e. the refractive index in the pump laser's propagation axis, Z, becomes different from those in the orthogonal X and Y axes. Therefore the refractive index also becomes different in the Z axis from the field off value. This occurs at double the frequency of the pump laser, so that these two characteristics features isolate the effect. In general the refractive index is made up of a weighted combination of the second order orientational averages observed in the simulation (Fig. 2), and is also related to the measurable power absorption coefficient through the Kramers Kronig equations. The experiment can therefore proceed by measuring, at twice the pump laser frequency, the change in the power absorption coefficient produced in the sample by the pump laser with a probe laser appropriately timed, tuned and detected. The contemporary technology for this experiment is well established in the probe being timed to follow the pump at a convenient interval with optical delay lines, consisting of beam splitters and mirrors as in the sub-picosecond optical Kerr effect [23]. The latter is usually detected however by a change in the plane of polarisation of the probe. In the frequency doubled optical Stark effect, the probe need not be polarised.

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References