SPECTRAL SPLITTING DUE TO A CIRCULARLY POLARISED PUMP LASER: LASER ZEEMAN SPECTROSCOPY

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Theoretical prediction is made for various types of molecular Zeeman spectroscopy due to a circularly polarised pump laser, in which optical rectification produces a pattern of spectral splitting mediated by the imaginary antisymmetric part of the frequency-dependent molecular polarisability. The hyperfine part of this splitting, in which the nuclear spin quantum number plays a role, leads to the expectation of laser-induced resonance effects akin to conventional nuclear magnetic resonance (NMR) and electron spin resonance (ESR). Experimental conditions for the observation of "laser Zeeman" spectral effects are defined using double resonance and saturation in mode-locked lasers for ultra high resolution.

Introduction

The well-known Zeeman effect in atomic and molecular spectroscopy depends to first order on the dot product of the molecular magnetic dipole moment **m** and the applied static magnetic flux density **B**. The magnetic dipole moment is proportional to the sum of orbital (**L**) and spin (**2S**) angular momenta through the respective gyromagnetic ratios. The hyperfine details depend on the contribution to **m** of the nuclear spin angular momentum quantum number I. Both **m** and **B** are axial vectors (rank one tensors) which have negative motion reversal symmetry (T) and positive parity inversion symmetry (P). The conventional linear and quadratic Zeeman effects due to **B** and B^2 respectively are both observed in atomic and molecular gases and liquids by application of strong magnetic fields: Zeeman[1] was the first to show the effect in sodium vapour placed between the pole pieces of a strong electromagnet, and since then it has become the basis for countless investigations of both atomic and molecular ensembles.[2,3] A concise but comprehensive account is given in Chapter 11 of Townes and Schawlow.[2] The development of the subject in terms of group theory has been described in detail by Piepho and Schatz.[3] The interesting analogy between the Zeeman and coherent optical resonance effects has been described by Steinfeld[4] in the context of coherent optical and double resonance techniques.

In this paper we develop the theory of a fundamentally new type of spectral effect which is named "laser Zeeman spectroscopy" because of its close formal similarity to the Zeeman effect due to $\mathbf{B}$. The laser Zeeman effect is the spectral splitting due to a circularly polarised electromagnetic field, the interaction Hamiltonian being a product of the imaginary part of the atomic or molecular polarisability, $i\alpha_{ij}''$, and the conjugate product of the non-linear optical phenomenon[5–7] of optical rectification. In Sec. 1 the interaction Hamiltonian is developed as the dot product of two T negative, P positive vector quantities in close formal analogy with the equivalent Hamiltonian of the conventional Zeeman effect.

Section 2 discusses the quantisation of the polarisability tensor α_{ij}'', which is an antisymmetric polar tensor transforming as a T negative, P positive axial vector quantity $\varepsilon_{ijk}\alpha_{jk}''$ using fundamental tensor algebra. The vector α_i'' in the laser Zeeman effect plays the same role as the magnetic dipole moment in the conventional Zeeman effect, has the same symmetry as angular momentum, and depends on the angular momentum quantum numbers L, $2S$, and I through constants akin to the gyromagnetic ratios of the Zeeman effect and magnetic resonance. The selection rule for transitions between states in laser Zeeman spectroscopy of atoms and molecules depends on the quantum number M as in the conventional Zeeman effect.

Section 3 is a description of the types of effect expected in laser Zeeman spectroscopy of simple molecules, using as illustrations Hunds coupling cases (a) and (b) in diatomics, in formal analogy with the description by Townes and Schawlow[2] of the same effects in conventional Zeeman spectroscopy. The theory is extended to hyperfine effects involving the nuclear quantum number I and nuclear quadrupole effects, leading to the expectation of nuclear and electron paramagnetic resonance due to a circularly polarised pump laser, in analogy with NMR and ESR spectroscopy due to $\mathbf{B}$.

Section 4 anticipates some experimental conditions for the observation of laser Zeeman spectroscopy by double resonance techniques at ultra high resolution in systems selected for resonance coincidencies with pump lasers such as a circularly polarised carbon dioxide or Nd:YAG system.

1. The Interaction Hamiltonian for Laser Zeeman Spectroscopy

The fundamental external physical property responsible for the laser Zeeman effect is the conjugate product of the circularly polarised laser

$$\boldsymbol{\pi} = \mathbf{E}_L^+ \times \mathbf{E}_L^- = -\mathbf{E}_R^+ \times \mathbf{E}_R^- = 2E_0^2 i\mathbf{k} \ , \tag{1}$$

which is phase independent and therefore exists in the steady state and does not time-average to zero. Here, the subscripts R and L refer to right and left circularly polarised components respectively, and the superscripts $+$ and $-$ to plus and minus conjugates of the electric field strength $\mathbf{E}$ (in volts m^{-1}) of the electromagnetic field. In Eq. (1), $\mathbf{k}$ is a unit vector in the z-axis of the laboratory frame (x, y, z) and i denotes the square root of minus one. The conjugate product is therefore a purely

imaginary axial vector which is negative to motion reversal symmetry T and positive to parity reversal P. It reverses sign with the circular polarity of the laser, and is fundamentally responsible[8-10] for bulk magnetisation due to a circularly polarised laser, the inverse Faraday effect. Recently, it has been shown to be responsible for circular and forward-backward birefringence[11,12] in molecular ensembles. The theory of the A term[13] of the former effect is responsible for Zeeman splitting as developed in this paper.

The vector π_i can be expressed as a rank two polar antisymmetric tensor through the algebraic tensor product

$$\pi_i = \varepsilon_{ijk}\pi_{jk} , \tag{2}$$

where ε_{ijk} is the Levi Civita symbol, the rank three totally antisymmetric unit tensor. It is proportional to the electric field strength squared, and the interaction Hamiltonian must therefore be a scalar formed by the contraction

$$\Delta H = -\frac{1}{2}\alpha_{ij}\pi_{ij} , \tag{3}$$

where α_{ij} is in general a complex dynamic molecular polarisability[13] mediating the effect of electromagnetic field on the molecule. The complex dynamic polarisability is well known to be made up of

$$\alpha_{ij} = \alpha'_{ij} - i\alpha''_{ij} , \tag{4}$$

where the real part is symmetric in its indices and T positive, and the imaginary part is antisymmetric and T negative. To obtain the real Hamiltonian, the imaginary part must multiply the purely imaginary $i\alpha''_{ij}$ to give

$$\Delta H = i\alpha''_{ij}\pi_{ij} = -\alpha''_z E_{0z}^2 , \tag{5}$$

which can be expressed as a product of two T negative, P positive axial vector quantities:

$$\Delta H = -\frac{1}{2}\alpha_i\pi_i = -\alpha''_i E_0^2 i , \tag{6}$$

in close formal analogy with the Hamiltonian for the conventional Zeeman effect

$$\Delta H_B = -m_i B_i . \tag{7}$$

2. Quantisation of the Imaginary Part of Polarisability

The electronic gyromagnetic ratio is well-known as the proportionality constant between the magnetic dipole moment and electronic orbital ($\mathbf{L}$) and spin ($2\mathbf{S}$) angular momenta. Similarly, the nuclear gyromagnetic ratio is the proportionality constant between the nuclear magnetic dipole moment and the nuclear spin quantum number $\mathbf{I}$. Analogously, we define the quantity γ_π as the proportionality constant between

the vector α_i'' and the electronic total angular momentum $\mathbf{L} + 2\mathbf{S}$, and the quantity $\gamma_{\pi n}$ as that between α_i'' and the nuclear spin angular momentum $\mathbf{I}$:

$$i\alpha_i'' = \gamma_\pi (L_i + 2S_i) , \tag{8}$$

$$i\alpha_i'' = \gamma_{\pi n} I_i . \tag{9}$$

This is reasonable on the grounds of fundamental symmetry, because the axial vectors α_i'', $\mathbf{L}$, $2\mathbf{S}$, and $\mathbf{I}$ are all T negative, P positive quantities so that γ_π and $\gamma_{\pi n}$ are scalars.

The interaction Hamiltonian of the laser Zeeman effect can therefore be written as

$$\Delta H = \gamma_\pi (L_i + 2S_i)(E_0^2)_i - \gamma_{\pi n} I_i (E_0^2)_i \tag{10}$$

in terms of E_0^2 and the new atomic or molecular constants. This puts the Hamiltonian in a form where it can be developed with vector coupling models as in the conventional Zeeman effect, models which allow predictions to be made about the nature of the laser Zeeman spectrum.

The selection rules for transitions between energy levels in laser Zeeman spectroscopy are identical, from Eqs. (8) and (9), to those in the conventional Zeeman effect given by

$$\Delta J = 0; \quad \Delta M = 0, \pm 1 , \tag{11}$$

where M takes the values

$$J, J - 1, \dots , -J$$

of the total angular momentum quantum number J.

Conventionally, when the probe microwave field of the Zeeman effect is parallel[2] to $\mathbf{B}$, $\Delta M = 0$, giving the π components of the effect; and when the two fields are perpendicular, $\Delta M = \pm 1$, giving the σ components. In laser Zeeman spectroscopy, the static magnetic flux density is replaced by π of a circularly polarised pump laser, such as a carbon dioxide or Nd:YAG laser, giving the possibility of infrared (or visible)/radio frequency double resonance in order to detect the fine, hyperfine, and superhyperfine[14-17] spectral structures of the laser Zeeman effect. This also gives rise to the interesting possibility of saturation and multiphoton laser Zeeman spectroscopy as discussed in Sec. 4.

The useful formal analogy between the conventional and laser Zeeman effects can be carried further and developed following Townes and Schawlow,[2] provided it is borne in mind that the two spectroscopies give information on different fundamental molecular properties. This is detailed in Sec. 3 for molecular spectra.

3. Some Simple Laser Zeeman Effects in Molecular Spectroscopy

The Hamiltonian (10), initially neglecting hyperfine interactions, can be developed with the well-known Hund vector coupling models.[2] In the weak coupling limit, $\mathbf{L}$ and $\mathbf{S}$ precess about the molecular axis, which precesses about the total electronic

angular momentum $\mathbf{J}$. In the presence of the conjugate product $\boldsymbol{\pi}$, $\mathbf{J}$ precesses about $\boldsymbol{\pi}$ with projection $\mathbf{M}$ in the direction of $\boldsymbol{\pi}$. This allows the Hamiltonian (10) to be rewritten as

$$\Delta H = -((\Lambda + 2.002\Omega)\gamma_\pi M E_{0z}^2)/(J(J+1)) \tag{12}$$

with Λ and Ω defined by

$$\Omega = \mathbf{k_a} \cdot \mathbf{J}; \quad \Lambda = \mathbf{k_a} \cdot \mathbf{L}, \tag{13}$$

where $\mathbf{k_a}$ is a unit vector in the molecular axis. As in the conventional Zeeman effect, this produces $2J+1$ equally spaced laser Zeeman lines corresponding to the different possible values of M.

The extent of the splitting is determined by the ratio of the interaction energy $\alpha_z'' E_{0z}^2$ to the reduced Planck constant. This introduces interesting differences from the conventional Zeeman effect, because the value of the imaginary polarisability can be increased dramatically by tuning the pump laser. This is clear from the definition of α_{ij}'' in its antisymmetric polar tensor form from the time-dependent Schrödinger equation

$$\alpha_{\alpha\beta}'' = -\alpha_{\beta\alpha}'' = -\frac{\delta}{\hbar} \sum_{j \neq n} \frac{\omega}{\omega_{jn}^2 - \omega^2} \operatorname{Im}\left(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle\right), \tag{14}$$

where

$$\omega_{jn} = \omega_j - \omega_n \tag{15}$$

is the transition frequency from state n to state j, and μ_α and μ_β are electric dipole moments. Clearly, if the circularly polarised pump laser is tuned to the frequency ω_{jn} we have

$$\omega \doteq \omega_{jn}, \tag{16}$$

and the denominator in Eq. (14) becomes very small. Double resonance is obtained under this condition by tuning the probe radio frequency field to a Zeeman transition *caused by the pump laser itself*, a technique which can be identified conveniently as infrared/radio frequency double resonance Zeeman spectroscopy. The hyperfine detail of this spectroscopy is equivalent to "nuclear electromagnetic resonance".

Hund's case (b) can be written in direct analogy to Eq. (11–5) of Townes and Schawlow as

$$\Delta H = -\frac{1}{2J(J+1)}\left[\Lambda^2\frac{(N(N+1)+S(S+1)-J(J+1))}{N(N+1)}\right.$$
$$\left. + 2.002(J(J+1)+S(S+1)-N(N+1))\right]M\gamma_\pi E_{0z}^2 \tag{17}$$

in their notation, but with $\mathbf{B}$ replaced by $\boldsymbol{\pi}$ and with $\mathbf{m}$ replaced by $i\alpha_i''$.

The Hamiltonian for the laser Zeeman effect can be written in terms of the Landé g_J factor

$$\Delta H = -g_J M \gamma_\pi E_{0z}^2, \tag{18}$$

which is of the order of unity for molecules with net angular momentum, as in the conventional Zeeman effect.[2] Otherwise, g is dominated by the nuclear spin angular momentum $\mathbf{I}$. In general, however, the g factor depends on the rotational angular momentum $\mathbf{J}$ and other momenta. In the laser Zeeman effect, if the g factors in states J_1 and J_2 are g_1 and g_2 respectively, and if the transition frequency between J_1 and J_2 is ν_0, the spectrum will be a series of lines defined by

$$\nu = \nu_0 + (g_2 - g_1)M\gamma_\pi E_{0z}^2/h \tag{19}$$

for $\Delta M = 0$ (π components), and

$$\nu = \nu_0 + [(g_2 - g_1)M \pm g_1]V_\pi E_{0z}^2/h \tag{20}$$

for $\Delta M = M_2 - M_1 = \pm 1$ (σ components), with M_2 the lower state. This spectral detail depends on the imaginary part of the molecular polarisability, which can be amplified greatly by resonance to the circularly polarised pump frequency. In general the g factors contain hyperfine (nuclear) contributions, which cause "nuclear electromagnetic resonance" as the radio/microwave frequency field is swept to the same frequency as that of a transition frequency between hyperfine states. This closely parallels the well-known technique of NMR.

If the molecular structure is such that

$$g_1 = g_2 \; , \tag{21}$$

then there is no π laser Zeeman effect, and in the σ effect; there are only two frequencies.

For observation of the σ lines, in general, the electric field of the microwave waveguide should be perpendicular to π of the laser, so that the direction of propagation of the circularly polarised pump laser is parallel to the length, or broadest faces, of the waveguide, in the z-axis of the laboratory frame. This can be achieved by actually incorporating the waveguide in the pump laser cavity, as in the conventional technique of infrared/radio frequency double resonance,[14-17] provided the pump laser is circularly polarised. No laser Zeeman effect can be observed if there is no circular polarisation of the pump laser, which can be useful to test for experimental artifacts.

The general appearance of the laser Zeeman spectrum is expected to be similar to that sketched in Fig. (11–1) of Townes and Schawlow,[2] but will also depend on the way the pump laser frequency is tuned to a natural transition frequency of α_{ij}'', giving, in principle, a great deal of information. Additionally, it is possible to use circularly polarised probe microwave radiation, as well as circularly polarised pump laser, with the added advantages discussed in pp. 288 ff. of Ref. 2.

Considering now the interesting case when the hyperfine structure due to $\mathbf{I}$ is taken into account, the first order Hamiltonian is modified to

$$\Delta H_2 = -\frac{1}{2}\left[\gamma_\pi g_J \mathbf{J} \cdot \boldsymbol{\pi} + \gamma_{\pi n} g_I \mathbf{I} \cdot \boldsymbol{\pi}\right] \; . \tag{22}$$

If this is much smaller than the hyperfine energy, so that π does not disturb the coupling between **J** and **I**, the vector coupling model gives the Landé type Hamiltonian

$$\Delta H_2 = [-\gamma_{\pi n} g_I (I(I+1) + F(F+1) - J(J+1))$$
$$- \gamma_\pi g_J (J(J+1) + F(F+1) - I(I+1))] \frac{M_F E_{0z}^2}{2F(F+1)} , \qquad (23)$$

where F is the total angular momentum quantum number, and M_F its projection on π of the pump laser. For a diamagnetic molecule, both terms of the laser Zeeman effect described by (23) are roughly equal in magnitude, giving considerable extra spectral details which can be used in gases for analytical purposes in close analogy to conventional NMR in liquids.

There appears to be an important potential advantage of laser Zeeman spectroscopy over the conventional effect because the latter is confined to molecules in the ground electronic state, where there is no net electronic angular momentum in most molecules. In the laser Zeeman effect however, used with a circularly polarised laser such as Nd:YAG to pump the molecule into an excited electronic state, it appears possible to observe electronic laser Zeeman effects in molecules in which net electronic angular momentum is absent in the ground state. This can be thought of simply as the conjugate product spinning the molecule through interaction with $i\alpha_i''$. An interesting example of what might be expected from such a mechanism can be based on the conventional Zeeman spectrum of nitric oxide, which is in a $^2\pi$ state which allows transitions of the type described in Fig. 11.3 of Ref. 2, the hyperfine part of which is similar to a conventional liquid state NMR spectrum. In this state the J number of NO is $3/2$, so that the M_J states are $3/2$, $1/2$, $-1/2$, and $-3/2$, each of which is further split into $M_I = 1, 0, -1$ states. Each M_J state would therefore be expected to show hyperfine structure in laser Zeeman spectroscopy. Another example is that of oxygen, where there would be laser Zeeman effect on p type triplets, giving a more complicated spectrum than for NO.

4. Conditions of Observation, Double Resonance Techniques

Symmetric tops and asymmetric tops will have more complicated laser Zeeman spectra in analogy with the conventional Zeeman effect, the case of HDO being particularly interesting because its $4\nu_{OH}$ state coincides with the Nd:YAG pump frequency.[18,19] The use of such coincidencies between pump laser and natural transition frequencies introduces the techniques of double resonance, for example, infrared double resonance,[14] or infrared/radio frequency double resonance,[15] and the closely related area of super-high resolution saturation spectroscopy.[17] In each of these techniques, an intense circularly polarised pump laser would be used to induce the laser Zeeman effect and to simultaneously amplify the mediating dynamic imaginary polarisability defined in Eq. (14) through coincidence with a natural transition frequency ω_{jn}.

One of the techniques of infrared double resonance has been used,[14] for example, to investigate dynamic Stark modulation in multiple infrared photon excitation. Laser Zeeman effects would be generated, in principle, by using a circularly polarised pump infrared laser with a probe tuned to the same frequency, the pump being much more intense than the probe. For example, the pump can be a carbon dioxide laser tuned to a transition frequency of sulfur hexachloride.[14]

Another possible method of detecting laser Zeeman structure at high resolution would be infrared/radio or microwave frequency double resonance.[15,16]. In this technique, a circularly polarised carbon dioxide laser is used with a radio or microwave frequency probe applied to a cell placed inside the laser cavity. For example, this type of spectrum is produced conventionally for a vapour such as methyl iodide by selecting a coincidence of a methyl iodide transition with a carbon dioxide laser frequency. Probe radio frequencies are also chosen so that they coincide with a natural molecular transition, for example the 246 MHz ground state of methyl iodide, or the 400 MHz first rotational excited state.

To optimise conditions for the laser Zeeman effect, a circularly polarised carbon dioxide laser with high power level would be used, and the probe field swept to detect laser Zeeman structure due to the Hamiltonian (22). The spacing of this structure ought to depend on the square of the electric field strength of the pump laser, and thus on the fourth power of the intensity in watts per unit area, multiplied into the value of the polarisability vector α_i''. Transitions between extra energy levels caused by the circularly polarised pump laser would be detected as absorptions of the radio or microwave frequency probe. In this technique, a method would have to be used for ensuring that the pump is circularly polarised, so that the sample cell may have to be situated outside the pump laser cavity, and the latter circularly polarised with a Nicol prism/quarter-wave plate, or some other devices. In this type of experiment, strong laser Zeeman effects would be anticipated if the molecule were chosen to have a net electronic angular momentum as well as coincidence with a pump laser line. In this respect it may be advantageous to use a circularly polarised visible frequency solid state laser such as a Nd:YAG rather than a carbon dioxide laser in the mid infrared and a microwave frequency waveguide probe to detect the laser Zeeman lines. In this context the pump laser replaces the magnet of conventional Zeeman effect apparatus (vector $\boldsymbol{\pi}$ replaces vector $\mathbf{B}$).

It may be advantageous in this configuration to simplify the expected laser Zeeman effect to its essentials by using an atomic vapour such as sodium as sample. There is a fairly close coincidence between the sodium D line at 589 nm, for example, and the 530 nm Nd:YAG line. A much closer coincidence is that between the third O–H stretching overtone of HOD and the 720 nm Nd:YAG line, but in this case the expected laser Zeeman spectrum would be a much more complicated structure of the asymmetric top molecule HOD. Another close coincidence is that between the 540 nm $'E_{ua} \leftarrow {}'A_{1g}$ low energy Q_1 transition of a D_{4h} porphyrin chromophore, where a simple broadened laser Zeeman spectrum may be observable in analogy with the conventional effect in porphyrins due to $\mathbf{B}$.[13]

It appears probable, finally, that interesting laser Zeeman features not anticipated by these simple arguments will be found when experiments are carried out on real systems. These are expected to give a wide variety of new fundamental information concerning the interaction of molecules and electromagnetic fields.

Acknowledgments

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