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# Semi-classical theory of laser-induced circular birefringence, resonance, and optical activity in scattered radiation

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The semi-classical theory of pump laser-induced circular birefringence, spectral Zeeman type splitting, dichroism, and ellipticity is developed with reference to a novel technique called laser ESR and NMR. The theory, in terms of molecular property tensors and transition tensors, is also applied to Rayleigh/Raman optical activity in light scattered from a probe laser co-axial with the pump. Optical rectification is shown to be the pump laser property responsible for these new effects, which parallel those due to static magnetic flux density ***B***, and which are based on analogy with the inverse Faraday effect, the ability of a circularly polarised pump laser to induce magnetisation. The interaction Hamiltonian is developed in terms of the conjugate product of the pump laser and a new fundamental atomic/molecular property called the electronic orbital/spin polarisability, an antisymmetric second rank polar tensor which transforms as a rank-one axial vector analogous with the atomic/molecular magnetic dipole moment. it is shown that optical rectification in the pump laser produces, through the conjugate product, the complete range of effects customarily generated by ***B***, including NMR and ESR, quantum Hall effect and so on.

## 1. Introduction

It is well known that static magnetic flux density ***B*** can generate a wide range of useful spectral phenomena, including nuclear magnetic resonance, electron paramagnetic resonance, circular birefringence (the Faraday effect), spectral splitting (the normal, anomalous and quadratic Zeeman effects), and induced optical activity in scattered light (Rayleigh and Raman). These effects can be treated in terms of molecular property tensors such as dynamic multipole moments and transition polarisabilities, for example, by a classical treatment of electromagnetic radiation and quantum treatment of its interaction with atoms and molecules through the time-dependent Schrödinger equation. This is known as "semi-classical" theory, well described, for example, in ref. [1]. An interesting new forward–backward birefringence and dichroism due to ***B*** [2–5] as recently been proposed by Wagnière and Meier [2,3] and developed by Barron and Vrbancich [4,5] with semiclassical theory. A fuller theory requires quantisation of the electromagnetic field, with zwitterbewegung, but all the known results of quantum field theory relevant to this paper can be derived by appropriate forms of semi-classical theory. Appropriate application of ***B*** has also been instrumental in the discovery of parity violation (non-conservation) in nuclear properties [6–8], leading to the unification at CERN of the electromagnetic and weak forces, a major fundamental achievement of contemporary natural philosophy. ***B*** also plays a role in the quantum Hall effect, in superconductivity, and in a large number of other known phenomena such as neutron scattering.

It would be interesting, therefore, to have available experimental and theoretical supplements for ***B***, which is negative to motion reversal (T) and positive to parity inversion (P), and forms a first-order interaction Hamiltonian through the atomic or molecular magnetic dipole moment, with the same T and P symmetries. In this paper, it is shown that the conjugate product $\boldsymbol{\pi}$ of a pump laser, such as a small, commercially available, pulsed Nd:YAG, produces, in principle, the complete range of phenomena customarily generated with a magnet, and attributed to the static magnetic flux density ***B***. The argument is supported by the experimentally verified [9–11] inverse Faraday effect, which is magnetisation produced by optical rectification in a circularly polarised

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pump laser (a combination, for example, of a Nd:YAG, quarter-wave plate and Nicol prism; or a piezoelectric modulator; or a circularly polarising optical filter, wire grid, or reflective holographic grating). The conjugate product $\boldsymbol{\pi}$ is negative to T and positive to P and forms a first-order interaction Hamiltonian through a novel fundamental atomic/molecular property which is called the dynamic electronic orbital or spin polarisability $\boldsymbol{\alpha}''$. The latter is a T negative, P positive, rank-one axial tensor (a vector), equivalent through the Levi-Civita symbol ($\epsilon_{ijk}$) with an antisymmetric second-rank polar tensor [1],

$$\alpha''_i = \epsilon_{ijk}\alpha''_{jk}\,, \tag{1}$$

made up of components of the T negative, P positive complex part [1] of the dynamic electronic polarisability. (Note that the Einstein tensor summation convention over repeated indices has been used in eq. (1), as in the rest of this paper.)

The first-order interaction Hamiltonian between $\pi_i$ and $\alpha''_i$ is developed in section 2, in direct analogy with that between $\boldsymbol{B}$ and the magnetic dipole moment $\boldsymbol{m}$. The latter is well known to have both orbital and spin components, because it is proportional to quantised orbital and spin angular momentum through the well known gyromagnetic ratio [12]. In analogy, the dynamic molecular property $\alpha''_i$ also has orbital and spin components, and is proportional to the respective angular momenta through a constant $\gamma_\pi$ analogous to the gyromagnetic ratio. Since $\boldsymbol{\alpha}''$ transforms as an axial vector with the same T and P symmetries as $\boldsymbol{m}$, and is proportional to quantised atomic or molecular angular momentum, it is governed by the same selection rules as the atomic or molecular dipole moment operator. (This is similar to the equivalence described in p. 383 of ref. [1] between an antisymmetric polar scattering tensor, transforming as an axial vector, and the magnetic dipole moment operator.)

Section 3 develops the semi-classical theory of circular birefringence, dichroism and ellipticity due to $\boldsymbol{\pi}$ as observed in either a probe laser co-axial with the pump, or in broad band electromagnetic radiation, as in a contemporary interferometric spectrometer. The theory is expressed in $A$, $B$ and $C$ terms, in formal analogy with the semi-classical [1] theory of the Faraday and Zeeman effects, and similarities and differences are discussed with $A$, $B$ and $C$ terms produced by optical rectification and by the customary magnet.

The theory of the $A$ (Zeeman) term is developed to discuss interesting new "laser ESR" effects, and on that basis, "laser NMR" effects involving MHz/GHz resonances respectively with the electrons and nuclei of an atom or molecule. This leads, in principle, into a rich new field of analytical chemical physics, using a combination of $\boldsymbol{\pi}$ and $\boldsymbol{B}$.

Section 4 develops the semi-classical theory of Rayleigh and Raman optical activity due to optical rectification, using again a close formal analogy with the theory due to Barron, Buckingham, and co-workers [1] of light scattering optical activity due to $\boldsymbol{B}$. Similarities and differences are discussed between the scattered optical activity due to $\boldsymbol{\pi}$ and $\boldsymbol{B}$.

Finally, section 4 is a discussion of possible other applications of the phenomenon of magnetisation due to optical rectification in fields such as the Hall effect and neutron scattering, and in the search for P violation in molecular matter.

## 2. Interaction Hamiltonian and definition of orbital and spin electronic polarisability

The first-order interaction Hamiltonian between $\alpha''_i$ and the conjugate product $\pi_i$ of a pump laser must be a T positive, P positive, real scalar quantity, an energy. The conjugate product $\boldsymbol{\pi}$ of optical rectification is defined through the cross product of the two complex conjugates of the electric field strength (in V m$^{-1}$) of the classical electromagnetic field,

$$\boldsymbol{\pi} = \boldsymbol{E}_{\mathrm{L}}^{+} \times \boldsymbol{E}_{\mathrm{L}}^{-} = -\boldsymbol{E}_{\mathrm{R}}^{+} \times \boldsymbol{E}_{\mathrm{R}}^{-} = 2E_0^2\mathrm{i}\boldsymbol{k}\,. \tag{2}$$

Here the R and L subscripts denote respectively right and left circularly polarised, and the + and − superscripts the positive and negative complex conjugates, both being allowed solutions to Maxwell's equations. The conjugate product $\boldsymbol{\pi}$ is purely complex, and is a vector quantity directed in the $Z$ axis of the laboratory frame, in which $\boldsymbol{k}$ is a unit vector. It is related to the third Stokes parameter $S_3$ [1] by

$$\boldsymbol{\pi} = -\mathrm{i} S_3 \boldsymbol{k} \tag{3}$$

and vanishes if the laser is not at least partially circularly polarised. It changes sign if the laser is switched from R (clockwise rotation of the electric field in a plane when the laser travels towards an observer) to L (anticlockwise rotation). It is a T negative, P positive, axial vector [13–15] with the same P and T symmetries as $\boldsymbol{B}$. In consequence, optical rectification of a circularly polarised pulsed pump laser can produce magnetisation, and this was one of the first non-linear optical effects to be observed [9–11] using an early giant ruby laser, quarter-wave plate and Nicol prism.

It has been shown recently [16,17] that the purely complex product $\boldsymbol{\pi}$ produces direct electric polarisation in chiral media through the imaginary, T negative part of the molecular dynamical polarisability, defined [1] by

$$\alpha''_{\alpha\beta} = -\alpha''_{\beta\alpha} = -\frac{2}{\hbar} \sum_{j \neq n} \frac{\omega}{\omega_{jn}^2 - \omega^2} \operatorname{Im}(\langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle) , \tag{4}$$

where the transition frequency (rad $\mathrm{s}^{-1}$),

$$\omega_{jn} = \omega_j - \omega_n , \tag{5}$$

is defined between quantum states $n$ and $j$, and where $\mu_\alpha$ and $\mu_\beta$ are electric dipole moment operators. The sum in eq. (4) excludes the ground state $n$, and $\mathrm{i}\alpha''_{\alpha\beta}$ is a purely imaginary, second-rank polar tensor, antisymmetric in its subscripts. It is a T negative, P positive quantity which vanishes at static frequencies ($\omega = 0$).

The first-order interaction Hamiltonian between the two purely imaginary T negative, P positive quantities $\pi_i$ and $\mathrm{i}\alpha''_i$ is a real scalar, formed either by a contraction of their two second-rank antisymmetric polar tensor representations, or equivalently, their two first-rank axial vector representations. The Hamiltonian is, furthermore, a part of the general, semiclassical two-variable Taylor expansion [1] of energy in terms of the time-dependent electric and magnetic field strengths $E_i$ and $B_i$ of the classical electromagnetic field and quantised dynamic molecular property tensors. This Taylor expansion can be written in the two-variable tensor series [1,18]

$$\Delta H = -\tfrac{1}{2}(\alpha_{ij} E_i E_j + \alpha_{1ij} E_i B_j + \alpha_{2ij} B_i B_j + \alpha_{3ij} B_i E_j) + \ldots . \tag{6}$$

and we are specifically interested in the phase (frequency and wave vector) independent antisymmetric part of the tensor product $E_i E_j$ multiplying the complex part of the complete dynamic polarisability and equivalent to the conjugate product (2)

$$2E_0^2 \mathrm{i} \boldsymbol{k} \equiv \begin{pmatrix} 0 & 2E_0^2 \mathrm{i} & 0 \\ -2E_0^2 \mathrm{i} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} . \tag{7}$$

The antisymmetric part of the tensor $E_i E_j$ is

$$(\pi_i)_{\mathrm{L}} = \epsilon_{ijk} (E_j^+ E_k^-)_{\mathrm{L}} , \quad (\pi_i)_{\mathrm{R}} = -\epsilon_{ijk} (E_j^+ E_k^-)_{\mathrm{R}} , \tag{8}$$

i.e. is related to the conjugate product through the Levi-Civita symbol, and the complex part of the dynamic polarisability is given in the same terms by eq. (1). The interaction Hamiltonian is therefore

$$\Delta H_1 = \tfrac{1}{2} \mathrm{i} \alpha''_i \pi_i = \mp \alpha''_Z E_{0Z}^2 , \tag{9}$$

which can be compared directly with the Hamiltonian between magnetic flux density $B_i$ and the magnetic dipole moment $m_i$. The component symmetries in each case are the same, i.e. T negative, P positive $B_i$ and $m_i$, and $\pi_i$ and $\alpha''_i$.

It is well established that the magnetic dipole moment can be written in terms of the orbital ($L$) and spin ($2S$) quantised electronic angular momenta through the gyromagnetic ratio [12] $\gamma_e$:

$$m_i = \gamma_e (L_i + 2S_i) , \tag{10}$$

the factor of 2 (to a good approximation) being generated essentially from relativistic quantum field theory. The magnitude of $L_i$ in quantum mechanics is $[L(L+1)]^{1/2}\hbar$, and this has a classical counterpart. The spin of the electron, on the other hand, has no classical counterpart and is a fundamental property of elementary matter, its spin quantum number $S$ taking the values $1/2$ and $-1/2$ from the Dirac equation.

We make the ansatz

$$\mathrm{i}\alpha''_i = \gamma_\pi (L_i + 2S_i) , \tag{11}$$

that the vector polarisability $\alpha''_i$ is similarly proportional through a constant akin to the gyromagnetic ratio,

$$\gamma_\pi \propto \gamma_e / E_0 c , \tag{12}$$

to the fundamental electronic angular momenta $L_i$ and $2S_i$. This kind of relation is indicated by symmetry (because angular momentum is T negative, P positive in the non-relativistic limit) and because the constant $\gamma_\pi$ of the form (12) is indicated by the fact that the products $m_i B_i$ and $\frac{1}{2}\mathrm{i}\alpha''_i \pi_i$ are both energies, and are therefore proportional via a scalar constant. This ansatz leads immediately to the novel fundamental quantities $\gamma_\pi L_i$ and $2\gamma_\pi S_i$, which we call respectively orbital and spin electronic polarisability.

The ansatz also implies that the same quantum numbers $L$ and $S$ define both the magnetic dipole moment and the vector polarisability $\alpha''_i$, implying that selection rules on both $m_i$ and $\alpha''_i$ are the same. Specifically, the selection rule on the "magnetic" quantum number

$$M = L, L-1, \ldots, -L$$

is

$$\Delta M = 0, \pm 1 , \tag{13}$$

for spectral phenomena due to the conjugate product $\boldsymbol{\pi}$.

## 2. Circular birefringence, dichroism, and ellipticity changes due to the conjugate product of pump laser optical rectification

The possibility of forward/backward and circular birefringence, dichroism, and probe ellipticity changes due to a pump laser, as measured by a co-axial probe, was first put forward [19] on the grounds of symmetry, and named "spin chiral" birefringence/dichroism. Subsequently, different classes of spin chiral type forward backward and circular birefringence have been isolated theoretically [20], and order of magnitude estimates given. The two classes are generated by different conjugate products, class one being due to the type (2). In this section we develop the semi-classical theory of class one effects in close formal analogy with the semi-classical theory of the Faraday $A$, $B$, and $C$ terms due to $\boldsymbol{B}$ [1] first given in quantum mechanical form by Serber [21], and in terms of origin-independent molecular property tensors by Buckingham and Stephens [22].

The Voigt–Born perturbation

$$\alpha''_{ij}(B_Z) = \alpha''_{ij} + \alpha''_{ijZ} B_Z + \ldots \tag{14}$$

of the semi-classical theory of the Faraday effect is replaced by

$$\alpha''_{ij}(\pi_Z)=\alpha''_{ij}-i\alpha''_{ijZ}\pi_Z+\dots \tag{15}$$

This perturbation of the relevant imaginary [1] part of the atomic or molecular polarisability is caused by the conjugate product (2) of a circularly polarised pump laser co-axial with a linearly polarised probe traversing an achiral ensemble. It causes rotation of the plane of the probe, accompanied by circular dichroism and ellipticity changes in the probe.

In close analogy with the theory of the Faraday effect, the angle of rotation is given in the laboratory frame by

$$\Delta\theta\approx\tfrac{1}{2}\omega\mu_0 cl\frac{N}{d_n}E_0^2\sum_n\left(\langle\alpha''_{XYZ}(f)\rangle+\frac{\langle\alpha''_{Zn}\alpha''_{XY}(f)\rangle}{kT}\right), \tag{16}$$

where $\omega$ is the measuring frequency (rad $s^{-1}$), $\mu_0$ the permeability in vacuo in SI units, $c$ the velocity of light (m $s^{-1}$), $l$ the sample length (m), $N$ the number of molecules per meter, $d_n$ the quantum state degeneracy, $E_0^2$, the square of the pump laser electric field strength, is in $V^2$ $m^{-2}$, and $kT$ the thermal energy per molecule. The factor $f$ is the dispersive line shape function [1]. The ellipticity change in the probe is

$$\Delta\eta\approx\tfrac{1}{2}\omega\mu_0 cl\frac{N}{d_n}E_0^2\sum_n\left(\langle\alpha''_{XYZ}(g)\rangle+\frac{\langle\alpha''_{Zn}\alpha''_{XY}(g)\rangle}{kT}\right), \tag{17}$$

where $g$ is the absorptive lineshape function [1].

The circular birefringence and dichroism due to $\boldsymbol{\pi}$ can be written in formal analogy with the magnetic electronic [1] $A$, $B$, and $C$ terms, written in the molecule fixed frame, as follows:

$$\Delta\theta\approx-\frac{\mu_0 clNE_0^2}{3\hbar}\left[\frac{2\omega_{jn}\omega^2}{\hbar}(f^2-g^2)A+\omega^2 f\left(B+\frac{C}{kT}\right)\right], \tag{18}$$

$$\Delta\eta\approx-\frac{\mu_0 clNE_0^2}{3\hbar}\left[\frac{4\omega_{jn}\omega^2}{\hbar}fgA+\omega^2 g\left(B+\frac{C}{kT}\right)\right], \tag{19}$$

for a quantum transition from $n$ to $j$, where $n$ is the state of lower energy, usually the ground state. The $A$, $B$, and $C$ terms due to the pump laser's conjugate product are

$$A=\frac{3}{d_n}\sum_n(\alpha''_{jZ}-\alpha''_{nZ})\,\mathrm{Im}(\langle n|\mu_X|j\rangle\langle j|\mu_Y|n\rangle)\,,$$

$$B=\frac{3}{d_n}\sum_n\mathrm{Im}\left(\sum_{k\neq n}\frac{\langle k|\alpha''_Z|n\rangle}{\hbar\omega_{kn}}(\langle n|\mu_X|j\rangle\langle j|\mu_Y|k\rangle-\langle n|\mu_Y|j\rangle\langle j|\mu_X|k\rangle)\right.$$
$$\left.+\sum_{k\neq j}\frac{\langle j|\alpha''_Z|k\rangle}{\hbar\omega_{kj}}(\langle n|\mu_Y|j\rangle\langle k|\mu_Y|n\rangle-\langle n|\mu_Y|j\rangle\langle k|\mu_X|n\rangle)\right),$$

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

which represent a sum over transitions from component states of a degenerate set to an excited state $\psi_j$, which itself could be a member of a degenerate set. Note the $A$ term requires a definition of the vector polarisability $\alpha''_Z$ in states $n$ and $j$. The definition in state $n$ is eq. (4), and the definition in state $j$ is

$$\alpha''_{\alpha\beta,j}=-\alpha''_{\alpha\beta,j}=-\frac{2}{\hbar}\sum_{k\neq j}\frac{\omega}{\omega_{kj}^2-\omega^2}\,\mathrm{Im}(\langle j|\mu_\alpha|k\rangle\langle k|\mu_\beta|j\rangle)\,, \tag{20}$$

where $k$ is a state of higher energy than $j$. In writing the $A$, $B$, and $C$ terms in this way, weighted Boltzmann averaging [1] has been used with the interaction energy ratio $-\alpha''_Z E_{0Z}^2/kT$. A $Q$-switched and focused Nd:YAG laser produces $E_0$ of about $10^9$ V m$^{-1}$, and for an order of magnitude estimate of $10^{-38}$ C$^2$ m$^2$ J$^{-1}$ for $\alpha''_Z$ the ratio $\alpha''_Z E_{0Z}^2/kT$ is of the order unity at T = 300 K.

The $A$ term is responsible for Zeeman splitting by the pump laser of spectra measured by a tunable probe laser or co-axial broad band probe. In this context, note that in a right circularly polarised pump laser the photon has a $-\hbar$ projection in the $\boldsymbol{k}$ axis, producing a change $\Delta M = -1$ in the atomic or molecular quantum state. In a left circularly polarised probe, the photon is projected $\hbar$, and the selection rule is $\Delta M = 1$. In a linearly polarised pump the selection rule is $\Delta M = 0$. This is accounted for classically in eq. (2), where the left conjugate product is positive, and the right negative. The sign change produced by switching the pump from left to right circular polarisation is equivalent to the change produced in the Faraday effect by switching the direction of $\boldsymbol{B}$ relative to the propagation vector of the probe from parallel to antiparallel.

As in the $\boldsymbol{B}$ induced Faraday effect, the $A$ term due to $\boldsymbol{\pi}$ comes from the splitting of lines by $\boldsymbol{\pi}$ into right and left circularly polarised components (the equivalent of the normal Zeeman effect). The $B$ term due to $\boldsymbol{\pi}$ originates from the mixing of energy levels due to the pump laser, and the $C$ term is a change of electronic population of the pump-laser-split ground state. In each case the magnetic dipole moment operator of the Zeeman effect is replaced by an orbital/axial vector polarisability operator with the same P and T symmetries and $M$ quantum number selection rules. However, this molecular quantity as defined by eq. (4) is capable of amplification by resonance when the pump laser frequency is tuned to a natural transition frequency of the material being irradiated, so that

$$\omega_{jn} \approx \omega \tag{21}$$

in the denominator of eq. (4). This feature is absent in the conventional Zeeman effect due to $\boldsymbol{B}$.

In the latter, the $A$ and $C$ terms need degenerate ground or excited states to support diagonal matrix elements of the magnetic dipole moment operator, and these are available by symmetry [1] only in molecules with three fold or higher proper rotation axes. In the $\boldsymbol{\pi}$ induced $A$ and $C$ terms, on the other hand, the vector polarisabilities in states $n$ and $j$ exist in general in the presence and absence of degeneracy, from the definitions (4) and (20). Therefore, although the same selection rules appear to apply to the quantum number $M$, the induced $A$ and $C$ terms should be visible in molecules of lower symmetry than in the conventional $\boldsymbol{B}$ induced equivalents.

*Pump laser induced electron and proton spin resonance.* The discussion just given of the $\boldsymbol{\pi}$ induced $A$ and $C$ terms leads to the theoretical prediction of electron and nuclear spin resonance due to optical rectification, clearly of great potential value if verified experimentally. The origin of electron spin resonance with $\boldsymbol{\pi}$ is found in the quantum nature of the vector polarisability $\boldsymbol{\alpha}''$, which is proportional through eq. (11) to the sum of the orbital and spin angular momenta of the electron, the latter taking the values 1/2 and −1/2. If the probe is tuned to the resonance frequency $\omega_R$, it is absorbed when

$$\hbar\omega_R = E(1/2) - E(-1/2) = 2\hbar\gamma_\pi E_0^2 \tag{22}$$

which is electron spin resonance due to optical rectification. This depends on the $\Delta M = 1$ transition between the electron spin polarisability states 1/2 and −1/2. If the pump laser inputs the energy $\alpha''_Z E_{0Z}^2$, the resonance frequency range is roughly $\alpha''_Z E_{0Z}^2/\hbar$, which is in the GHz for an order of magnitude $10^{-38}$ C$^2$ m$^2$ J$^{-1}$ for the spin polarisability, and a pump laser electric field strength of the order $10^6$ to $10^8$ V m$^{-1}$. Conventional ESR spectrometers can therefore be adapted for use with the pump laser, using existing microwave frequency probes. Again, by tuning the pump to a natural transition frequency in the visible, for example, the vector polarisability can be increased greatly by this second type of resonance, giving the possibility of "double resonance".

A significant feature of conventional EPR/ESR due to $\boldsymbol{B}$ is retained when $\boldsymbol{B}$ is substituted by $\boldsymbol{\pi}$. This is coupling of electron to proton spins, caused in the $\boldsymbol{\pi}$ induced transition between electron orientation states by the interaction of the spin angular momenta of the electron with protons which have non-vanishing spin angular momentum quantum numbers. This hyperfine structure can be induced, under the right conditions, by the optical rectification of a pulsed laser, dispensing with the need for highly homogeneous magnets. In the triphenyl methyl radical, for example, the ***B*** induced hyperfine structure of one resonance peak due to this mechanism contains no less than 196 separate lines. A similar hyperfine structure is expected using $\boldsymbol{\pi}$ instead of ***B***, with the added possibilities of double resonance as discussed already, exploiting different pump laser frequencies and electric field strengths to produce a rich spectral variety for analytical purposes.

If the pump laser is used in the same $Z$ axis as the homogeneous magnet, the Hamiltonian becomes

$$\Delta H_1 = -\gamma_{\mathrm{N}} \boldsymbol{I}\cdot\boldsymbol{B} - \tfrac{1}{2}\gamma_\pi \boldsymbol{J}\cdot\boldsymbol{\pi}\,, \tag{23}$$

where $I$ is the nuclear spin angular momentum quantum number, $\gamma_{\mathrm{N}}$ is the nuclear gyromagnetic ratio, and the angular momentum $\boldsymbol{J}$ is the sum

$$\boldsymbol{J} = \boldsymbol{L} + 2\boldsymbol{S}\,.$$

The Hamiltonian (23) can be rewritten in the Landé form,

$$\Delta H_2 = -\gamma_{\mathrm{N}}\left(1 + \frac{I(I+1) - J(J+1)}{2J_{\mathrm{tot}}(J_{\mathrm{tot}}+1)}\right)\boldsymbol{J}_{\mathrm{tot}}\cdot\boldsymbol{B} - \frac{\gamma_\pi}{2}\left(1 - \frac{I(I+1) - J(J+1)}{2J_{\mathrm{tot}}(J_{\mathrm{tot}}+1)}\right)\boldsymbol{J}_{\mathrm{tot}}\cdot\boldsymbol{\pi}\,, \tag{24}$$

where

$$J_{\mathrm{tot}} = J + I, \ldots, |J - I|$$

is the total angular momentum quantum number. For $I \neq 0$ the customary NMR line, defined through the selection rule

$$\Delta M_I = \pm 1 \tag{25}$$

is split into a new pattern of lines dependent on the section rules

$$\Delta M_{J_{\mathrm{tot}}} = 0, \pm 1 \tag{26}$$

and on the individual values of $I$ and $J$. This has vast potential application in the analytical laboratory, because modifications to include $\boldsymbol{\pi}$ can be made in standard NMR instruments, including 2D and Fourier transform NMR, and NMR imaging for different nuclei, pump laser frequencies. and electric field strengths.

## 4. Optical activity in scattered probe radiation induced by pump laser optical recification

The P positive T negative conjugate product $\boldsymbol{\pi}$ induces optical activity in Raman and Rayleigh scattered radiation in the same way as the static magnetic flux density ***B***. The semi-classical theory of this type of optical activity is developed in this section with the vector polarisability $\boldsymbol{\alpha}''$ taking the role of magnetic dipole moment ***m***. The development is a close formal analogy with the theory of light scattering optical activity due to ***B*** given in detail in ref. [1].

The starting point of the theory is the Voigt–Born expansion (15) of the polarisability in terms of the conjugate product $\pi_Z$. In analogy with the theory of light scattering optical activity due to ***B***, a weighted Boltzmann average with energy ratio

$$V = -\alpha''_Z E_{0Z}^2 / kT \tag{27}$$

is applied to obtain laboratory frame weighted averages of the type

$$\begin{aligned}\langle \alpha_{XX}\alpha^*_{XY}\rangle_\pi = \mathrm{i}E_{0Z}^2 \langle &\alpha'_{XX}\alpha''^*_{XYZ} - \alpha''_{XX}\alpha'^*_{XYZ} + \alpha'_{XXZ}\alpha''^*_{XZ} - \alpha''_{XXZ}\alpha^*_{XY} \\ &+ (1/kT)(\alpha'_{XX}\alpha''^*_{XY}\alpha''_{Zn} - \alpha''_{XX}\alpha^*_{XY}\alpha''_{Zn}) + \ldots\rangle\,.\end{aligned} \tag{28}$$

Non-zero terms occur for $E_0^2 \equiv E_{0Z}^2$; for example

$$\langle \alpha'_{XX}\alpha''^{*}_{XYZ} \rangle = \alpha'_{\gamma\delta}\alpha''^{*}_{\epsilon\alpha\beta}\langle j_\alpha k_\beta i_\gamma i_\delta i_\epsilon \rangle = \tfrac{1}{30}(2\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha''^{*}_{\beta\gamma\delta} + \alpha'_{\alpha\alpha}\epsilon_{\beta\gamma\delta}\alpha''_{\gamma\delta\beta}) \,, \tag{29}$$

where the Greek subscripts, following ref. [1], refer to molecule-fixed frame quantities.

The Stokes parameters describing the radiation scattered from a probe laser parallel to the circularly polarised pump laser are supplemented by terms as follows describing the optical activity in the scattered probe radiation produced by the pump's conjugate product $\pi_Z$; e.g.,

$$\begin{aligned} S_0^{\mathrm{d}}(0^\circ) = -2KE_{0Z}^2[&2\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha''^{*}_{\beta\gamma\delta} + \alpha'_{\alpha\alpha}\epsilon_{\beta\gamma\delta}\alpha''^{*}_{\gamma\delta\beta} + 2\alpha''_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha'^{*}_{\gamma\beta\delta} + \alpha''_{\alpha\beta}\epsilon_{\alpha\beta\gamma}\alpha'^{*}_{\delta\delta\gamma} \\ &+ (1/kT)(2\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha''^{*}_{\beta\gamma}\alpha''_{\delta n} + \alpha'_{\alpha\alpha}\epsilon_{\beta\gamma\delta}\alpha''^{*}_{\gamma\delta}\alpha''_{\beta n})]P\sin 2\eta \,, \end{aligned} \tag{30}$$

$$S_1^{\mathrm{d}}(0^\circ) = S_2^{\mathrm{d}}(0^\circ) = 0 \,, \tag{31}$$

$$\begin{aligned} S_3^{\mathrm{d}}(0^\circ) = -2KE_{0Z}^2[&2\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha''^{*}_{\beta\gamma\delta} + \alpha'_{\alpha\alpha}\epsilon_{\beta\gamma\delta}\alpha''^{*}_{\gamma\delta\beta} + 2\alpha''_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha'^{*}_{\gamma\beta\delta} + \alpha''_{\alpha\beta}\epsilon_{\alpha\beta\gamma}\alpha'^{*}_{\delta\delta\gamma} \\ &+ (1/kT)(2\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha''^{*}_{\beta\gamma}\alpha''_{\delta n} + \alpha'_{\alpha\alpha}\epsilon_{\beta\gamma\delta}\alpha''^{*}_{\gamma\delta}\alpha''_{\beta n})] \,. \end{aligned} \tag{32}$$

These terms are formally identical with Barron's equations (3.5.45)–(3.5.47) of ref. [1], but implement $\pi_Z$ in place of $B_Z$ and the polarisability $\alpha''_Z$ in place of the magnetic dipole moment $m_Z$. As in scattered optical activity due to $\boldsymbol{B}$, that due to $\boldsymbol{\pi}$ of the pump laser does not lead to a circularly polarised component in the light scattered at 90° if the pump and probe lasers are parallel. Such a component can be generated in the scattered probe radiation, however, by a circularly polarised pump laser parallel to the scattered beam. Again in analogy with $\boldsymbol{B}$ induced scattered optical activity, the intensity of the scattered probe radiation depends on the degree of circularity of the incident probe only if the pump is parallel with the probe.

The circular intensity differences for scattering of probe radiation at 0°, 180°, and 90° due to optical rectification in a circularly polarised pump laser parallel to the incident probe radiation are found by analogy with the original theory of Barron and Buckingham [23] as follows, e.g.,

$$\begin{aligned} \Delta(0^\circ) = -2E_{0Z}^2[&2\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha''^{*}_{\beta\gamma\delta} + \alpha'_{\alpha\alpha}\epsilon_{\beta\gamma\delta}\alpha''^{*}_{\gamma\delta\beta} + 2\alpha''_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha'^{*}_{\gamma\beta\delta} + \alpha''_{\alpha\beta}\epsilon_{\alpha\beta\gamma}\alpha'^{*}_{\delta\delta\gamma} \\ &+ (1/kT)(2\alpha'_{\alpha\beta}\epsilon_{\alpha\gamma\delta}\alpha''^{*}_{\beta\gamma}\alpha''_{\delta n} + \alpha'_{\alpha\alpha}\epsilon_{\beta\gamma\delta}\alpha''^{*}_{\gamma\delta}\alpha''_{\beta n})] \\ &\times (7\alpha'_{\lambda\mu}\alpha'^{*}_{\lambda\mu} + \alpha'_{\lambda\lambda}\alpha'^{*}_{\mu\mu} + 5\alpha''_{\lambda\mu}\alpha''^{*}_{\lambda\mu})^{-1} \,, \end{aligned} \tag{33a}$$

$$\Delta(180^\circ) = \Delta(0^\circ) \,. \tag{33b}$$

(Note that there is a minor typographical error in Barron's [1] eqs. (3.5.48)–(3.5.53d), where "*kt*" should read "*kT*".)

In our eqs. (30)–(33) above the molecular property tensors are all expressed in the molecule-fixed frame, and the tensor summation convention is implied over repeated indices.

As in the theory of magnetically induced Raman scattered optical activity, there are contributory cross terms in Raman scattering due to optical rectification containing the real antisymmetric and imaginary symmetric parts of the transition polarisability tensors defined in ref. [1]. They are formally identical with eq. (3.5.51) of ref. [1] with the term $B_Z$ of those equations replaced by $E_{0Z}^2$; and the term $m_{Zn}$ replaced by $\alpha''_{Zn}$, the $Z$ component of the vector orbital/spin polarisability in quantum state $n$ as defined in eq. (4). These equations are not reproduced here due to their great algebraic complexity. (Note, however, that "*kt*" in Barron's eq. (3.5.51) should read "*kT*".)

As in the theory of magnetic Rayleigh and Raman optical activity, a simpler appreciation [1] of circular intensity difference

$$\Delta = \frac{I^{\mathrm{R}} - I^{\mathrm{L}}}{I^{\mathrm{R}} + I^{\mathrm{L}}} \tag{34}$$

in scattered probe radiation due to optical rectification in the pump laser may be found from

$$\Delta_X(90^\circ) = \frac{2\,\mathrm{Im}(\alpha_{XY}\alpha^*_{XX})}{\mathrm{Re}(\alpha_{XX}\alpha^*_{XX} + \alpha_{XY}\alpha^*_{XY})}\,, \tag{35}$$

$$\Delta_Z(90^\circ) = \frac{2\,\mathrm{Im}(\alpha_{ZY}\alpha^*_{ZX})}{\mathrm{Re}(\alpha_{ZX}\alpha^*_{ZX} + \alpha_{ZY}\alpha^*_{ZY})} \tag{36}$$

by writing the polarisabilities perturbed as in eq. (15) by the conjugate product of the pump laser, and taking a Boltzmann average. This procedure gives Rayleigh and Raman scattered optical activity associated with diagonal scattering transitions; but for off diagonal transitions the theory of Rayleigh and Raman optical activity in scattered probe radiation due to the circularly polarised pump laser is worked directly [1] from eqs. (35) and (36), giving information directly on the ground state Zeeman splitting due to $\pi_Z$.

Optical activity in scattered radiation due to $\pi_Z$ appears at this early stage of understanding to have an advantage over the equivalent phenomenon due to $B_Z$. This is because magnetic fields have little direct influence on molecular vibrational states, whereas $\pi_Z$ interacts with the molecule via the vector polarisability $\alpha''_Z$, which may be influenced considerably by tuning the pump to a vibrational transition of the molecule. In this context the vector polarisability is defined for pump induced probe Raman scattering through the Placzek approximation used by Barron [1],

$$\alpha_{\alpha\beta} \rightarrow (\alpha_{\alpha\beta})_{v_m v_n} = \langle v_m | \alpha_{\alpha\beta}(Q) | v_n \rangle\,, \tag{37}$$

between vibrational states $v_m$ and $v_n$.

Similar definitions can be used for the various possibilities engendered by electronic/vibrational coupling.

The discussion in ref. [1] of scattered magnetic optical activity is confined to resonance effects, but it appears possible to observe $\pi_Z$ induced optical activity in scattered probe radiation in *transparent* Raman scattering, for example, if the pump frequency is tuned to a natural electronic/vibrational transition of the molecule.

## 5. Discussion of other phenomena due to pump laser optical rectification

It appears possible to exploit the identical T and P symmetries of $\boldsymbol{B}$ and $\boldsymbol{\pi}$ in other interesting directions: wherever $\boldsymbol{B}$ has been used customarily, then so can $\boldsymbol{\pi}$. The discussion here is qualitative.

One of the most interesting possibilities is in the area of interaction of electron and neutron beams with circularly polarised pump lasers with finite $\boldsymbol{\pi}$. For example, the well known experiment of Wu et al. [24], proving P non-conservation, was originally performed with magnetic flux density to align the nuclear spin angular momentum $\boldsymbol{I}$ of $^{60}$Co, with subsequent measurement of the angular distribution of emitted electrons in a β decay process,

$$^{60}\mathrm{Co} \rightarrow {}^{60}\mathrm{N}_i^+ + \mathrm{e}^- + \bar{\nu}_e\,. \tag{38}$$

This concept can be repeated, in principle, with $\boldsymbol{\pi}$ of the pump laser substituted for $\boldsymbol{B}$, to probe further the non-conservation of parity in molecular and atomic ensembles.

It is also clear that magnetic effects in areas such as inelastic neutron scattering can be generated in principle by directing the pump laser parallel to the incident neutron beam, resulting in circular differential intensity differences similar to eq. (33) for light scattering.

Finally the Hall effect and quantum Hall effect can depend on applied magnetic flux density $\boldsymbol{B}$, and it appears that the conjugate product $\boldsymbol{\pi}$ would have similar effects in analogy.

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