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LASER ZEEMAN AND NMR SPECTROSCOPY: EFFECTIVE TORQUE AND LASER LARMOR PRECESSION

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Laser Zeeman effects are caused by optical rectification in an electromagnetic field, in close formal analogy with the well known effects of static magnetic flux density (B). The conjugate product ($\mathbf{\Pi}$) and dynamic molecular polarisability vector ($i\boldsymbol{\alpha}''$) form a torque formally analogous to that between the molecular magnetic dipole moment ($\mathbf{m}$) and B. This defines the Larmor frequency of precession, which is shown to be directly proportional to the square of the electric field strength (E_0, in volt m^{-1}) of the laser through a molecular constant analogous to the gyromagnetic ratio. Supercomputer simulation is used to show that this torque generates distinctive new ensemble averages (time cross correlation functions) which mediate the onset of circular birefringence and dichroism ("magnetic" optical activity). Resonance in the presence of a co-axial magnetic field leads to "laser NMR" effects, which are created simply in terms of the torque and Larmor precession.

Introduction

Zeeman[1] appears to have been the first to observe spectral broadening due to static magnetic flux density (B), known as the Zeeman effect. The quantum theory of the Faraday effect, due to Serber[2] and Rosenfeld[3] shows that its A term is responsible for Zeeman splitting,[4] and this was given new impetus by the semi-classical treatment of Buckingham and Stephens.[5] The development of the subject in terms of group theory is described in detail by Piepho and Schatz[6] and Steinfeld,[7] one of the earliest descriptions available is that of Townes and Schawlow.[8]

Recently, it has been shown theoretically[9–12] and numerically[13] that the conjugate product $\mathbf{\Pi}$ of a laser produces a range of spectral effects in close formal analogy with the Zeeman effect due to B. The atomic or molecular quantity mediating "laser Zeeman" spectroscopy is an axial vector α_i'' which transforms as a rank two antisymmetric polar tensor, the imaginary part of the dynamic polarisability, α_{ij}. The equivalent axial vector and polar tensor representations are linked mathematically by[4]

$$\alpha_i \equiv \alpha_i' - i\alpha_i'' \; ; \tag{1a}$$

$$\alpha_i'' = \varepsilon_{ijk}\,\alpha_{jk}'' \; ; \tag{1b}$$

where ε_{ijk} is the rank three totally antisymmetric unit tensor, the Levi-Civita symbol. As usual, summation over repeated tensor subscripts is implied (the Einstein notation). The axial vector α_i'' is negative to motion reversal (T) and positive to parity inversion (P). It is formally analogous to the magnetic dipole moment m_i which mediates the Zeeman effect. The interaction hamiltonian to first order of the laser Zeeman effect is[9–12]

$$\Delta H = -\frac{1}{2}\alpha_i \Pi_i = -\alpha_z'' E_0^2 |\mathbf{k}| \tag{2}$$

which is formally analogous to

$$\Delta H = -m_z B_z \tag{3}$$

of the magnetic (conventional) Zeeman effect.

It has been shown theoretically that the hamiltonian (2) produces circular[9] and forward backward[10] birefringence, spectral splitting[11] and effects analogous to those of B in ESR and NMR.[12] In chiral media, it also produces frequency dependent electric polarisation, which has been supercomputer simulated and animated in the dielectric (GHz) and far infrared frequency (THz) range.[13]

In Sec. 1 we define the Larmor frequency of precession due to the conjugate product $\mathbf{\Pi}$ of a circularly polarised laser, such as carbon dioxide or Nd:YAG. The torque used for this definition is that between $i\alpha_i''$ and Π_i, and this is shown by supercomputer simulation in Sec. 2 to produce distinctive ensemble averages which measure the thermodynamically averaged response of the ensemble to the circularly polarised laser's conjugate product. These are exemplified by the time cross correlation function (c.c.f.) between the linear center of mass velocity ($\mathbf{v}$) and angular velocity ($\boldsymbol{\omega}$) of a diffusing molecule in liquid water at 293 K, 1.0 bar:

$$C_1(t) = \frac{\langle v_i(t)\omega_j(0)\rangle}{\langle v_i^2\rangle^{1/2}\langle \omega_j^2\rangle^{1/2}} . \tag{4}$$

Finally, Sec. 3 introduces a frequency dependent (oscillating) measuring field in the same Z axis as the propagation vector of the circularly polarised pump laser, and defines resonance conditions using a simple classical treatment formally analogous to those used in the elementary theory of NMR. The new features are called "laser NMR" and "laser NMR relaxation" effects, and are identified with the nuclear hyperfine structure of laser Zeeman spectroscopy.

1. The Laser Larmor Precession Frequency

The "laser Larmor" precession to be described here is due to a torque

$$\mathbf{Tq} = E_0^2 \boldsymbol{\alpha}'' \times \mathbf{k} \tag{5}$$

which produces precession of $\boldsymbol{\alpha}''$ around the direction of $\mathbf{k}$. The latter is defined in a circularly polarised laser as

$$\boldsymbol{\Pi} = \mathbf{E}_{\mathrm{L}}^{+} \times \mathbf{E}_{\mathrm{L}}^{-} = -\mathbf{E}_{\mathrm{R}}^{+} \times \mathbf{E}_{\mathrm{R}}^{-} = 2\,E_0^2\,i\,\mathbf{k} \tag{6}$$

where the subscripts L and R denote left and right circularly polarised, respectively, and the superscripts + and − denote plus or minus conjugation. E_0 denotes the electric field strength in volts m^{-1} of the laser, and $\mathbf{k}$ is a unit vector in the propagation direction of the laser.[9–13]

A classical analysis of the motion of the dynamic polarisability vector $\boldsymbol{\alpha}''$ can be made in close formal analogy with the analysis of the motion of $\mathbf{m}$ in a static magnetic field B.[7] The torque[5] is the basis of this treatment and is the rate of change of angular momentum by definition. The polarisability vector $\boldsymbol{\alpha}''$ and angular momentum ($\mathbf{J}$) are both T negative, P positive, quantities, and are related by a scalar quantity γ_π analogous to the gyromagnetic ratio:

$$i\boldsymbol{\alpha}_i'' = \gamma_\pi J_i = \gamma_\pi(L_i + 2.002\,S_i)\ . \tag{7}$$

(In relativistic quantum mechanics J has an electronic spin ($2.002\mathbf{S}$) as well as orbital ($\mathbf{L}$) component.)

The classical equation of motion of $\boldsymbol{\alpha}''$ in a field $\boldsymbol{\Pi}$ is therefore

$$\frac{d\boldsymbol{\alpha}''}{dt} = \gamma_\pi E_0^2\,\boldsymbol{\alpha}'' \times \mathbf{k} \tag{8}$$

whose solution[7] is the precesson of α'', in which its Z component is constant and the X and Y components rotate with a constant magnitude in a plane perpendicular to the Z axis with frequency $\gamma_\pi E_0^2$, the precession frequency due to the conjugate product $\boldsymbol{\Pi}$ of the laser.

The "laser Larmor frequency" can be emphasised by transforming the equation of motion (8) to a rotating coordinate system in order to find[7] the motion of the axial vector $\boldsymbol{\alpha}''$ at an angular frequency $|\boldsymbol{\Omega}|$ to be specified. Following the conventional treatment in Chapter 11 of Steinfeld[7] for example, gives

$$\begin{aligned}\frac{d\boldsymbol{\alpha}''}{dt} &= (\boldsymbol{\alpha}'' \times \mathbf{k})\gamma_\pi E_0^2 - \boldsymbol{\Omega} \times \boldsymbol{\alpha}'' \\ &= \boldsymbol{\alpha}'' \times (\gamma_\pi E_0^2 \mathbf{k} + \boldsymbol{\Omega})\ .\end{aligned} \tag{9}$$

Choosing the frequency

$$\boldsymbol{\Omega} = -\gamma_\pi E_0^2 \mathbf{k} \tag{10}$$

implies

$$\frac{d\boldsymbol{\alpha}''}{dt} = \mathbf{0} \tag{11}$$

i.e. that the vector $\boldsymbol{\alpha}''$ appears time invariant in the rotating frame. The frequency $\gamma_\pi E_0^2$ is the laser Larmor precession frequency of the dynamic atomic or molecular polarisability in the circularly polarised laser. In other words $\boldsymbol{\alpha}''$ precesses about the propagation axis of the laser (the Z axis).

We have shown classically that optical rectification in a circularly polarised pump laser produces atomic and molecular dynamic polarisability precession analogous with the precession of the magnetic moment $\mathbf{m}$ about applied static magnetic flux density B. In principle, therefore, the laser field can be used for the observation of hyperfine resonance akin to those in NMR. This is discussed further in Sec. 3 of this paper, where we consider the effect of $\boldsymbol{\Pi}$ on a co-axial, oscillating, and measuring magnetic field. At the laser Larmor frequency ω_L the effect of the pump laser's $\boldsymbol{\Pi}$ on the motion of $\boldsymbol{\alpha}''$ can be ignored,[7] and serves to establish energy differences between M angular momentum quantum levels defined by

$$J = L + 2.002S$$

$$M = J, \quad J-1, \ldots, -J \ .$$

2. Supercomputer Simulation of the Effects of the Torque[8]

The molecular dynamics computer simulation of torques of the type (8) was first used[14] in 1982 to generate the Langevin function and dynamical response characteristics of a molecular ensemble subjected to a strong, static, electric field. In 1985, the presence of an electric field induced c.c.f. of the type (4) was demonstrated in the laboratory frame.[15,16] Since then the technique has been used to reveal several new diffusion phenomena such as the decoupling effect[17] and fall transient acceleration.[18] Recently it has been applied to novel asymmetric correlation functions induced by shear stress[19–21] using non-equilibrium techniques.

In order to simulate the torque classically, an approximation is needed to the semi-classical definition[4] of the vector $\boldsymbol{\alpha}''$:

$$\alpha''_\gamma = \varepsilon_{\alpha\beta\gamma}\alpha''_{\alpha\beta} = -\frac{2}{\hbar}\left(\frac{\omega}{\omega_{jn}^2 - \omega^2}\right) \times \mathrm{Im}\ \varepsilon_{\alpha\beta\gamma}\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle \tag{12}$$

for a transition between the quantum states n and j. Here μ_α and μ_β are orthogonal electric dipole moments defined in the molecule fixed frame (α, β, γ). The transition frequency is

$$\omega_{jn} = \omega_j - \omega_n \tag{13}$$

in radian s^{-1}, and it is assumed that there is no absorption or dispersion of the pump laser, applied at frequency ω, so that the lineshape function[4] is effectively zero. The pump laser is applied therefore in a transparent part of the spectrum.

The symmetry of the molecule fixed frame quantity

$$\text{Im } \varepsilon_{\alpha\beta\gamma} \langle n | \mu_\alpha | j \rangle \langle j | \mu_\beta | n \rangle$$

is that of an axial vector, and is the same symmetry as angular momentum, represented by the well known R symbols of the molecular point group character tables.[22] In the water molecule for example, of C_{2v} symmetry, there are three independent components, denoted $R_\gamma(A_2)$; $R_\beta(B_1)$; and $R_\alpha(B_2)$ in the last column of the character table. This means that α has three independent components in the molecule fixed frame, denoted α''_α, α''_β, and α''_γ, respectively. This gives a classical representation for α'' to be used in the computer simulation.

The representation of the conjugate product $\mathbf{\Pi}$ is straightforward because it is phase independent, proportional to the square of the electric field strength and directed in the Z axis of the laboratory frame.

2.1. *Simulation conditions*

Using a rotation matrix consisting of unit vector components in the three principal molecular moments of inertia[23] of the water molecule, the vector $E_0^2\mathbf{k}$ was first transformed into the molecule fixed frame.[13] A frame invariant value of

$$\omega_{ij} = 0.9\,\omega \tag{14}$$

was used to define the amplitude of α''_γ. The components α''_γ, α''_β, and α''_α were coded in the arbitrary ratio 7:5:3 in the absence of experimental data. The torque (8) was evaluated in frame (α, β, γ) and back transformed finally into the laboratory frame (X, Y, Z), where it was incorporated in the forces loop[23] of the code.

The simulation proceeded at 293 K and 1.0 bar, using a liquid sample of 108 water molecules, with the intermolecular potential described in Ref. 23, p. 287. An integration time step of 0.5 fs was used and the c.c.f.[4] evaluated over two contiguous segments of about 2,500 time steps each. This gave the noise level illustrated in Fig. 1, which shows that the (X, Y) and (Y, X) elements of the c.c.f. are mirror images. The c.c.f. is therefore that of a molecular Coriolis acceleration[24,25]

$$C_1(t) = \frac{\langle \mathbf{v}(t) \times \boldsymbol{\omega}(0) \rangle}{\langle v^2 \rangle^{1/2} \langle \omega^2 \rangle^{1/2}} \tag{15}$$

in the laboratory frame induced by the conjugate product of the applied laser field. The latter was enough to raise the energy of the system by 19.5 KJ/mole,

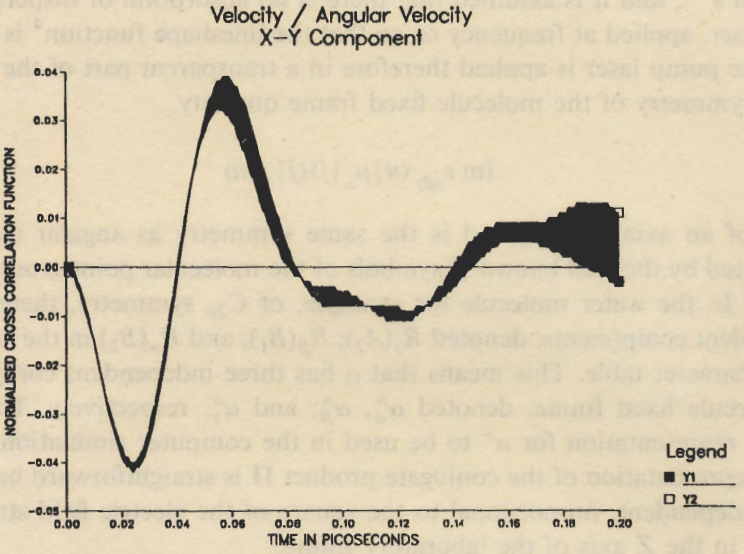

Fig. 1. The XY component

$$C_{XY}(t) = \frac{\langle v_X(t)\omega_Y(0)\rangle}{\langle v_X^2\rangle^{1/2}\langle\omega_Y^2\rangle^{1/2}}$$

of the Coriolis time correlation function of water in the laboratory frame induced by the laser conjugate product interacting with the imaginary part of the dynamic polarisability of water. The YX component (not shown) was also computed, and is the mirror image.

i.e. injected about 1.0 kT per molecule into the ensemble. For an order of magnitude[9] for α'' of about $10^{-38}\,J^{-1}C^2\,m^2$; this means that the electric field strength of the laser was of the order 10^7 volt m^{-1}; easily obtainable[26] in a pulsed Nd:YAG for example. The simulation is therefore carried out under accessible practical conditions. As fully described in the literature,[14–18,23] the system was allowed to reequilibrate into a Π-applied steady state before computing the c.c.f. (4), (15). In this steady state the computed rotational and translational temperatures were satisfactorily within the range of the input temperature of 293 K, and the computed pressure fluctuated about 1.0 bar for an input liquid density of 1.0 gm/cm^3. The simulation was carried out on the IBM 3090-6S of the Cornell National Supercomputer Facility.

The simulation allows the effect of the torque (8) to be measured on water spectra in the far infra red region,[23] where an anisotropy was observed in the Fourier transform[27] of the far infra red power absorption coefficient. The component in the Z axis differed from those in the X and Y axes in frequency dependence. This was also observed for the Fourier transform of the dielectric loss at lower frequency regions than the far infra red.[27] Higher frequency regions were not accessible to the simulation, but these results demonstrate clearly the

dynamical effect of the torque (8) which is accompanied[9] by the development of circular birefringence and dichroism[4] formally analogous to the Faraday effect of B (magnetic electronic circular dichroism).

It is interesting to note that the c.c.f. in Fig. 1 is a P negative, T positive quantity (a Coriolis acceleration) produced by the torque (8), which has the same symmetry as the torque[14]

$$\mathbf{Tq}_E = -\boldsymbol{\mu} \times \mathbf{E}_s \tag{16}$$

between an electric dipole moment ($\boldsymbol{\mu}$) and static electric field $\mathbf{E}_s$.[14]

The appearance in the laboratory frame of a c.c.f., that is, a Coriolis acceleration can be clarified analytically as a direct consequence of the fact that the simulation evaluated a torque (the time derivative of an angular momentum) in the moving, molecule fixed, frame, and transformed back into the laboratory frame. This procedure introduces laboratory frame Coriolis and centripetal accelerations[23–25] through the well known theorem of dynamics:

$$[\ddot{\mathbf{r}}]_{\alpha,\beta,\gamma} = [\ddot{\mathbf{r}} - 2\boldsymbol{\omega} \times \mathbf{v} - \dot{\boldsymbol{\omega}} \times \mathbf{r} + (\boldsymbol{\omega} \times \mathbf{r})]_{X,Y,Z} \tag{17}$$

applied to a position vector $\mathbf{r}$ in the molecule fixed frame, and back transformed into the laboratory frame.

The ensemble averaged Coriolis acceleration $2\langle \mathbf{v}(t) \times \boldsymbol{\omega}(0) \rangle$ is therefore one of the characteristic liquid (or gas) phase responses of the sample to the conjugate product of the circularly polarised laser, and accompanies the precession of $\boldsymbol{\alpha}''$ around $\boldsymbol{\Pi}$.

3. Pump/Probe Effects, Laser Induced Hyperfine Resonance at GHz Frequencies

In this section we introduce a probe electromagnetic field at GHz frequencies propagating in the same, Z, axis as the circularly polarised pump laser, and consider resonances observed with the probe field in direct analogy to NMR and ESR, where static magnetic flux density takes the part of our circularly polarised pump laser. The probe GHz field has an oscillating magnetic flux density described[7] by

$$\mathbf{B}_1(t) = B_{10}(\mathbf{i} \cos \omega t + \mathbf{j} \sin \omega t) \tag{18}$$

at the angular frequency ω. Here $\mathbf{i}$ and $\mathbf{j}$ are unit vectors mutually perpendicular to the propagation axis of the probe.

The equation of motion of the pump probe system is

$$\frac{d\mathbf{m}}{dt} = \mathbf{m} \times (\gamma_\pi \boldsymbol{\Pi} + \gamma_e \mathbf{B}_1(t)) \tag{19}$$

where γ_e is the gyromagnetic ratio, so that the magnetic moment **m** of the atom or molecule precesses around a new effective field direction[7]

$$\mathbf{B}_{\text{eff}} = \frac{\gamma_e}{\gamma_\pi} B_{10}\,\mathbf{i} + \left(E_0^2 - \frac{\omega}{\gamma_\pi}\right)\mathbf{k} \ . \tag{20}$$

At the laser Larmor frequency

$$\omega_{\text{L}} = \gamma_\pi E_0^2 \doteqdot \frac{\alpha'' E_0^2}{\hbar} \tag{21}$$

we have resonance, and probe radiation is strongly absorbed in direct analogy to the basic principle of NMR or ESR spectroscopy. In this condition the magnetic moment **m** undergoes circular motion[7] in the *jk* plane in the rotating frame of reference introduced in Sec. 1. The effect of the probe field oscillating at the laser Larmor frequency is to change the alignment of the magnetic moment from parallel to **Π** of the pump laser to antiparallel, i.e. from **k** to $-\mathbf{k}$. This is equivalent in the simplest (spin only[7]) quantum mechanical scenario to a change of the M spin quantum number from $+1/2$ to $-1/2$, again in close formal analogy with NMR and ESR. The structure seen spectroscopically is equivalent to the hyperfine detail of laser Zeeman spectroscopy,[11] involving in general Landé coupling between several different quantum numbers.[28]

Therefore, a new type of resonance spectroscopy can be developed in principle by using a circularly polarised pump laser instead of the magnet of a conventional NMR or ESR spectrometer.

If the probe field is applied for a time

$$t = \frac{\pi}{2}\omega_{\text{L}}^{-1} = \frac{\pi}{2\gamma_\pi E_0^2} \tag{22}$$

then the angle of rotation of the magnetic moment is

$$\theta = \gamma_\pi E_0^2 t = \frac{\pi}{2} \ . \tag{23}$$

If applied for a time π/ω_{L}, the angle of rotation is π, and the direction of the magnetic moment is reversed. If applied finally for $2\pi/\omega_{\text{L}}$, then θ is 2π, and the moment is rotated back to its original position. This is the equivalent of 90°, 180°, and 360° pulses in conventional NMR.[7]

3.1. *The laser Bloch equations*

We introduce the phenomenological "laser Bloch equations" to define relaxation effects of magnetisation due to the conjugate product **Π** of a circularly polarised pump laser, and can be written as the longitudinal and transverse

dynamical effect of the torque (8) which is accompanied[9] by the development of circular birefringence and dichroism[4] formally analogous to the Faraday effect of B (magnetic electronic circular dichroism).

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applied to a position vector $\mathbf{r}$ in the molecule fixed frame, and back transformed into the laboratory frame.

The ensemble averaged Coriolis acceleration $2\langle \mathbf{v}(t) \times \boldsymbol{\omega}(0) \rangle$ is therefore one of the characteristic liquid (or gas) phase responses of the sample to the conjugate product of the circularly polarised laser, and accompanies the precession of $\boldsymbol{\alpha}''$ around $\boldsymbol{\Pi}$.

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at the angular frequency ω. Here $\mathbf{i}$ and $\mathbf{j}$ are unit vectors mutually perpendicular to the propagation axis of the probe.

The equation of motion of the pump probe system is

$$\frac{d\mathbf{m}}{dt} = \mathbf{m} \times (\gamma_\pi \boldsymbol{\Pi} + \gamma_e \mathbf{B}_1(t)) \tag{19}$$

components

$$\frac{d\mathbf{m}_z}{dt} = N\gamma_\pi E_0^2(\boldsymbol{\alpha}'' \times \mathbf{k})_z + \frac{\mathbf{m}_0 - \mathbf{m}_z}{T_1} \tag{24}$$

and

$$\frac{d\mathbf{m}_\perp}{dt} = N\gamma_\pi E_0^2(\boldsymbol{\alpha}'' \times \mathbf{k})_\perp - \frac{\mathbf{m}_0 - \mathbf{m}_\perp}{T_2} \tag{25}$$

where the magnetisation $\mathbf{M}$ is simply $N\langle\mathbf{m}\rangle$. The longitudinal component is M_Z, in the direction of propagation of the pump laser, and the transverse components are mutually perpendicular, M_X and M_Y. As in conventional NMR, the T_1 process is associated with the relaxation of laser induced magnetisation in the Z axis, parallel to the circularly polarised pump laser. The T_1 process is an irreversible relaxation of $\mathbf{M}_Z$ from its initial value at the instant t to a final value at $\mathbf{M}_0$, and is named here "laser induced spin lattice relaxation", in which the alignment of the magnetic moment due to the circularly polarised pump laser is destroyed by thermodynamic fluctuations in the atomic or molecular ensemble, a fall transient process.[18] The T_2 process, as in NMR, destroys coherence between molecules magnetised by the circularly polarised pump laser, and is called here "laser induced spin spin relaxation".

Conclusions

It has been shown that a circularly polarised pump laser produces resonance effects formally similar to those in NMR and ESR, including Larmor precession, spin lattice, and spin spin relaxation. The effect of the torque between the conjugate product $\boldsymbol{\Pi}$ and the polarisability vector α'' has been supercomputer simulated to reveal the presence of characteristic new ensemble averages which accompany the magnetisation produced by the laser.

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