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The Role of Net Angular Momentum in Pump/Probe Spectroscopy: Absorption, Refringence, Scattering, and Nuclear Resonance

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Applied net angular momentum (**J**) has the same role in spectroscopy as applied magnetic flux density (**B**), both having the same parity and motion reversal symmetry. This simple statement appears to have profound consequences, especially in the context of nonlinear optics, where **J** can be generated by a pump laser. These are explored for pump/probe spectroscopy involving absorption, refringence, and scattering in the semiclassical Rayleigh theory. It is shown that there are phenomena analogous to those induced by **B**, exemplified by the spin chiral class of circular and axial birefringence/dichroism (analogues of the Faraday and Wagnière/Meier effects produced by **B**); and pump laser-induced Rayleigh/Raman optical activity (analogues of scattered optical activity induced by **B**). Nuclear effects of the pump laser-induced **J** are introduced as nuclear electromagnetic resonance (NER). © 1991 Academic Press, Inc.

INTRODUCTION

It is well known that magnetic flux density **B** and net angular momentum (**J**) have the same parity (P) and motion reversal (T) symmetries. It appears clear, therefore, that **J** can play the role of **B** in spectroscopy and optics: on the surface a simple enough statement, but one which appears to have profound consequences for modern physics (*1*). There have been a few papers on the role of **J** in the relativistic context of ether drag, catalyzed by J. J. Thompson (*2*) a few years after the first Michelson/Morley experiment. Thompson considered translational ether drag, and his result was arrived at independently by Fermi (*3*). Much later, rotational ether drag was observed meticulously by R. V. Jones (*4*) and analyzed relativistically by Player (*5*). Recently, Barron has briefly mentioned the possibility of optical phenomena induced by **J** (*6*), and the present author, inspired by this remark, has given a nonrelativistic (*7*) and relativistic (*8*) theory of circular and axial birefringence induced by net angular momentum induced mechanically by ultracentrifuging a rod in the manner of R. V. Jones (*4*).

In this paper, we provide a fairly detailed first theory of absorption, refringence, scattering, and nuclear resonance phenomena induced by the conjugate product

$$\boldsymbol{\pi} = \frac{\partial \mathbf{E}^{+}}{\partial t} \times \mathbf{E}^{-} \tag{1}$$

of the electric field intensity (**E**) of the pump at an angular frequency ω in radians per second. In this equation $\mathbf{E}^{+}$ is the positive complex conjugate of the classical Maxwellian electromagnetic field, and $\mathbf{E}^{-}$ is the negative complex conjugate, defined in more detail in Eqs. (16)–(18) of this paper. Note that the product (1) has the

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positive P and negative T symmetries of angular momentum but has the units of (volts/meter)^2 radians second^{-1}. It is denoted "effective pump laser angular momentum" (π), and is the basis of nonlinear optical rectification effects (*9–13*).

In Section 1, the basic points of the semiclassical theory are summarized, following Barron's standard treatment (*14*) of work by the Buckingham school. This sets up equations for subsequent sections of this paper which deal with a few of the many optical phenomena induced by π of the pump and measured by a probe laser. The latter can be circularly, plane, or unpolarized, absorbed, refracted, scattered, or reflected. In Section 2, the frequency dependent circular birefringence and dichroism due to π is introduced, in a manner akin to the theory of the Faraday effect. In Section 3, equations are given for the accompanying frequency dependent axial birefringence and dichroism (15–20), and the order of magnitude compared with the effect of Section 2. In Section 3, the theory of the effect of π on Rayleigh and Raman optical activity (21–25) is given, in close analogy with the theory of magnetic Rayleigh and Raman optical activity. This is optically active and frequency dependent scattering of the probe laser stimulated by π of the pump laser, again a novel type of spectroscopy. Finally in Section 4, a short description is given of another consequence of π, nuclear electromagnetic resonance (NER), akin to the well known NMR effect of $\mathbf{B}$. The resonance condition is defined through the effect of π on the nuclear spin characteristics of the molecule being investigated with the pump/probe system.

Clearly these are only a very few of the phenomena to be expected from the seemingly simple realization that π can play the role of $\mathbf{B}$ in molecular and atomic spectroscopy. There are other fundamental effects of the pump laser, akin, for example, to Zeeman splitting. All of these new techniques are potentially interesting in fundamental physics, for example, in the search for parity violation (*26*), and useful for the analytical laboratory. The treatment in this paper is in the nonrelativistic approximation, but, clearly, a pump laser can spin a molecule at relativistic angular momenta, requiring a fuller treatment than offered here. In contemporary understanding, the complete evaluation of pump laser angular momentum effects requires relativistic quantum field theory with unification of the electromagnetic and weak forces.

1. SEMICLASSICAL THEORY IN THE NONRELATIVISTIC APPROXIMATION; RAYLEIGH MODEL OF REFRINGENT SCATTERING

Much of the theory of this paper follows the standard work by Barron (*14*), which developed the Rayleigh theory of refringent scattering for general application in terms of complex, dynamic, molecular property tensors, whose origins are firmly rooted in quantum mechanics.

The interaction of a molecule with a radiative field is based on such work as that of Placzek (*27*), Born and Huang (*28*), and Buckingham (*29*), and to first order in the electric and magnetic components of the field, it can be expressed, following Ref. (*14*), as the induced dipole moment

$$\mu_i = \alpha'_{1ij}E_{j0} + \frac{\alpha''_{1ij}}{\omega}\dot{E}_{j0} + \alpha'_{2ij}B_{j0} + \frac{\alpha''_{2ij}}{\omega}\dot{B}_{j0} + \frac{1}{3}A'_{ijk}E_{jk0} + \frac{1}{3}\frac{A''_{ijk}}{\omega}\dot{E}_{jk0} + \cdots \qquad (2)$$

Here α'_{1ij} and α''_{1ij} are the real and imaginary components of the complex molecular dynamical polarizability, and α'_{2ij} and α''_{2ij} are the equivalents for the Rosenfeld tensor. The problem of origin dependence is circumvented, following Buckingham's method, by the use of the electric dipole/electric quadrupole tensor A_{ijk}, which premultiplies the gradient of the electric field component of the electromagnetic (radiation) field.

We extend Eq. (2) with a second-order Taylor expansion in the electric field **E** and its time derivative $\dot{\mathbf{E}}$

$$\mu_i = \alpha'_{1ij}E_{j0} + \frac{\alpha''_{1ij}}{\omega}\dot{E}_{j0} + \frac{1}{2!}\left[\beta_{1ijk}(E_jE_k)_0 + \frac{\beta_{2ijk}}{\omega}(E_j\dot{E}_k)_0 + \frac{\beta_{3ijk}}{\omega}(\dot{E}_jE_k)_0 + \frac{\beta_{4ijk}}{\omega^2}(\dot{E}_j\dot{E}_k)_0\right] + \alpha'_{2ij}B_{j0} + \frac{\alpha''_{2ij}}{\omega}\dot{B}_{j0} + \frac{1}{3}A'_{ijk}(E_{jk})_0 + \frac{1}{3}\frac{A''_{ijk}}{\omega}\dot{E}_{jk0} + \cdots \tag{3}$$

an expansion which shows tensor field products such as $\dot{E}_iE_j$ premultiplied by appropriate rank three molecular property tensors. It can be shown (*9*) that the antisymmetric components

$$\mathbf{E}^+ \times \mathbf{E}^-; \qquad \mathbf{E}^+ \times \mathbf{B}^-; \qquad \mathbf{B}^+ \times \mathbf{B}^-; \cdots$$

are the ones responsible for the second-order phenomenon of optical rectification (*30*). Clearly,

$$\beta_{1ijk}(E_jE_k)_0$$

and

$$\frac{\beta_{2ijk}}{\omega}(\dot{E}_jE_k)_0 = i\beta_{2ijk}(E_jE_k)_0 \tag{4}$$

have the same symmetry characteristics (*31*). Our "effective pump laser angular momentum" $\boldsymbol{\pi}$ derives from this Taylor expansion to second order in the electric field. Clearly, there are other terms of this kind, such as $\mathbf{B}^+ \times \mathbf{B}^-$, and so on.

The conjugate product

$$\mathbf{E}^+ \times \mathbf{E}^- = \pm 2E_0^2 i\mathbf{k}, \tag{5}$$

where **k** is a unit vector in the Z axis of the laboratory frame results in a single Z axis component of $2E_0^2$, denoted by $2E_{0Z}^2$. The interaction energy of this term with the molecule is written (Appendix 1)

$$V = -E_{0Z}^2(\alpha''_{1XY} - \alpha''_{1YX}) \equiv -E_{\mathrm{p}}^2\alpha''_1, \tag{6}$$

where α''_1 is the appropriate component of the real, molecular dynamical polarizability tensor, expressed in frame (X, Y, Z) of the laboratory. In the semiclassical theory of Ref. (*14*), and for a frequency ω_{lm} of transition between energy levels l and m this results in the following perturbation of the wavefunction of such a quantum transition

$$\Psi'_l = \Psi_l - \frac{E_{\mathrm{p}}^2}{\hbar}\sum_{l\neq m}\frac{1}{\omega_{lm}}\langle l|\alpha''_1|m\rangle\Psi_m, \tag{7}$$

where $\hbar$ is the Planck constant divided by 2π. The equivalent energy perturbation is denoted

$$V'_l = V_l - \langle l|\alpha''_1|l\rangle E_{\mathrm{p}}^2 \tag{8}$$

and the frequency separation of perturbed levels becomes

$$\omega_{ln} = \omega_{ln} - (\alpha''_l - \alpha''_n)E_{\mathrm{p}}^2/\hbar. \tag{9}$$

For a conservative order of magnitude 10^{-38} J^{-1} C^2 m^2 for α''_1 and for $\hbar = 1.055 \times 10^{-34}$ J sec, the frequency splitting in radians sec^{-1} is

$$\omega'_{ln} - \omega_{ln} \doteqdot 10^{-4}E_{\mathrm{p}}^2, \tag{10}$$

where E_{p} is the pump laser's electric field strength in volts meter^{-1}. In a small, commercially available Nd:YAG laser, the electric field strength E_{0Z} can reach (*32*) 10^9 V m^{-1} by Q-switching and simultaneously focusing. It is clear that the splitting in Eq. (10) can be easily measurable.

Defining a dynamical polarizability in the quantum state m as

$$\alpha''_m = \langle m|\alpha''_1|m\rangle \tag{11}$$

and using (*14*)

$$\frac{1}{(\omega_{ln}^2 - \omega^2)} \doteqdot \frac{1}{(\omega_{ln}^2 - \omega^2)}\left[1 + \frac{2\omega_{ln}(\alpha''_{l1} - \alpha''_{n1})E_{\mathrm{p}}^2}{\hbar(\omega_{ln}^2 - \omega^2)}\right] \tag{12}$$

we obtain from perturbation theory the following expression for the tensor $\alpha^{(1)''}_{ijZ}$ which mediates the effect of $\boldsymbol{\pi}$ on a molecule of an ensemble. This expression shows that the interaction of $\boldsymbol{\pi}$, with the same P and T symmetry as $\mathbf{B}$, is as well defined in the standard semiclassical theory of a molecule in a radiation field. This provides a firm basis for the further analysis of new effects that follows in this paper. The quantum mechanical expression for $\alpha^{(1)''}_{1ijZ}$ is

$$\begin{aligned}
\alpha^{(1)''}_{1ijZ} = -\frac{2}{\hbar^2}\sum_{l\neq n}\Bigg\{&\frac{2\omega_{ln}}{(\omega_{ln}^2 - \omega^2)^2}(\alpha''_{l1} - \alpha''_{n1})\mathrm{Im}(\langle n|\mu_i|l\rangle\langle l|\mu_j|n\rangle)\\
&\times\sum_{m\neq n}\frac{1}{\omega_{mn}(\omega_{ln} - \omega^2)}\mathrm{Im}[\langle m|\alpha''_1|n\rangle(\langle n|\mu_i|l\rangle\\
&\times\langle l|\mu_j|m\rangle - \langle n|\mu_j|l\rangle\langle l|\mu_i|m\rangle)]\\
&+\sum_{m\neq l}\frac{1}{\omega_{ml}(\omega_{ln}^2 - \omega^2)}\mathrm{Im}[\langle l|\alpha''_1|m\rangle(\langle n|\mu_i|l\rangle\\
&\times\langle m|\mu_j|n\rangle - \langle n|\mu_j|l\rangle\langle m|\mu_i|n\rangle)]\Bigg\}.
\end{aligned} \tag{13}$$

One of the most important of the molecular property tensors of the semiclassical theory (*14*) is the zeta tensor

$$\zeta_{ijk} = \zeta'_{ijk} - i\zeta''_{ijk}, \tag{14}$$

where

$$\zeta'_{ijk} = \frac{1}{c}\left[\frac{\omega}{3}(A''_{ijk} + A''_{jik}) + \epsilon_{lki}\alpha'_{2jl} + \epsilon_{lkj}\alpha'_{2il}\right] \tag{15}$$

and

$$\zeta''_{ijk} = -\frac{1}{c}\left[\frac{\omega}{3}(A'_{ijk} - A'_{jik}) + \epsilon_{lki}\alpha''_{2jl} - \epsilon_{lkj}\alpha''_{2il}\right]. \tag{16}$$

Here A_{ijk} is the complex molecular electric dipole/electric quadrupole tensor; α_{2ij} is the Rosenfeld tensor; and ϵ_{ijk} is the Levi–Civita symbol. Equation (3.4.11) of Ref. (*14*) summarizes the rate of change of intensity, azimuth, ellipticity, and degree of polarization of a quasi-monochromatic light wave passing through a dilute, optically active, birefringent, and absorbing ensemble of molecules. This equation embraces a large number of phenomena (*14*). Some of these are "activated" by an influence which is negative to T and positive to P. This has been ascribed almost universally to **B**, but it is important to note, following the third principle of group theoretical statistical mechanics (gtsm) (*33–36*), that other influences with the same P and T symmetries will activate new spectroscopic phenomena. This appears to be a simple, but profound (*1*), development.

In the basic Rayleigh/Barron theory for the refringent intensity and polarization changes, the imaginary part of the complex, frequency dependent, molecular polarizability tensor component α''_{1XY} contributes in the same way as the zeta tensor component ζ''_{XYZ}. However, ζ''_{XYZ} is negative to T and vanishes in the absence of a time-odd influence. If this is applied, however, in the direction of the propagation vector of the probe laser, the perturbed ζ''_{XYZ} no longer vanishes. Following principle three of gtsm, the symmetry of the external influence has been imparted to a quantity, an ensemble average, of the same symmetry. The latter is revealed to the observer.

2. CIRCULAR BIREFRINGENCE DUE TO EFFECTIVE PUMP LASER ANGULAR MOMENTUM π

Having this realization in hand it becomes straightforward to adapt the semiclassical Rayleigh theory of the Faraday effect to give equations for circular birefringence induced by effective pump laser angular momentum. In a small Nd:YAG pump laser, for example, this can be induced at second order by the four possible conjugate products of nonlinear optical rectification from Eq. (3)

$$\mathbf{E}_{\mathrm{L}}^{+} \times \mathbf{E}_{\mathrm{L}}^{-} = -\mathbf{E}_{\mathrm{R}}^{+} \times \mathbf{E}_{\mathrm{R}}^{-} = 2E_0^2 i\mathbf{k} \tag{17}$$

$$\mathbf{E}_{\mathrm{L}}^{+} \times \mathbf{B}_{\mathrm{L}}^{-} = \mathbf{E}_{\mathrm{R}}^{+} \times \mathbf{B}_{\mathrm{R}}^{-} = 2E_0B_0\mathbf{k} \tag{18}$$

$$\mathbf{B}_{\mathrm{L}}^{+} \times \mathbf{B}_{\mathrm{L}}^{-} = -\mathbf{B}_{\mathrm{R}}^{+} \times \mathbf{B}_{\mathrm{R}}^{-} = 2B_0^2 i\mathbf{k}. \tag{19}$$

Here $\mathbf{k}$ is a unit vector in the Z axis, along which both the pump and probe lasers are aligned; $\mathbf{E}_{\mathrm{L,R}}^{\pm}$ is the electric field strength and $\mathbf{B}_{\mathrm{L,R}}^{\pm}$ is the magnetic flux density of the pump laser, whose angular frequency is ω. Note that the first pair of conjugate products reverses sign with the circular polarity of the pump, and the second reverses sign with the direction of the pump with respect to the plane polarized probe. All four products remove the phase of the pump laser, and all four survive time averaging. In all cases the symmetries of the conjugate products are negative to T and positive to P. The most intense effect is that in E_0^2, which, in a small, focused Nd:YAG laser, can reach $10^{18}\,(\mathrm{V/m})^2$ (*32*). Conjugate products of this type have been used phenomenologically by Baranova and Zel'Dovich (*37*) in the context of enantiomer separation by a radiofrequency laser. Optical rectification, which they describe, is a well known phenomenon of nonlinear optics (*9–13*), and in consequence it should be straightforward to adapt it for the new spectroscopies introduced here.

The net pump laser angular momentum from Eq. (1) is now used in a Voigt/Born perturbation (*14*) to first order to activate the polarizability tensor element responsible for circular birefringence and dichroism measured by the probe laser

$$\alpha''_{1XY}(\boldsymbol{\pi}) = \alpha''_{1XY} + \alpha^{(1)''}_{1XYZ}\pi_Z + \cdots . \tag{20}$$

This parallels the standard Voigt/Born perturbation in the theory of the Faraday effect

$$\alpha''_{1XY}(\mathbf{B}) = \alpha''_{1XY} + \alpha^{(B)''}_{1XYZ}B_Z + \cdots . \tag{21}$$

The rotation of the plane of polarization of the probe laser from (20) is given immediately from Rayleigh/Barron theory (*14*) as

$$\Delta\theta \doteq \tfrac{1}{2}\omega\mu_0 clN\langle \alpha''_{1XY}(f) + \alpha^{(1)''}_{1XYZ}(f)\pi_Z\rangle, \tag{22}$$

where μ_0 is the permeability *in vacuo*, c is the velocity of light, l is the sample length, N is the number of molecules per meter, and where

$$\langle \alpha''_{1XY}(f) + \alpha^{(1)''}_{1XYZ}(f)\pi_Z\rangle$$

is the absorptive (*14*) part of the tensor components. The $\langle\ \ \rangle$ denotes a Boltzmann weighted average (*14*) with potential energy

$$V(\Omega) = -E_{0Z}^2\alpha''_{1XY}. \tag{23}$$

Evaluating this average (*14*) gives the expression (Appendix 1)

$$\Delta\theta \doteq \frac{1}{6}\,\omega\mu_0 clNE_{0Z}^2\left(\epsilon_{\alpha\beta\gamma}\alpha^{(1)''}_{1\alpha\beta\gamma}(f) + \alpha''_{1\alpha\beta}(f)\,\frac{\alpha''_{1\alpha\beta}}{kT}(f)\right), \tag{24}$$

where kT is the energy per molecule and where the tensor component subscripts refer to the molecule fixed frame (*14*).

Note that this is strictly valid for $E_{\mathrm{p}}^2\alpha''_1 \ll kT$ in a dilute solution. An order of magnitude estimate is given in Appendix 2.

Clearly there are many spectroscopic possibilities which spring from this type of circular birefringence. The molecular property tensors upon which it depends are in general frequency dependent, as in the Faraday effect. The effect conserves parity and reversality in all ensembles (*14, 38*), as in the Faraday effect, so that it is not confined to chiral molecules. The angle of rotation changes sign with the circular polarity of the pump laser, and the rotation depends on the factor E_0^2. The property tensor $\alpha^{(1)''}_{1XYZ}$ is a new and specific probe of molecular spectroscopy. Finally, there are analogous effects due to the other three possible conjugate products of optical rectification, Eqs. (17)–(19). These are easily distinguishable, however, from their different field dependencies, i.e., E_0^2, E_0B_0, and B_0^2.

Before proceeding to pump laser-induced axial birefringence, note that gyrotropic birefringence (*14*) is also produced by $\boldsymbol{\pi}$, through the zeta tensor ζ_{ijk}. The latter contributes to polarization and intensity changes in just the same way as the real symmetric dynamic polarizability (*14*) responsible for linear birefringence, but needs an additional time-odd, parity even influence, traditionally **B**. However, this can equally well be $\boldsymbol{\pi}$, and the latter can be very big in a system such as a *Q*-switched and focused Nd:YAG laser (*32*). Consequently, gyrotropic birefringence due to $\boldsymbol{\pi}$ is expected to be an easily observable effect.

3. AXIAL BIREFRINGENCE DUE TO $\boldsymbol{\pi}$

Axial birefringence due to a static magnetic field was introduced in 1982 by Wagnière and Hutter (*39–41*) and is another fundamentally important effect of **B** in spectroscopy. From the third principle of gtsm, we immediately have the possibility of an analogous effect due to $\boldsymbol{\pi}$. Here we again rely on the Rayleigh/Barron semiclassical theory to describe the latter in terms of molecular property tensors in the nonrelativistic approximation. In this case (*14, 38*) the zeta tensor is activated by π_Z, and axial birefringence is observed with an *unpolarized* probe in the same *Z* axis as the pump Nd:YAG laser. The refractive index measured by the probe differs as the circular polarity of the pump is switched from right to left. The effect is frequency dependent, and conserves reversality (*14, 38*) because $\boldsymbol{\pi}$ has the same *P* and *T* symmetries as **B** of the original Wagnière/Meier effect (*39*). It conserves parity in chiral ensembles only, so the effect should vanish in achiral ensembles in the absence of parity violation. Therefore, if it is *observed* in achiral ensembles, it measures *P* violation (*42–45*) in molecular ensembles, a very desirable goal in itself. Because the frequency of the powerful pump laser can be made to resonate with the probe, tiny *P* violating quantum transitions could well be amplified enormously, to the point where they become observable in terms of axial birefringence in achiral molecular ensembles. The resonance condition would be similar to that described in Section 5 for nuclear electromagnetic resonance spectroscopy.

The treatment of axial birefringence due to $\boldsymbol{\pi}$ given here follows that by Barron and Vrbancich (*38*) for **B**. The attenuated absorption intensity for the unpolarized probe propagating in *Z* is their Eq. (3.2), viz.

$$I \doteqdot I_0\exp(-\tfrac{1}{2}N\omega\mu_0 cl(\alpha'_{1XX}(g) + \alpha'_{1YY}(g) + \zeta'_{XXZ}(g) + \zeta'_{YYZ}(g)))\,, \qquad (25)$$

where I_0 is the initial intensity. Expressions are then given in Ref. (*38*) for the real and imaginary parts of the refractive index measured by an incoherent superposition of right and left circularly polarized components of the unpolarized probe laser. Both refractive and absorption indices of the probe become different when the pump's circular polarization is switched from left to right, and this is the axial birefringence due to $\boldsymbol{\pi}$.

In the presence of $\boldsymbol{\pi}$ the zeta tensor becomes activated. The components ζ'_{XXZ} and ζ'_{YYZ} in Eq. (25) become measurable through axial birefringence. They are

$$\zeta'_{XXZ} = \frac{2}{c}\left(\frac{\omega}{3}A''_{XXZ} + \alpha'_{2XY}\right) \qquad (26)$$

and

$$\zeta'_{YYZ} = \frac{2}{c}\left(\frac{\omega}{3}A''_{YYZ} - \alpha'_{2YX}\right) \tag{27}$$

We consider Voigt/Born perturbations linear in π_Z of the Rosenfeld and electric dipole/electric quadrupole tensor components

$$\alpha'_{2XY}(\boldsymbol{\pi}) = \alpha'_{2XY} + \alpha'_{2XYZ}\pi_Z + \cdots \tag{28}$$

$$\alpha'_{2YX}(\boldsymbol{\pi}) = \alpha'_{2YX} + \alpha'_{2YXZ}\pi_Z + \cdots \tag{29}$$

$$A''_{XXZ}(\boldsymbol{\pi}) = A''_{XXZ} + A''_{XXZZ}\pi_Z + \cdots \tag{30}$$

and

$$A''_{YYZ}(\boldsymbol{\pi}) = A''_{YYZ} + A''_{YYZZ}\pi_Z + \cdots. \tag{31}$$

As for circular birefringence, these must be subjected to a Boltzmann thermodynamic average with the potential energy

$$V(\Omega) = -E_{\mathrm{p}}^2\alpha''_1 \equiv -E_{0Z}^2(\alpha''_{1XY} - \alpha''_{1YX}). \tag{32}$$

The axial birefringence due to $\boldsymbol{\pi}$ is the difference

$$n'(\pi_Z \upuparrows K_Z) - n'(\pi_Z \updownarrows K_Z),$$

where **K** is the propagation vector of the probe laser, which clearly relies on the components of the activated zeta tensor, subjected to thermodynamic averaging. In a dilute solution for $E_{0Z}^2\alpha''_{1XY} \ll kT$ we have

$$(n^{\upuparrows} - n^{\updownarrows}) \doteqdot 2\mu_0 cNE_{0Z}^2\left\{\frac{1}{3}\epsilon_{\alpha\beta\gamma}\alpha'_{2\alpha\beta\gamma}(f) + \frac{1}{30kT}((4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}) \right.$$
$$\left. \times(\alpha'_{2\alpha\gamma}\alpha''_{1\beta\delta} - \alpha'_{2\beta\gamma}\alpha''_{1\alpha\delta})) + \frac{\omega}{45}(3A''_{\alpha\alpha\beta\beta}(f) - A''_{\alpha\beta\beta\alpha}(f)) + \cdots\right\} \tag{33}$$

with tensor components defined now in the molecule fixed frame. An order of magnitude estimate of the effect is given in the Appendix. The power level of the pump laser can be increased to the point where the axial birefringence, which depends on E_{0Z}^2 becomes accurately measurable. A convenient experimental arrangement would be to send radiation from the pump and probe down the arms of a Rayleigh interferometer (*38*), which is very sensitive to changes in refractive index. The pump circular polarization is left in one arm and right in the other, and the axial dichroism in the power absorption coefficient can be analyzed directly with a contemporary Fourier transform Michelson interferometer if a broad band probe beam is used instead of a monochromatic probe laser. The broad band probe exits from the Michelson interferometer, is sent through the Rayleigh interferometer, and the resulting interferogram picked up on a liquid helium cooled detector, preamplified, lock-in amplified, and numerically Fourier transformed. The interferogram is a combination of the Michelson component and the Fraunhoffer pattern of the two entrance slits of Rayleigh's interferometer.

4. OPTICALLY ACTIVE RAMAN AND RAYLEIGH SCATTERING DUE TO $\boldsymbol{\pi}$

Magnetic Rayleigh/Raman optical activity was developed theoretically and experimentally by Buckingham and Barron and is described on p. 380 of Ref. (*14*). The radiation scattered from a probe laser becomes optically active by applying a magnetic field to the sample parallel to the incident probe laser. For 90° scattering

$$\Delta_X(90^\circ) = \frac{2\,\mathrm{Im}(\alpha_{1XY}\alpha^*_{1XX})}{\mathrm{Re}(\alpha_{1XX}\alpha^*_{1XX} + \alpha_{1XY}\alpha^*_{1XY})} \tag{34}$$

and

$$\Delta_Z(90^\circ) = \frac{2\,\mathrm{Im}(\alpha_{1ZY}\alpha^*_{1ZX})}{\mathrm{Re}(\alpha_{1ZX}\alpha^*_{1ZX} + \alpha_{1ZY}\alpha^*_{1ZY})}, \tag{35}$$

where

$$\Delta = (I^{\mathrm{R}} - I^{\mathrm{L}})/(I^{\mathrm{R}} + I^{\mathrm{L}}) \tag{36}$$

is the dimensionless circular intensity difference (*14*). The scattering is described in Eqs. (34) and (35) by laboratory frame components of complex molecular polarizability tensors and complex conjugates described by a superscripted asterisk. The magnetic field **B** activates optical activity in several different ways, and in consequence, so does $\boldsymbol{\pi}$. The latter activates the polarizabilities through a Voigt/Born expansion to first order in π_Z. Consequently, in analogy with the effect of **B**, there are several new optically active scattering phenomena due to $\boldsymbol{\pi}$ of a pump laser parallel to the incident probe. These can be subclassified into $\boldsymbol{\pi}$ induced Rayleigh and Raman effects associated with diagonal scattering transitions, and with off-diagonal transitions, which probe the analogue of ground state Zeeman splitting due to $\boldsymbol{\pi}$. There is also optically active resonance, as well as transparent, Raman scattering due to $\boldsymbol{\pi}$, together with the interesting prospect of double resonance, when both probe and pump are tuned to the same frequency of a vibrational fundamental, for example. There is the additional advantage that $\boldsymbol{\pi}$ is expected to have a much more direct influence on vibrational spectra than **B**, because $\boldsymbol{\pi}$ is electromagnetic in origin, and Raman scattering in general is a phenomenon which depends on electronic states excited by electromagnetic fields.

Clearly, as soon as it is realized that $\boldsymbol{\pi}$ is a "symmetry clone" of **B**, new horizons appear.

The theory of Raman/Rayleigh optical activity due to $\boldsymbol{\pi}$ is now initiated, following the available methodology for **B** in Ref. (*14*), pp. 143 ff. The effect due to $\boldsymbol{\pi}$ conserves parity and reversality in all molecular ensembles and the main contribution in Rayleigh scattering is due to interference between waves generated by polarizability tensor components respectively perturbed and unperturbed by $\boldsymbol{\pi}$ of the pump laser. It is measured by scattered probe radiation, in the same way that the effects of Sections 2 and 3 are measured by the probe, not the pump, which plays the role of **B**. Therefore scattered pump radiation must be removed carefully by filtering around the pump frequency. Scattered optically active radiation from the probe can be observed at any angle, but the theory simplifies considerably for 90° scattering.

The same considerations apply for Raman optical activity due to $\boldsymbol{\pi}$, but the interference is now between unperturbed symmetric transition polarizability components, $(\alpha_{ij})^{\mathrm{s}}_{mn}$, and antisymmetric components, $(\alpha_{ij})^{\mathrm{a}}_{mn}$, perturbed by $\boldsymbol{\pi}$, and vice versa (*14*).

In both Rayleigh and Raman contexts the Voigt/Born perturbation due to $\boldsymbol{\pi}$ of the complex, frequency dependent, molecular polarizability is

$$\alpha_{ij}(\boldsymbol{\pi}) = \alpha'_{1ij} + \alpha'_{1ijk}\pi_k - (\alpha''_{1ij} + \alpha''_{1ijk}\pi_k) + \cdots \tag{37}$$

and polarizability conjugate products such as $\alpha_{1XX}\alpha^{*}_{1XY}$ are Boltzmann averaged with the potential energy (32). We obtain expressions for optically active scattering due to $\boldsymbol{\pi}$ analogous to those for **B** given in Eqs. (3.5.45)–(3.5.53) of Ref. (*14*). The most general expressions for the Stokes parameters for optically active scattering due to $\boldsymbol{\pi}$ are the analogues of Barron's Eqs. (3.5.51), p. 145 of Ref. (*14*). These are given in Appendix 3 because of their complexity.

The Stokes parameters of Appendix 3 contain cross terms between $(\alpha'_{ij})^{\mathrm{a}}_{mn}$ and $(\alpha''_{ij})^{\mathrm{s}}_{mn}$ which are responsible for resonance Raman scattering from the probe due to $\boldsymbol{\pi}$. "Resonance" in this context refers to the probe frequencies.

As in magnetic Raman/Rayleigh scattering, the intensity of the scattered light depends only on the degree of circularity of the incident probe for given circular polarity of the pump. The Stokes parameters switch sign if the pump is switched from right to left circular polarity for a given circular polarity of the probe.

Finally, we note that the effect can also be generated by a pump laser at a suitable angle, say 45°, mixing with the already scattered radiation from a probe laser. This technique would automatically remove the danger of artifacts from scattering of the pump radiation, which is, of course, much more intense than the probe. The pump cannot be at right angles to the scattered probe radiation, because there would be no component of $\boldsymbol{\pi}$ in the direction of the latter. Clearly, the pump cannot be in the same direction as the scattered probe, because its intensity would probably destroy the detector system, or it would otherwise block off the scattered probe radiation from the detector system. (In this context, a magnetic field can always be generated parallel or antiparallel with the scattered probe radiation.)

5. NUCLEAR ELECTROMAGNETIC RESONANCE (NER)

This is a symmetry clone of nuclear magnetic resonance (NMR) which is well described in the literature through interaction Hamiltonians such as

$$\Delta H_1 = -\gamma_N \mathbf{I} \cdot \mathbf{B} \tag{38}$$

between applied magnetic flux density (**B**) and quantized nuclear spin. In Eq. (38), γ_N is the magnetogyric ratio and I is the nuclear spin quantum number. With analogous symmetries, the interaction Hamiltonian between $\boldsymbol{\pi}$ and **I** can be expressed as

$$\Delta H_2 = -\gamma_{EM} \mathbf{I} \cdot \boldsymbol{\pi}, \tag{39}$$

where γ_{EM} is a nuclear coefficient called the nuclear gyroptic ratio. The derivation of its electronic counterpart is described in terms of the optical Zeeman effect later in this section. The resonance condition of NER is described by solving the Schrödinger equation with the quantity

$$\boldsymbol{\alpha}_I \equiv \mathrm{V}_{EM} \mathbf{I} \tag{40}$$

which is analogous with the nuclear magnetic moment. The energy of the nucleus in the eigenstate $|I, \alpha_I\rangle$ is the eigenvalue in the equation

$$\Delta H_2 |I, \alpha_I\rangle = -\gamma_{EM} \pi_Z I_Z |I, \alpha_I\rangle, \tag{41}$$

i.e.,

$$E(\alpha_I) = -\gamma_{EM} \pi_Z I_Z. \tag{42}$$

The probe radiation stimulates transitions between states with the selection rule

$$\Delta\alpha_I = \pm 1 \tag{43}$$

determined by the properties of I. The transition rate is greatest at the resonance condition

$$\hbar\omega_{\mathrm{R}} = E(\alpha_I - 1) - E(\alpha_I) = \gamma_{EM} \hbar \pi_Z \tag{44}$$

$$\omega_{\mathrm{R}} = \gamma_{EM} \pi_Z \tag{45}$$

where an intense absorption of the probe radiation is observed. As in NMR, the probe frequency may be maintained constant while varying ("tuning" or "sweeping") π through several available orders of magnitude and pump frequencies. A vice-versa technique can also be applied.

If NER is observed experimentally, it is expected that the local π at the nucleus will differ from the applied π through shielding by the electrons, i.e., by a shielding constant akin to NMR, resulting in a chemical shift and a new technique for the analytical laboratory, susceptible to refinements akin to Fourier transform NMR, and all the nuclear effects usually associated with NMR, such as spin–spin and spin–orbit coupling, relaxational NMR, Overhauser enhancement, and so forth.

The magnitude of the effect depends on the constant γ_{EM} in Eq. (39), which must have the same P and T symmetry as γ_N, but whose order of magnitude depends on the properties of the nucleus itself. The spin quantum number ranges from 0 to 6 in different nuclei, and is $\frac{1}{2}$ in the proton. If resonance is observed in nuclei in which I vanishes, it may be an indication of P violation, with more interesting consequences.

NER can be looked upon as the hyperfine detail of the spectral splitting due to the conjugate product π, described by the A term of the Serber representation (*38*) of Eq. (B2) of Appendix 2, viz.

$$\Delta\theta = \frac{-\mu_0 c l N E_0^2}{3\hbar} \left(\frac{2\omega_{jn}\omega^2}{\hbar} (f^2 - g^2) A + \omega^2 f \left(B + \frac{C}{kT} \right) \right), \tag{46}$$

where

$$A = \frac{3}{d_n} \sum_n (\alpha_j'' - \alpha_n'') \mathrm{Im}(\langle n|\mu_X|j\rangle\langle j|\mu_Y|n\rangle);$$

$$B = \frac{3}{d_n} \sum_n \mathrm{Im}\Bigg(\sum_{k \neq n} \Bigg[\sum_{k \neq n} \frac{\langle k|\alpha_Z''|n\rangle}{\hbar\omega_{kn}} (\langle n|\mu_X|j\rangle\langle j|\mu_Y|k\rangle - \langle n|\mu_Y|j\rangle\langle j|\mu_X|k\rangle)$$

$$+\sum_{k\neq j}\frac{\langle j|\alpha''_Z|k\rangle}{\hbar\omega_{kj}}\left((\langle n|\mu_X|j\rangle\langle k|\mu_Y|n\rangle-\langle n|\mu_Y|j\rangle\langle k|\mu_X|n\rangle)\right]\Bigg)$$

$$C=\frac{3}{d_n}\sum_n\alpha''_Z\mathrm{Im}(\langle n|\mu_X|j\rangle\langle j|\mu_Y|n\rangle).$$

As in the conventional Zeeman effect, these equations represent a sum over transitions from component states of a degenerate set to an excited state Ψ_j, which itself can be a member of a degenerate set of degeneracy d_n.

In this representation, the optical Zeeman effect is the A term, expressed in terms of the angular polarizability in states n and j. The definition in state n is Eq. (11), and that in state j is

$$\begin{aligned}\alpha''_{\alpha\beta,j}&=-\alpha''_{\beta\alpha,j}\\&=\frac{-2}{\hbar}\sum_{k\neq j}\frac{\omega}{\omega_{kj}^2-\omega^2}\mathrm{Im}(\langle j|\mu_\alpha|k\rangle\langle k|\mu_\beta|j\rangle),\end{aligned}\tag{47}$$

where k is a state of higher energy than j. In writing the A, B, and C terms in this way, weighted Boltzmann averaging has been used with the interaction energy

$$V(\Omega)=-\alpha''_Z E_0^2.\tag{48}$$

By Q-switching or mode locking and simultaneously tuning the circularly polarized pump laser to resonance, this energy can easily be of the order of kT itself at 300 K.

Note that in this A term description of the optical Zeeman effect, a right circularly polarized pump laser delivers a photon with $-\hbar$ projection in the Z axis, producing a change $\Delta M=-1$ in the atomic or molecular quantum state. In a left circularly polarized pump, the photon is projected $\hbar$, and the selection rule is $\Delta M=1$. In a linearly polarized pump, the selection rule is $\Delta M=0$, and there is no optical Zeeman effect. This is accounted for classically in Eq. (17), where the left conjugate product is positive, and the right is negative. The sign change produced by switching the pump from left to right in the optical Zeeman effect is equivalent to reversing the direction of the magnetic field in the conventional Zeeman effect. As in the conventional effect, the A term due to π of the optical Zeeman effect represents the splitting of lines into right and left circularly polarized components. The magnetic dipole moment operator of the conventional effect is replaced by the angular polarizability of the optical effect.

Therefore the Hamiltonian of the optical Zeeman effect can be represented as

$$\Delta H_{0Z}=-\alpha''_Z E_0^2=-\gamma_\pi M_J E_0^2\hbar,\qquad M_J=J,J-1,\ldots,-J,\tag{49}$$

where M_J is the Z axis component of the total electronic/nuclear angular momentum quantum number, with selection rule

$$\Delta M_J=\pm1.\tag{50}$$

If probe electromagnetic radiation of angular frequency ω_p in radians per second is directed at the atom or molecule being irradiated by π_i of the pump laser, resonance occurs when

$$\omega_{\mathrm{p}} = \gamma_{\pi} E_0^2 \qquad (51)$$

in the MHz/GHz range for a pump laser electric field strength of 10^5 to 10^7 V m^{-1}, assuming a conservative order of magnitude (*28*) of 10^{-38} J^{-1} C^2 m^2 for the orbital polarizability. This can be amplified greatly by tuning the pump laser to a natural transition frequency ω_{jn} of Eq. (47), implying the need for a much lower pump electric field strength.

The angular polarizability, α''_Z, appearing in Eq. (49) is a quantized axial vector with positive P and negative T symmetries, the same fundamental symmetries as quantized angular momentum. It can be seen that angular polarizability and angular momentum are proportional, and it follows that $i\alpha''_i$ can be written

$$i\alpha''_i = \gamma_{\pi}(L_i + 2.002 S_i), \qquad (52)$$

where γ_{π} is a "gyroptic ratio" between the optical conjugate product and the fundamental atomic or molecular electronic angular momenta—the orbital L_i and the spin $2.002 S_i$. The nuclear equivalent is Eq. (39).

Therefore, we have the important result that the spectral effects of the conjugate product (17) can be developed theoretically in terms of the quantum theory of angular momentum, which in one form or another is the basis for much of quantum mechanics and spectroscopy.

The optical Zeeman effect and NER are two of the important consequences of this realization. If the effects of laser inhomogeneity can be surmounted, using, for example, the techniques of photon echo, it is possible that NER or "optical NMR" will attain the analytical usefulness of conventional NMR.

The formal analogy between the optical and conventional Zeeman effects can be developed further, for example, in diatomics, in terms of the well known Hund vector coupling models; and the theory is formally identical to descriptions such as those of Townes and Schawlow (*14*), Chap. 11, with the magnetic dipole moment replaced by the angular polarizability and the magnetic flux density of the conventional Zeeman effect by the quantity E_0^2, the square of the electric field strength of the pump laser, for example, an excimer pumped, circularly polarized, dye laser.

DISCUSSION

This paper rests on the conjugate product $\boldsymbol{\pi}$, which has the same symmetry as **B**. This type of conjugate product appears in Eq. (3) of Baranova and Zel'Dovich (*37*), who used it to describe a spinning electric field. It follows that a spinning electric field can be substituted for the pump laser to look at lower frequency effects of $\boldsymbol{\pi}$, e.g., in the radiofrequency range. Again, by symmetry cloning **B** with $\boldsymbol{\pi}$, we can expect a whole variety of spectroscopic effects typically ascribed to **B**. One of these might be an effect analogous to Zeeman splitting, but caused by the rotating electric field. As early as 1920, Born (*46*) realized that a rotating electric field can cause bulk (hydrodynamic) rotation of a liquid, suspended, for example, in a thin walled vessel on a torsion wire, an effect observed by Lertes (*47*), Grossetti (*48*), and Dahler (*49*). Splitting akin to the Zeeman effect is also expected from $\boldsymbol{\pi}$ of the pump laser, where the rotation frequency of the electric field is much higher.

Finally all these effects conserve parity and reversality of the complete experiment (*14*), the Wigner principles, because the relative symmetries of π and the propagation vector, **K**, of the probe are akin to the relative symmetries of **B** and **K**. Further discussion of this point has been given elsewhere by Barron and Vrbancich (*38*), and by the present author (50–52).

APPENDIX I

This appendix provides some technical details of the calculation of angle of rotation in π induced circular birefringence.

The interaction energy of the molecule with the pump electromagnetic field is expanded as

$$V(\Omega) = -\mu_i E_i - \tfrac{1}{2}\alpha_{1ij} E_i E_j - \cdots, \tag{A1}$$

where α_{ij} is the complex molecular polarizability. The term

$$-\tfrac{1}{2}\alpha_{1ij} E_i E_j$$

is a tensor contraction. We are interested specifically in the contraction

$$-\tfrac{1}{2}\alpha_{1ij}(\mathbf{E}_{\mathrm{L}}^{+} \times \mathbf{E}_{\mathrm{L}}^{-})_{ij}$$

with

$$(\mathbf{E}_{\mathrm{L}}^{+} \times \mathbf{E}_{\mathrm{L}}^{-})_{ij} = \begin{bmatrix} 0 & 2E_{0Z}^{2} i & 0 \\ -2E_{0Z}^{2} i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{A2}$$

and

$$\alpha_{1ij} \equiv \alpha'_{1ij} - i\alpha''_{1ij} \tag{A3}$$

as the complex molecular polarizability. Using the rule for tensor contraction

$$a_{ij}b_{ij} = a_{XX}b_{XX} + a_{XY}b_{XY} + a_{XZ}b_{XZ} + a_{YX}b_{YX} + a_{YY}b_{YY} + a_{YZ}b_{YZ} + a_{ZX}b_{ZX} + a_{ZY}b_{ZY} + a_{ZZ}b_{ZZ} \tag{A4}$$

we obtain the energy of interaction of the conjugate product $\mathbf{E}_{\mathrm{L}}^{+} \times \mathbf{E}_{\mathrm{L}}^{-}$ with the molecular polarizability as

$$V(\Omega) = -E_{0Z}^{2}(\alpha''_{1XY} - \alpha''_{1YX}) = -2E_{0Z}^{2}\alpha''_{1XY}. \tag{A5}$$

This is used in Eq. (23) to derive Eq. (24) using the Boltzmann average (*14*)

$$\langle X(\Omega)\rangle = \langle X(\Omega)\rangle_0 - \frac{1}{kT}\langle X(\Omega)V(\Omega)\rangle + \cdots, \tag{A6}$$

where

$$\langle X(\Omega)\rangle_0 = \langle \alpha''_{1XY} + 2\alpha^{(1)''}_{1XYZ}\mathrm{E}_{0Z}^{2}\rangle_0 \tag{A7}$$

is the unweighted component of this average. The other component is

$$\frac{1}{kT}\cdot 2E_{0Z}^{2}\langle \alpha''_{1XY}\alpha''_{1XY}\rangle + \cdots O(\mathrm{E}_{0Z}^{4}). \tag{A8}$$

Thus, in Eq. (22) of the text

$$\langle \alpha''_{1XY}(f) + \alpha^{(1)''}_{1XYZ}(f)\pi_Z \rangle = 2\langle \alpha^{(1)''}_{1XYZ} \rangle E^2_{0Z} + \frac{2E^2_{0Z}}{kT}\langle \alpha''_{1XY}\alpha''_{1XY} \rangle. \tag{A9}$$

The weighted averages in this equation are finally transformed into the molecule fixed frame using the general tensor transformation rules and algebra of Ref. (*14*), Chap. 4. We have

$$\langle \alpha^{(1)''}_{1XYZ} \rangle = \tfrac{1}{6}\epsilon_{\alpha\beta\gamma}\alpha^{(1)''}_{1\alpha\beta\gamma} \tag{A10}$$

and

$$\langle \alpha''_{1XY}\alpha''_{1XY} \rangle = \tfrac{1}{6}\alpha''_{1\alpha\beta}\alpha''_{1\alpha\beta} \tag{A11}$$

giving Eq. (24) of the text.

Similarly, Eq. (33) of the text is obtained from the laboratory frame Boltzmann averages in (*38*)

$$\begin{aligned}(n^{1\uparrow} - n^{1\downarrow}) \doteqdot 2\mu_0 cNE^2_{0Z}\Big\{&\langle \alpha'_{2XYZ} \rangle - \langle \alpha'_{2YXZ} \rangle + \frac{1}{kT}(\langle \alpha'_{2XY}\alpha''_{1XY} \rangle \\ &- \langle \alpha'_{2YX}\alpha''_{1XY} \rangle) + \frac{\omega}{3}(\langle A''_{XXZZ} \rangle + \langle A''_{YYZZ} \rangle) + \cdots\Big\}.\end{aligned} \tag{A12}$$

The average $\langle \alpha'_{2XY}\alpha''_{1XY} \rangle$ for example is expressed in the notation of Ref. (*14*) as

$$\begin{aligned}\langle \alpha'_{2XY}\alpha''_{1XY} \rangle &= \langle i_\alpha i_\beta j_\gamma j_\delta \rangle \alpha'_{2\alpha\gamma}\alpha''_{1\beta\delta} \\ &= \frac{1}{30}(4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma})\alpha'_{2\alpha\gamma}\alpha''_{1\beta\delta}\end{aligned}$$

which finally gives Eq. (33) using the fact that the real part of the polarizability is even and the imaginary part is odd to index reversal.

APPENDIX 2

Order of magnitude estimates of the effects of Eqs. (24) and (33) are made in this appendix as follows. It appears that the angle of rotation due to π is easily measurable. Take an angular frequency (ω) in the visible of 10^{15} rad sec^{-1}, $\mu_0 = 4\pi \times 10^{-7}$ J m^{-1} A^{-2}, $c = 3 \times 10^8$ m sec^{-1}, a sample length of 1.0 m, a conservative order of magnitude of 10^{-38} J^{-1} C^2 m^2 for $\alpha''_{1\alpha\beta}(f)$, and $kT = 4 \times 10^{-21}$ J at 300 K; and for $N = 6 \times 10^{26}$ molecules m^{-3}

$$\Delta\theta \doteqdot 10^{-12} E^2_{0Z} \text{ rad} \tag{B1}$$

for the angle of rotation due to

$$\Delta\theta = \frac{1}{6}\omega\mu_0 clNE^2_{0Z}\alpha''_{1\alpha\beta}\frac{\alpha''_{1\alpha\beta}}{kT} + \cdots. \tag{B2}$$

This is within range of a spectropolarimeter even for an unfocused Nd:YAG laser operating in continuous mode. There appears no need even for pulsing or *Q*-switching. As in the Faraday effect there will be an accompanying dichroism, circular birefringence, and optical rotatory dispersion, both in chiral and achiral materials. The effect occurs in all polarizable ensembles. Clearly, by utilizing the contemporary laser technology of pulsing, *Q*-switching, and focusing, the angle of rotation can become enormous, possibly large enough to measure directly the enantiomeric energy in equivalence (*53*).

In contrast, the axial birefringence of Eq. (33) is a far smaller effect, needing for observation the full power of a focused and *Q*-switched Nd:YAG laser, and fast detector system technology. Following Barron and Vrbancich, and using an order of magnitude of 10^{-34} A^2 J^{-1} m^3 sec for $\alpha'_{2\alpha\gamma}$, we obtain

$$n^{\uparrow\uparrow} - n^{\uparrow\downarrow} \doteqdot 10^{-23} E_{0Z}^2. \tag{B3}$$

For a *Q*-switched and focused Nd:YAG laser delivering 10^{18} (V/m)^2, the axial birefringence is of the order 10^{-5} at 300 K. This is about a thousand times larger under these conditions than the equivalent magnetochiral effect (*38*). If a highly polarizable chiral material is chosen with a large optical rotatory power, such as a helical biomacromolecule, or a cobalt complex as suggested in Ref. (*38*), it is probable that the axial effect can be increased to an order of magnitude well within range of a Rayleigh refractometer.

APPENDIX 3

Here we provide expressions for π induced light scattering optical activity using the expressions given by Barron *et al.* (*54*) in the laboratory frame (X, Y, Z) for the depolarization ratio due to π in the X and Z axes. The light scattering geometry is as in Ref. (*54*), with **B** replaced by π. Here, the superscripts R and L refer to the scattered *probe* radiation, whose electric field intensity is denoted by $E_0^{(\mathrm{p})}$. R is a distance from the scattering center which is large in comparison with molecular dimensions. The depolarization ratio for the probe radiation is, using Ref. (*53*) and averaging with the potential energy (23) of the text,

$$\Delta_\alpha = (I_\alpha^{\mathrm{R}} - I_\alpha^{\mathrm{L}})/(I_\alpha^{\mathrm{R}} + I_\alpha^{\mathrm{L}}), \tag{C1}$$

where

$$A = (\omega^4 \mu_0 E_0^{(\mathrm{p})2})/(16\pi^2 c R^2) \tag{C2}$$

$$I_X^R - I_X^{\mathrm{L}} = A\,\mathrm{Im}(\alpha_{1XY}\alpha^*_{1XX}) \tag{C3}$$

$$I_Z^{\mathrm{R}} - I_Z^{\mathrm{L}} = A\,\mathrm{Im}(\alpha_{1ZY}\alpha^*_{1ZX}) \tag{C4}$$

$$I_X^{\mathrm{R}} + I_X^{\mathrm{L}} = \frac{A}{2}\,\mathrm{Re}(\alpha_{XX}\alpha^*_{XX} + \alpha_{XY}\alpha^*_{XY}) \tag{C5}$$

$$I_Z^{\mathrm{R}} + I_Z^{\mathrm{L}} = \frac{A}{2}\,\mathrm{Re}(\alpha_{ZX}\alpha^*_{ZX} + \alpha_{ZY}\alpha^*_{ZY}). \tag{C6}$$

The products of polarizabilities in these expressions are perturbed by π of the pump laser. After Boltzmann averaging for π in the Z direction of the incoming probe beam, we have

$$I_X^{\mathrm{R}} - I_X^{\mathrm{L}} = 2AE_{0Z}^2 \langle \alpha'_{1XX}\alpha''^{*}_{1XYZ} - \alpha''_{1XX}\alpha'^{*}_{1XYZ} + \alpha'_{1XXZ}\alpha''^{*}_{1XZ} - \alpha''_{1XXZ}\alpha'^{*}_{1XY} + \frac{1}{kT}(\alpha'_{1XX}\alpha''^{*}_{1XY}\alpha''_{1XY} - \alpha''_{1XX}\alpha'^{*}_{1XY}\alpha''_{1XY})\rangle + \cdots \quad \text{(C7)}$$

for the numerator of Δ_X. It is seen that this is proportional to the square of the electric field intensities both of the pump and of the probe. In consequence it appears that the effect can be easily large enough for observation with a Nd:YAG pump.

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