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FREQUENCY DEPENDENT ELECTRIC POLARISATION DUE TO OPTICAL RECTIFICATION: EFFECT ON FAR INFRA RED BANDSHAPES.

by
M. W. Evans,
Theory Center,
Cornell University,
Ithaca,
NY 14853,
U.S.A.,
and
G. Wagnière,
Physical Chemistry Institute,
University of Zurich,
Winterthurerstrasse 190,
Zurich, CH 8057,
Switzerland.

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Abstract

The symmetry principles governing the non-linear interaction of intense laser radiation with molecular ensembles show that dynamical interaction phenomena exist in the ensemble even though the induced frequency dependent polarisation be purely imaginary, and unobservable in the static limit. An example is computer simulated in the S enantiomer of bromochlorofluoromethane, showing clear effects on the orientational and rotational velocity correlation functions and by Fourier transform, the dielectric and far infra red spectra. Conditions are suggested for its experimental observation and order of magnitudes calculated for the appropriate mediating tensors.

Introduction

The interaction of intense electromagnetic radiation with molecular ensembles may be described using time dependent perturbation theory, a quantum mechanical approach which has led

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recently to the discovery of several new birefringence effects, exemplified by the forward (1-3) and inverse (4) magnetochiral effects. A symmetry classification of these effects has recently been proposed (5-9) in terms of group theoretical statistical mechanics (g.t.s.m.), and its three principles (10-12). This classification indicates the presence of several other analogous phenomena (13-16), prominent among which is electric rectification (17), a phenomenon of non-linear optics which is treated in this letter with molecular dynamics computer simulation. This simulation method is based on the incorporation of appropriate extra torques in the forces loop of a standard molecular dynamics program. It has been shown, furthermore, that these torques may contain a real component (18) when the corresponding induced polarisation is purely imaginary (4), implying that there is a frequency dependent dynamical effect of the intense laser field even when there is no real part to the complex polarisation. An example of a hidden variable dynamical phenomenon in the electric rectification effect is investigated here with computer simulation in the S enantiomer of bromochlorofluoromethane, a chiral ensemble. It is found that the real component of the torque gives rise to clear spectral effects, which can be measured experimentally, for example in the far infra red and higher frequency regions of the electromagnetic spectrum.

1. Frequency Dependent Polarisation due to Optical Rectification.

The quantum mechanical expression for optical rectification has been given explicitly by Ward (19). This expression for the purely real, static, electric polarisation induced to second order by the radiation consists of double sums over all eigenstates of the unperturbed molecular system. The individual terms in these sums contain in the numerators products of matrix elements of the system-field interaction. In the denominators appear the transition energies of the system, the frequency of the radiation field, and appropriate damping factors (19). If one is primarily interested in the symmetry properties of the effect, it is therefore sufficient to consider the numerators, which are of general form

$$\underset{\sim}{\mu}(\underset{\sim}{\mu}' \cdot \underset{\sim}{E}_-)(\underset{\sim}{\mu}'' \cdot \underset{\sim}{E}_+) \qquad -(1)$$

where $\underset{\sim}{\mu}$, $\underset{\sim}{\mu}'$ and $\underset{\sim}{\mu}''$ designate matrix elements of the electric dipole operator and $\underset{\sim}{E}_-$, $\underset{\sim}{E}_+$ are electric field vectors complex conjugate to each other. Upon isotropic averaging, expression (1) splits up into a real factor pertaining to the molecular susceptibility multiplied by a field factor

$$(\underset{\sim}{\mu} \cdot \underset{\sim}{\mu}' \times \underset{\sim}{\mu}'')(\underset{\sim}{E}_- \times \underset{\sim}{E}_+) \qquad -(2)$$

This field factor, $\underset{\sim}{E}_- \times \underset{\sim}{E}_+$, either vanishes if the radiation is linearly polarised, or is imaginary in the case of circular polarisation. Even in an optically active fluid, the induced electric d.c. polarisation is therefore not directly observable.

However, the polarisation induced in the individual molecules couples to the electromagnetic field, resulting in a torque of generic form

$$\langle T_{q_k} \rangle = \langle \beta_{ijk} E_j E_k \times E_j \rangle \qquad -(3)$$

where β_{ijk} has the units of the molecular hyperpolarisability tensor, with 27 scalar elements in general. This torque contains real contributions which do not average out in the ensemble (18). Its dynamic influence may be interpreted on the basis of group theoretical statistical mechanics (10-12).

The tensor $E_j E_k$ (with nine scalar elements in general) may be decomposed into a trace (rank zero tensor) component $D^{(0)}$ under R_3, an axial vector (rank one tensor) transforming as $D^{(1)}$ and a symmetric rank two tensor, transforming as

$$\langle \underset{\sim}{T_q} \rangle_0 = \langle (\underset{\sim}{\beta}\, \underset{\sim}{E}_- \cdot \underset{\sim}{E}_+) \times \underset{\sim}{E}_\pm \rangle \qquad -(4)$$

$$\langle \underset{\sim}{T_q} \rangle_1 = \langle (\underset{\sim}{\beta}\, \underset{\sim}{E}_- \times \underset{\sim}{E}_+) \times \underset{\sim}{E}_\pm \rangle \qquad -(5)$$

$$\langle \underset{\sim}{T_q} \rangle_2 = \langle (\beta\, \underset{\sim}{E}_- \underset{\sim}{E}_+) \times \underset{\sim}{E}_\pm \rangle \qquad -(6)$$

Assuming a plane wave as described by expression (8) below, we notice that if the radiation is linearly polarised and $\underset{\sim}{E}_\pm$ is

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real, then $\langle \underset{\sim}{T_q} \rangle_0$ will be real, $\langle \underset{\sim}{T_q} \rangle_1$ will vanish and $\langle \underset{\sim}{T_q} \rangle_2$ may be made to vanish by an appropriate choice of the laboratory coordinate system. If the radiation is circularly polarised, then $\underset{\sim}{E}_- = \underset{\sim}{E}_+^*$ is complex. Both $\langle \underset{\sim}{T_q} \rangle_0$ and $\langle \underset{\sim}{T_q} \rangle_1$ will be complex and contain real contributions; $\langle \underset{\sim}{T_q} \rangle_2$ will vanish for a circularly polarised wave as given by expression (4).

The torque $\langle \underset{\sim}{T_q} \rangle$ in a circularly polarised laser thus has both real and imaginary parts. In consequence, the real part of a torque component such as $\langle (\underset{\sim}{\beta} \underset{\sim}{E}_-^{(L)} \times \underset{\sim}{E}_+^{(L)}) \times \underset{\sim}{E}_\pm^{L,R} \rangle$ has a dynamical effect on the ensemble which can be observed numerically in the time correlation functions and experimentally in their Fourier transforms revealed as measurable spectra. It is a dynamical effect because the induced polarisation vanishes at zero frequency.

2. Computer Simulation

Computer simulation of this dynamical effect proceeds as outlined in the appendix of ref. (18). In the simulation, we have illustrated the effect by confining attention to the torque component

$$\langle \underset{\sim}{T_q} \rangle_1 = \langle (\underset{\sim}{\beta} \underset{\sim}{E}_-^L \times \underset{\sim}{E}_+^L) \times \underset{\sim}{E}_+^L \rangle \quad - (7)$$

where (R) and (L) denote right or left circularly polarised, and the + or − signs denote complex conjugates of the field (17). This gives the four possibilities

$$\underset{\sim}{E}_-^L = E_0(\underset{\sim}{i} + i\underset{\sim}{j})\exp(-i\theta_L) \; ; \; \underset{\sim}{E}_-^R = E_0(\underset{\sim}{i} - i\underset{\sim}{j})\exp(-i\theta_R)$$

$$\underset{\sim}{E}_+^L = E_0(\underset{\sim}{i} - i\underset{\sim}{j})\exp(i\theta_L) \; ; \; \underset{\sim}{E}_+^R = E_0(\underset{\sim}{i} + i\underset{\sim}{j})\exp(i\theta_R)$$

$$- (8)$$

where $$\theta_L = \omega t - \underset{\sim}{\kappa}_L \cdot \underset{\sim}{r} \; ; \; \theta_R = \omega t - \underset{\sim}{\kappa}_R \cdot \underset{\sim}{r} \quad - (9)$$

are the phases in IUPAC convention.

The phases are approximated by

$$\theta \doteqdot \theta_L \doteqdot \theta_R = \omega t \qquad - (10)$$

and incorporating the real part of the torque into the forces loop of the program TETRA (20), coded for 108 molecules of (S bromochlorofluoromethane, a chiral ensemble. The torque (7) involves independent scalar elements of the molecular [21] hyperpolarisability in the correct C_1 symmetry, which in the absence of known experimental or ab initio numerical data were coded in from data on methane. This procedure was adopted only TO ILLUSTRATE THE PRESENCE OF THE EFFECT in one of the simplest available chiral ensembles, and further work would involve the ab initio computation of all molecule fixed frame, scalar elements using a modofication of a package such as HONDO (22).

The molecules interacted with a site site potential (16, 23)

$$\phi_{ij} = \sum\sum\left(\left\{4\epsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\right\} + \frac{q_i q_j}{r_{ij}}\right) \quad -(11)$$

$\sigma(C-C) = 3.4$ Å $\qquad \epsilon/k(C-C) = 35.8$ K

$\sigma(H-H) = 2.8$ Å $\qquad \epsilon/k(H-H) = 10.0$ K

$\sigma(F-F) = 2.7$ Å $\qquad \epsilon/k(F-F) = 54.9$ K

$\sigma(Br-Br) = 3.9$ Å $\qquad \epsilon/k(Br-Br) = 218.0$ K

$\sigma(Cl-Cl) = 3.6$ Å $\qquad \epsilon/k(Cl-Cl) = 158.0$ K

and their rotational and translational equations of motion were integrated with a time step of 50.0 fs on the CNSF IBM 3090-6S. The orientation and rotational velocity auto-correlation functions (a.c.f.'s) of the ensemble were evaluated in the field applied steady state using two field frequencies of 10.0 THz and 1.0 THz respectively. These are roughly similar to the frequency of a Q-switched CO_2 laser. The correlation functions were evaluated in contiguous segments with running time averaging. The laser fields employed were powerful enough to show clearly the presence of changes in the time dependence of correlation functions (and thus in the frequency dependence of bandshapes) and were energetically equivalent to about 25 kJ per mole at a temperature of 293 K at 1 bar.

3. Results : Dielectric and far Infra red Spectral Effects due to Optical Rectification.

We have simulated the orientational a.c.f. of the permanent molecular dipole moment for the S enantiomer and racemic mixture. This is defined by

$$C_1(t) = \langle \mu_{0i}(t)\mu_{0j}(0)\rangle / \langle \mu_0^2 \rangle \quad - (11)$$

where < > denote ensemble averaging, and where μ_0 denotes the permanent molecular electric dipole moment . In this field-free equilibrium there are no orientational cross correlation functions (c.c.f.'s), which are off diagonal elements of (11). The same c.f. was simulated for applied fields of 1.0 THz and 10.0 THz, each in the S enantiomer. At the lower frequency, anisotropy in the orientational a.c.f. components was observed for a laser beam propagating in the Z axis of (X, Y, Z). This was accompanied by the development of off diagonal c.c.f. elements of orientation. At the higher frequency the anisotropy was lessened considerably, but the time dependencies of the a.c.f. elements were clearly different from the average at field-free equilibrium. Four off diagonal c.c.f. elements of orientation were detected in the field applied steady state.

The rotational velocity a.c.f. at field-free equilibrium in the S enantiomer, defined by

$$C_2(t) = \langle \dot{\mu}_{0i}(t)\dot{\mu}_{0j}(0)\rangle / \langle \dot{\mu}_0^2 \rangle \quad - (12)$$

was simulated as the Fourier transform of the far infra red bandshape. Results were obtained in the steady state, with an applied 1.0 THz field, and 10.0 THz field. There was a clear bandshape effect at both frequencies, at 10.0 THz the a.c.f. becomes highly oscillatory, and at the lower frequency the development was observed of interesting asymmetric c.c.f. elements, reminiscent of those simulated by Evans and Heyes { 24 } in the context of couette flow. The rotational velocity a.c.f. is essentially part of the Fourier transform of the far infra red frequency spectrum of the ensemble (power absorption coefficient and frequency dependent refractive index), and in consequence, time resolved techniques and powerful laser pulse trains can be used to evaluate experimentally the effect of electric rectification, a non-linear "hidden variable" dynamical effect in the far infra red and higher frequencies into the visible and beyond. Right and left circularly polarised pulse trains from a power laser are sent down the two arms of a Rayleigh interferometer { 8 }, and the sensitivity of the instrument is used to measure the refractive and absorption index changes due to the various hidden variable effects exemplified in this paper. The sensitivity of this instrument can reach one part in one hundred million under practical conditions. The spectral resolution of the new "hidden variable" effect is achieved with a combination of Michelson and Rayleigh interferometers, the former being used to analyse the frequency dependence of the axial birefringence of the hidden variable effect, the latter as a sensitive measuring instrument of small differences in refractive index. The combined interferogram at the detector is made up of the Michelson interferogram, as in a contemporary Bomem, Nicolet, or Bruker design, and the Rayleigh interferogram, a Fraunhoffer pattern from the input slits of the Rayleigh interferometer. The same set up can be used to detect magnetochiral birefringence, and, with a piezzo-optic modulator, circular dichroism caused by hidden variable dynamics.

4. Molecular Property Tensors and Order of Magnitude Estimates.

In order to estimate the order of magnitude of the molecular property tensor mediating the effect of the conjugate product

$$\underset{\sim}{\Pi} = \underset{\sim}{E}_{+}^{L} \times \underset{\sim}{E}_{-}^{L} = -\underset{\sim}{E}_{+}^{R} \times \underset{\sim}{E}_{-}^{R} = 2E_0^2\, i\, \underset{\sim}{k} \quad -(13)$$

on spectral features in the dielectric and far infra red, we use standard semi-classical theory { 25 } with an interaction hamiltonian

$$\Delta H = -\frac{1}{2}\alpha_{\alpha\beta}\Pi_{\alpha\beta} \qquad -(14)$$

The axial conjugate product vector $\underset{\sim}{\pi}$ is negative to motion reversal T and positive to parity inversion P, and is equivalent to a second rank antisymmetric polar tensor. A real, scalar, hamiltonian is obtained from the tensor ($\pi_{\alpha\beta}$) by contraction with another T negative, P positive, antisymmetric dynamic polarisability tensor (25)

$$\alpha_{\alpha\beta} = \alpha'_{\alpha\beta} - i\,\alpha''_{\alpha\beta} \qquad -(15)$$

The hamiltonian (14) is therefore

$$\Delta H = -\alpha''_Z E_0^2 \qquad -(16)$$

where α''_Z is the orbital/spin electronic polarisability, proportional to the sum of orbital and spin electronic angular momenta

$$\alpha''_Z = \gamma_\pi \left(L_Z + 2.002\, S_Z \right) \qquad -(17)$$

From the time dependent Schrodinger equation

$$\alpha''_{\alpha\beta} = -\alpha''_{\beta\alpha}$$

$$= -\frac{2}{\hbar} \sum_{j \neq n} \frac{\omega}{\omega_{jn}^2 - \omega^2} \mathrm{Im}\left(\langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle \right) \qquad -(18)$$

for a transition from state n to j at the frequency

$$\omega_{jn} = \omega_j - \omega_n \qquad -(19)$$

where $\mu_{\alpha,\beta}$ are electric dipole moments.

The product $\underset{\sim}{\pi}$ is clearly independent of the phase of the electromagnetic field, but is generated by a frequency dependent electromagnetic field. The time dependent Schrodinger equation must be used, therefore, to find an expression for the T and P negative molecular property tensor χ_{ij} that mediates the induction of a dynamic molecular dipole moment μ_i by the conjugate product π_j :

$$\mu_i = X_{ij}\pi_j + \dots \qquad \text{— (20)}$$

Elementary time dependent perturbation theory expresses the tensor in the form

$$X_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\langle n|\mu_\alpha|j\rangle\langle j|\alpha_\beta|n\rangle}{\omega_{jn}} \qquad \text{— (21)}$$

where α_β is given in eqn. (18).

Note that this is T and P negative, and for an electronic vector polarisability $\underset{\sim}{\alpha}$ of the order 10^{-38} J^{-1} C^{2} m^{2} ; a dipole moment of the order 10^{-30} C m; and for a transition frequency of the order 10^{15} rad s^{-1} ; its order of magnitude is about 10^{-51} C^{3} m^{3} J^{-2} , about the same as that of the first electric hyperpolarisability. However, $X_{\alpha\beta}$ differs from the customary γ_{ijk} because the latter is observable in achiral and chiral ensembles, and has a non-vanishing static component. The new dynamic property tensor $X_{\alpha\beta}$ appears only in chiral ensembles because of parity conservation. If observed in achiral ensembles there would be parity non-conservation, itself an important effect.

Finally we express the analogous (4) inverse Faraday effect (experimentally observed magnetisation due to $\underline{\pi}$) through the closely related molecular property tensor Y_{ij} :

$$m_i = Y_{ij}\pi_j + \dots \qquad \text{— (22)}$$

where m_i is the magnetic dipole moment due to π_j . Perturbation theory gives the result

$$Y_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\langle n|m_\alpha|j\rangle\langle j|\alpha_\beta|n\rangle}{\omega_{jn}} \qquad \text{— (23)}$$

which is similar to Wagniere's eqn. (18) of ref (4) for the paramagnetic contribution to the inverse Faraday effect, in which equation the equivalent of spin polarisability is expressed hrough the cross product of electric dipole moments.

Eqns. (21) and (23) compare directly the new effect this paper and the well known inverse Faraday effect. The latte occurs in all ensembles, because the symmetry of π_j is the same as that of the T negative, P positive magnetic dipole mome m_i, so that Y_{ij} is P positive, T positive. The inverse Faraday effect is much smaller than the new effect of eqn (21), implying that the latter is easily observable by using, for example, time integrated transient far infra red Fourier transform spectroscopy, with pulses of circularly polarised Nd:YAG laser radiation to generate π_j. The induced dynamic polarisation is picked up as a dielectric loss in a capacitance/inductance circuit of the type used in non-linear dielectric spectroscopy (26), for example, with the strong electric field replaced by the pulsed and circularly polarised Nd:YAG pump laser.

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