Review of optical NMR and ESR*

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The theory of optical NMR and ESR is reviewed for site selective investigation of complex systems in solution, such as folded proteins. Optical NMR and ESR is based on the ability of a circularly polarised, visible frequency, laser to give up the angular momentum of its photons to electrons of the sample, thus creating a magnetic moment whose magnitude is the Bohr magneton per photon. This effect is accompanied by other mechanisms of angular momentum transfer, such as the inverse Faraday effect. The magnetic dipole moment produced by the photon interacts with the strong static magnetic field of the NMR or ESR instrument, giving site selective resonances which can be mapped using conventional two-dimensional and enhancement techniques.

Introduction

The role of speculation in natural philosophy has always been critically important, yet too much of it is traditionally unwelcome – dismissal as 'mere speculation' is always risked by the radical. Such dismissal is itself unscientific if the 'speculation' happens to be based on rational extrapolation, or more interestingly, quantum leaps of the imagination. Who dares criticise the quantum now? Perhaps there are speculators who will, and they must be encouraged.

In this short review, I accept the quantum, but propose the development of what I hope will be a useful new technique, which I call, for want of a better term, 'optical NMR/ESR'. It is based on the ability of visible frequency circularly polarised electromagnetic radiation to give up quanta of angular momentum to electrons in complex samples such as folded proteins in solution. These are essentially quanta of the optically induced magnetic dipole moment. The intensity (watts per square centimetre) of light is proportional to the number of light quanta (photons) per unit volume multiplied by its angular frequency (ω in rad s^{-1}), and the reduced Planck constant h. It follows that there is much more intensity per photon at visible frequency than at the radio frequencies, because ω for the former is about 100,000 to a million times bigger. The number of photons per unit volume is also increased for a given ω by using more watts per centimetre squared, *i.e.* by increasing the light intensity, which is proportional to light energy per unit

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volume. The latter is proportional to the square of the amplitude of the oscillating electric field strength (volts per centimetre) of the light beam. By increasing both frequency and intensity simultaneously, the number of available photons per unit volume becomes much greater. There are many more photons in an intense visible frequency laser than in a radio frequency beam.

The quantum theory of radiation[1] argues that the photon is handed, *i.e.* there can be a right handed and left handed photon, characterised by a quantum number M. This is a consequence of the fact that circularly polarised, visible frequency, light has a classical angular momentum per unit volume, known as 'angular momentum density'. This was shown experimentally by Beth[2] long before the invention of lasers by measuring the bulk rotation of a doubly refracting plate about the axis of propagation of circularly polarised, visible, radiation. The angular momentum of light in quantum theory is:

$$|\mathbf{M}| = n_0 M h \qquad (1)$$

and is therefore proportional to the number of photons per unit volume (n_0) multiplied by the quantum number M and the reduced Planck constant (or Dirac constant[3]) h. When a photon is absorbed by an atom or molecule, all its angular momentum is given to an electron. For a left circularly polarised laser, this transfer is described by a change of +1 in the magnetic quantum number M, and −1 for a right circularly polarised laser. If there is a very large number of available photons in an intense, visible frequency laser, more than one photon may be absorbed, and more than one unit of angular momentum may be given to the same electron. In one photon absorption, each circularly polarised photon contributes either +h or −h units of angular momentum to the electron as it is absorbed. In general, M can be any integer (positive or negative) excluding zero. The value zero is excluded theoretically on the grounds of gauge invariance and the fact that the photon has no rest mass.[1]

This is the basis of the electric dipole transition rule:

$$\Delta L = \pm 1$$
$$\Delta M = 0, \pm 1 \qquad (2)$$

for an electron, where M can range from −L to +L of the angular momentum quantum number L. Note that the electronic value M = 0 is allowed, and the change ΔM = 0 for photon to electronic angular momentum transfer is also allowed. L for the electron can range from 0 to n − 1, where n is the principal electronic quantum number[4] (not to be confused with the number of photons per unit volume, denoted n_0). Thus M represents components of L, the orbital angular momentum quantum number, about a preferred direction, such as Z of the laboratory frame. For n = 1, only one unit of electronic angular momentum can occur, the L = 0 unit, which is given the label s. For n = 2, L can be 0 or 1 (s and p orbitals) and so on. For L = 1, M can be either −1, 0 or +1, for L = 2, M can be −2, −1, 0, 1 and 2. Note that for a given L, all the M values have the same energy, *i.e.* are degenerate in the absence of an influence (such as a strong static magnetic field) which removes the degeneracy, so that transitions between different M levels occur at different frequencies for a given L.

The basis of optical NMR/ESR is that angular momentum is proportional to magnetic dipole moment, the elements of this relation as described in section 1. The magnetic dipole moment (**m**) per photon given to the electron of an atom or

molecule during absorption of circularly polarised radiation is of the order of the Bohr magneton. This induced dipole moment produces the energy $-\mathbf{m}\cdot\mathbf{B}$ through interaction with the externally applied static magnetic flux density **B** of the NMR or ESR magnet. This energy is measured as resonance frequency, and is site selective. Different resonating protons of a protein, for example are affected to different extents by the visible frequency photons available from the circularly polarised laser, and the two-dimensional NMR spectrum characterises this site selective nature.

Here I estimate the order of magnitude of the frequency shift expected in the NMR or ESR spectrum as a function of the laser energy per unit volume, *i.e.* of the frequency and of the number of photons per unit volume. I then give a brief description of additional magnetisation effects of circularly polarised light, such as the inverse Faraday effect,[5,6] which may become important in very intense laser beams. Finally a speculative discussion is given of the likely uses of laser NMR and ESR.

The light induced magnetic dipole moment

A magnetic dipole moment is created by a loop of moving charge, a current, I (amps), and its magnitude is IA where A is the area of the loop.[7] In the atom, the moving charge is the electron, and the area is that of the electronic orbit. The direction of the magnetic dipole moment is normal to the plane of the orbit, and the effective magnetic dipole moment of a point electronic charge (e), of mass m_e, moving in a circular orbit of radius r can be written as:

$$|\mathbf{m}| = (e/2m_e)|\mathbf{L}| \equiv -\gamma_e|\mathbf{L}| \qquad (3)$$

where **L** is the orbital angular momentum. The latter is written as $h\hat{\mathbf{L}}$ where $\hat{\mathbf{L}}$ is the dimensionless angular momentum operator,[8] and the quantity γ_e is the gyromagnetic ratio. The product $-\gamma_e h$ is the Bohr magneton, the atomic unit of magnetic moment.

The effect of an external magnetic field **B** is to make possible the distinction between various possible orientations of the magnetic dipole moment and consequently of the electronic orbit. If the magnetic dipole moment is orientated at an angle θ to the direction of **B**, a torque:

$$\begin{aligned} |\mathbf{Tq}| &= -|\mathrm{mB}|\sin\theta \\ &= |\mathbf{m}\times\mathbf{B}| \end{aligned} \qquad (4)$$

is set up between the field and dipole, which attempts to reorient the dipole antiparallel to the field. The integral of this torque with respect to θ is the work done against the field, which is the dot product:

$$W = \int |\mathbf{Tq}|\,d\theta = |\mathrm{mB}|\cos\theta = \mathbf{m}\cdot\mathbf{B} \qquad (5)$$

It follows that a magnetic dipole moment in a magnetic field **B** has a potential energy which is the same in magnitude as the work done but opposite in sign; thus,

$$\Delta E = -\mathbf{m}\cdot\mathbf{B} \qquad (6)$$

In quantum theory this energy has discrete values, and the energy of a single electron atom is changed by:

$$\Delta E_L = -\gamma_e \mathbf{L}\cdot\mathbf{B} \qquad (7)$$

assuming that the orbit size is unaffected by **B**.

This is the well known basis of conventional nuclear magnetic resonance and electron spin resonance spectroscopy, Zeeman splitting, and a variety of other important phenomena.[7,10] The powerful new techniques of two-dimensional enhancement NMR introduced in the last decade[11] rely on this same basic mechanism, with the additional electron nuclear spin interactions of Overhauser enhancement.[12] Transitions between energy levels of equation (7) are detected with radio frequency fields, in the 100 MHz range for NMR and the 100 GHz range for ESR. Many ingenious variations on the basic principle are now used routinely to great effect, for example protein structure determination in solution,[13] and NMR/ESR constitutes a large proportion of the current research literature of physical chemistry.

The usefulness of NMR and ESR for structure determination arises, among a variety of other factors, from the chemical shift.[14] The magnetic fields seen by different proton sites, for example, differ from the applied field:

$$\mathbf{B}_{eff} = \mathbf{B}(1-\sigma) \qquad (8)$$

through the chemical shift factor σ. Thus, different proton sites in a folded protein, for example,[13] will resonate at different frequencies, characteristic of the environment at each site. This allows the two-dimensional NMR mapping[15] of a protein through its various different proton resonances. Many of these occur at much the same frequency (the chemical shift is measured in parts per million), and since there are only a few amino acid residues per protein, the overlapping of proton resonances is often a technological constraint, even with the strongest available magnetic flux densities **B** (Tesla).

The absolute frequency separation of proton resonances in a protein can be changed by changing the energy equation (7). This can be done in two ways: (1) by increasing **B** (using a strong magnet); or, (2) by increasing the effective magnetic dipole moment **m** associated with each proton resonance. The first technique has been used for many years, but the second appears never to have been explored experimentally. Optical NMR/ESR is one way of increasing the effective **m** by optically injecting angular momentum into the sample using a visible frequency, circularly polarised laser of up to a few hundred watts per centimetre squared intensity.

The laser is tuned to near an absorption frequency in the visible region of the spectrum of the sample. At angular frequency ω the energy of the laser is $n_o h\omega$, where n_o is the number of photons per unit volume, and its angular momentum about the axis of propagation (Z) is $n_o Mh$. Absorption of one photon will promote an electron from one orbital to another of higher energy, *i.e.* into an excited orbital state, the energy difference between the orbitals of higher and lower energy being:

$$E_f - E_i = h\omega \qquad (9)$$

per absorbed photon. This transition must be allowed by selection rules on quantum numbers[7] and is accompanied by the injection of one unit of angular

momentum, this being +h per photon for left circularly polarised laser radiation and –h for the right handed counterpart.

Therefore, the absorption of energy from the laser represented by equation (9) is accompanied by the creation of:

$$|\mathbf{m}| = \gamma_e h \qquad (10)$$

units of magnetic dipole moment, where γ_e is the Bohr magneton. It follows that one Bohr magneton unit of moment is created per photon. The greater the number of photons per unit volume, n_o, the greater the number of units of induced magnetic dipole moment in the sample. The more energy, $h\omega$, per photon, the greater the difference equation (9), *i.e.* more energetic transitions become possible, between higher n states, (*e.g.* L = 1 to L = 2, p to d states for high n states). Such high n transitions are not possible with radio frequency photons because there is not enough energy per photon. Electronic (Δn) transitions are usually observed spectroscopically at visible and ultra violet frequencies.

This is a critical difference, therefore, between conventional NMR/ESR and optical NMR/ESR. In the latter, transitions between electronic angular momentum states are induced by the energetic circularly polarised, visible frequency, laser.

The total angular momentum of the laser is more accurately[15] written as:

$$|\mathbf{M}| = n_o{}^{L,M} Mh \qquad (11)$$

where $n_o{}^{L,M}$ is associated with quantum numbers L and M. The total laser angular momentum obeys the commutation relations:[15]

$$[M_x, M_y] = ihM_z;$$
$$M_x{}^2 + M_y{}^2 + M_z{}^2 = h^2L(L+1) \qquad (12)$$

so that its magnitude is proportional to $[L(L + 1)]^{1/2}$. Therefore, as the angular momentum increases, L increases, and the more the allowed values of M for each L of each photon.

The angular momentum M of the laser carries with it the capability of imparting $n_o{}^{L,M}\gamma_e h$ units of magnetic dipole moment to the atom which absorbs the energetic, visible frequency, photon according to the selection rules on n, L and M. For example, if the absorption of a photon causes a transition from a p to d orbital (L = 1 to L = 2), transitions $\Delta M = \pm 1$ are allowed from the three degenerate M electronic states of L = 1 to the five degenerate M electronic states of L = 2. For a left photon, $\Delta M = +1$ and vice versa. The unit of magnetic moment imparted for a $\Delta M = 1$ transition is $|h\gamma_e|$, the Bohr magneton. After absorbing the photon, the electron is in the d orbital, with five allowed values of M. In the absence of the laser it would be in the lower energy p orbital, with three allowed values of M. Applying the magnetic field of the NMR or ESR spectrometer removes the degeneracy of the five allowed M values. The ESR or NMR resonance appears at higher frequencies, because the magnitude of the orbital electronic angular momentum, and therefore the magnetic dipole moment, is proportional to $[L(L + 1)]^{1/2}$, and there are more possible resonances, because three-fold degeneracy has been replaced by five-fold degeneracy. In the presence of a field **B** this degeneracy is removed, there are five different energy levels instead of three in the absence of the laser.

The ESR and NMR spectra are affected in a variety of ways by the presence of the laser.

Order of magnitude estimates

The discussion of the effect of a circularly polarised laser starts with the hydrogen atom, in particular the first Lyman transition at 1,215.67 Å in the ultra-violet. This is the Lyα line of the hydrogen atom, which is the wavelength at which the quantum transition occurs from the electronic state n = 1 to n = 2, where n is the principal quantum number.[4] The electron in the ground state of the hydrogen atom is described by the quantum numbers:

$$n = 1, l = 0, m_l = 0, s = 1/2, m_s = 1/2, -1/2 \qquad (13)$$

which, for one electron, follow from the rules:[3]

$$l = 0, 1, ..., n - 1; \; m_l = -l, ..., l$$
$$s = 1/2; \; m_s = -s, ..., s \qquad (14)$$

By tuning a laser in a vapour of hydrogen atoms to the frequency of the Lyα transition, a photon is absorbed and the electron is prepared in a higher energy condition, governed by the selection rules of the hydrogen atom quantum numbers. Depending on the circular polarisation of the laser, the condition of the electron is described as follows:

$$n = 2, l = 1, m_l = +1, s = 1/2, m_s = 1/2, -1/2 \qquad (15)$$

for left circularly polarised radiation;

$$n = 2, l = 1, m_l = \text{“} \; s = 1/2, m_s = 1/2, -1/2 \qquad (16)$$

for right circularly polarised radiation; and

$$n = 2, l = 1, m_l = 0, s = 1/2, m_s = 1/2, -1/2 \qquad (17)$$

for linearly polarised radiation.

A transition from state (13) to any of the states (15), (16), or (17) involves a change of hydrogen atom energy, which is determined by the principal quantum number n. The selection rule $\Delta l = +1$ for absorption implies that l must change from 0 to 1. There is no change in electron spin quantum number, so that $\Delta s = 0$. The energy needed to change from the ground state (13) to any of the states (15) to (17) is provided by the laser tuned to 1,215.67 ↓. In state (15), for example, produced by a left circularly polarised laser at this wavelength, note that $m_l = l = 1$, and it is no longer equiprobable that the electron occupy any of the states $m_l = -1, ..., 1$. Similarly, after absorption of a right handed photon from a right circularly polarised laser, the magnetic quantum number in the prepared state is confined to $m_l = -1$. In a linearly polarised laser, it is confined to $m_l = 0$.

Using a laser at a given frequency and specific polarisation it is possible to prepare the electron of the hydrogen atom in a higher energy state by transfer of a photon from the laser to the electron.

In an ensemble of N hydrogen atoms a significant population is found in the laser prepared condition, depending on the energy available in the laser, which is proportional to the number of photons per unit volume multiplied by the angular frequency and reduced Planck constant. Having prepared the electron population in this way the second stage of the experiment consists of using an ESR or NMR spectrometer to study transitions between Zeeman states of the prepared atoms. The static magnetic flux density B_Z of the spectrometer is applied in the same Z axis as the propagation axis of the laser. It shifts the energy of the *prepared* electron by an amount determined by the magnetic spin and orbital quantum numbers m_s and m_l, and by the interaction between the electron's spin and orbital angular momentum.

If the applied magnetic field is strong enough to enable us to neglect the spin orbit coupling, the spectrum simplifies, as we shall see. In the presence of spin orbit coupling in the prepared state, transitions between Zeeman states are described in general by the energy change:

$$\Delta H \equiv h\omega = (g_{j1}m_{j1} - g_{j2}m_{j2})\mu_B B_Z \qquad (18)$$

where the total angular momentum quantum numbers j and m are defined through the Clebsch-Gordan series:[3]

$$\begin{aligned} &j = l + s,\ l + s - 1,\ldots,\ |l - s|; \\ &m_j = m_l + m_s \end{aligned} \qquad (19)$$

and where the Landé factor is defined in general by:

$$g_j = [1 + [j(j + 1) + s(s + 1) - l(l + 1)]/2j(j + 1)] \qquad (20)$$

Note that the Landé factor depends indirectly on the principal electronic quantum number n, because n determines allowed values of l, and therefore of j.

We are now in a position to work out the effect of the laser, applied to the first Lyman line, on the ESR and NMR spectrum of atomic hydrogen.

In the absence of the laser, the electron is in the ground state (13). Beringer and Heald[16] were among the first to measure the ESR spectrum of H in the ground state, which consists of the transition $m_j = -1/2$ to $m_j = +1/2$; $\Delta m_I = 0$ at 9,185.5046 MHz for their applied magnetic flux density. Here $\Delta m_I = 0$ is the change in the nuclear spin magnetic quantum number, signifying the presence of hyperfine coupling between electron and nuclear spin. In the following, we neglect for the moment the effect of hyperfine coupling in the prepared state, and focus on the coupling between the electronic spin and orbital angular momenta.

The frequency 9,185.5046 MHz was arrived at by injecting microwave radiation at this frequency into the ground state hydrogen atom, whose electron absorbs photon energy, and undergoes a quantum transition from the lower energy state ($m_j = -1/2$) to the higher energy state ($m_j = 1/2$), satisfying the selection rule $\Delta m_j = +1$ for transitions between the two ground Zeeman states. When the energy difference between these states coincides exactly with the applied radio frequency, absorption of a photon occurs, as observed experimentally by a net lowering of the power level at the microwave detector. At 9,185.5046 MHz, this signifies the presence of the π_1 ESR line of the ground state of atomic hydrogen. This is described by the resonance condition:

$$h\omega_R = (g_{1/2}m_{1/2} - g_{-1/2}m_{-1/2})\mu_B B_Z \qquad (21)$$

where ω_R is the angular frequency of the microwave probe radiation, $g_{1/2}$ is the Landé factor in the state $m_{1/2} = 1/2$, and $m_{-1/2}$ is the Landé factor in the state $m_{-1/2} = -1/2$, and is the Bohr magneton. In the ground state $l = 0$, and in consequence:

$$g_{1/2} = g_{-1/2} = 2 \tag{22}$$

the single observable resonance frequency is:

$$\omega_R = 2\mu_B B_Z/h \tag{23}$$

Having laser-prepared the H electron in one of the states (15) to (17), however, the ESR spectrum will consist of more than one line. This is easily seen by reference to Table 1, which summarises the allowed j and m_j state. Zeeman transitions between these states occur in the presence of the magnet according to the selection rules:[3]

$$\Delta j = 0 \pm 1; \Delta m_j = 0 \pm 1 \tag{24}$$

In the state prepared by the left circularly polarised laser (Table 1) these selection rules allow three resonance frequencies from equation (18), involving different Landé factors g_{j1} and g_{j2} due to the fact that $l = 1$ in the prepared state, allowing spin orbit coupling:

(1) $(j = 3/2, m_j = 1/2) \leftarrow (j = 1/2, m_j = 1/2)$; $w_R = (\mu_B B_Z)/3h$;

(2) $(j = 3/2, m_j = 3/2) \leftarrow (j = 1/2, m_j = 1/2)$; $w_R = (5/3)(\mu_B B_Z)/h$;

(3) $(j = 3/2, m_j = 3/2) \leftarrow (j = 3/2, m_j = 1/2)$; $w_R = (4/3)(\mu_B B_Z)/h$;

The state prepared by the right circularly polarised laser allows the three resonances:

(4) $(j = 1/2, m_j = -1/2) \leftarrow (j = 3/2, m_j = -1/2)$; $w_R = (1/3)(\mu_B B_Z)/h$;

(5) $(j = 1/2, m_j = -1/2) \leftarrow (j = 3/2, m_j = -3/2)$; $w_R = (5/3)(\mu_B B_Z)/h$;

(6) $(j = 3/2, m_j = -1/2) \leftarrow (j = 3/2, m_j = -3/2)$; $w_R = (4/3)(\mu_B B_Z)/h$;

and the state prepared by the linearly polarised laser allows:

(7) $(j = 3/2, m_j = 1/2) \leftarrow (j = 1/2, m_j = -1/2)$; $w_R = 2(\mu_B B_Z)/h$;

(8) $(j = 3/2, m_j = 1/2) \leftarrow (j = 1/2, m_j = 1/2)$; $w_R = (1/3)(\mu_B B_Z)/h$;

(9) $(j = 3/2, m_j = 1/2) \leftarrow (j = 3/2, m_j = -1/2)$; $w_R = (4/3)(\mu_B B_Z)/h$;

(10) $(j = 1/2, m_j = 1/2) \leftarrow (j = 3/2, m_j = -1/2)$; $w_R = (\mu_B B_Z)/h$;

(11) $(j = 1/2, m_j = -1/2) \leftarrow (j = 3/2, m_j = -1/2)$; $w_R = (1/3)(\mu_B B_Z)/h$;

(12) $(j = 1/2, m_j = 1/2) \leftarrow (j = 1/2, m_j = -1/2)$; $w_R = (2/3)(\mu_B B_Z)/h$;

Table 1 *Quantum numbers of the ground and laser prepared H electronic states.*

	n	l	m_l	s	m_s	j	m_j
Ground	1	0	0	1/2	1/2	1/2	1/2
	1	0	0	1/2	–1/2	1/2	–1.2
Laser prepared at 1,215.67 Å (n = 1 to n = 2)							
Left	2	1	1	1/2	1/2	3/2	3/2
circularly	2	1	1	1/2	–1/2	3/2	1/2
polarised	2	1	1	1/2	1/2	1/2	1/2
Right	2	1	–1	1/2	1/2	3/2	–1/2
circularly	2	1	–1	1/2	–1/2	3/2	3/2
polarised	2	1	–1	1/2	1/2	1/2	–1/2
Linearly	2	1	0	1/2	1/2	3/2	1/2
polarised	2	1	0	1/2	–1/2	3/2	–1/2
	2	1	0	1/2	1/2	1/2	1/2
	2	1	0	1/2	–1/2	1/2	–1/2

Significantly, the microwave resonance frequencies for the left and right circularly polarised laser are the same, although the quantum states between which these Zeeman transitions occur are different for the left (1 to 3) and right (4 to 6) circularly polarised lasers. For the linearly polarised laser there are six possible transitions, generating five resonance lines in the microwave, because two of the transition energies coincide. Clearly, the splitting of the original single π_1 ground state resonance of atomic hydrogen by a laser tuned to the Lyα frequency is a potentially useful phenomenon because it is characteristic of the atom and also of the energy level of the prepared electron. The simple analysis of this section, based on well known selection rules, is an indication of the wide scope of the technique. Some characteristics of optical ESR as described here in the simplest case are noteworthy.

(a) The ground state resonance has been split and shifted to lower frequencies, into the NMR range of frequencies, thus bringing the hydrogen atom ESR line of the ground state within range of an NMR spectrometer. This is due to spin orbit coupling, which is determined by Landé factors. For higher n states (for example n = 3, prepared by tuning a laser to the Lyβ line at 1,025.72 Å in the ultraviolet (n = 1 to n = 3), or the Balmer α line (n = 2 to n = 3) in the red part of the visible spectrum at 6,562.80 Å, the Landé factors become smaller, so that for the simple hydrogen atom, richer resonance patterns will become observable in the NMR range as the electron is prepared by the laser in higher and higher n states.

(b) In this analysis, no account has been taken of the interaction between the spin of the electron and of the nucleus, which is responsible for hyperfine structure.[16] Hyperfine interaction will enrich the spectrum further by splitting each electronic Zeeman state (described by l and m_l) into hyperfine states described by l, m_l, I

and m_I, where I is the nuclear spin quantum number, with m_I defining its allowed values.

(c) A fuller analysis requires consideration of population statistics in each electronic state. In general, after preparation by the laser, there will be a significant electronic population in the prepared state as well as a residual population in the ground state. The original resonance at 9,185.5046 MHz will still be observable in general, therefore, its (reduced) intensity depending on the residual ground state electronic population.

(d) No account has been taken of multi photon absorption. If the laser tuned to the Lyα line is intense enough to cause two photon absorption, the selection rules are extended to:

$$(l,m_l) \rightarrow (l+1, m_l+1) \rightarrow (l+2, m_l+2) \qquad (25)$$

for left circular polarisation, to:

$$(l, m_l) \rightarrow (l+1, m_l-1) \rightarrow (l+2, m_l-2) \qquad (26)$$

for right circular polarisation, to:

$$(l, m_l) \rightarrow (l+1, m_l) \rightarrow (l+2, m_l) \qquad (27)$$

for linear polarisation.[17] This gives rise to the possibility of more resonances in the microwave between multi photon Zeeman states, resonances which are within range of an NMR or ESR spectrometer.

When the spin orbit coupling is broken in favour of separate alignment[8] of spin and orbital electronic angular momentum, as in the Paschen Back effect,[3] the microwave resonances are no longer determined by j and m_j, but by l and m_l and by s and m_s. In general, in the state $n = 2$, $l = 1$, $m_l = -1, 0, +1$; $s = 1/2$, $m_s = -1/2$ and $+1/2$. Transitions can occur between the m_l and m_s Zeeman levels, a total of five levels. The microwave resonance spectrum will therefore record these transitions.

Finally in this section there are notable similarities between the use of a laser to prepare an electron in this way and the Overhauser effect,[9] where the electron resonance is saturated and the nuclear resonance intensity enhanced theoretically by a factor γ_e/γ_n, the ratio of electron and nuclear gyromagnetic ratios. Overhauser enhancement is the basic mechanism for several contemporary technologies, notably ENDOR and its two-dimensional developments.

The inverse Faraday effect

There is space here only for a brief mention of a mechanism of magnetisation by a circularly polarised laser which is proportional to the conjugate product:

$$\pi = \mathbf{E}_L^{+} \times \mathbf{E}_L^{-} = -\mathbf{E}_R^{+} \times \mathbf{E}_R^{-} = 2E_o^{2}\mathbf{k}i \qquad (28)$$

Here **E** denotes the electric field strength in V m^{-1} of the laser, the subscripts R and L denote right and left circular polarisation, and the superscripts + and − denote plus and minus conjugates of the electromagnetic plane wave.[18] In equation (28), the complex scalor E_o is the electric field strength amplitude, **k** a unit vector in the Z axis of the laboratory frame, and $i = (-1)^{1/2}$. The conjugate product has the same negative motion reversal symmetry (T) and positive parity inversion symmetry (P) as magnetic flux density **B**, and a circularly polarised

laser is capable in principle of lifting the degeneracy of Zeeman states in a similar way to an applied magnetic field **B**.[19–26] The theory of this effect is described at length elsewhere.[19,20]

There appears to be only one experimental measurement of the inverse Faraday effect in the literature, by Pershan *et al.* in 1965.[5] It was found that a *pulse* of circularly polarised ruby laser radiation of 10^7 W cm^{-2} produced bulk magnetisation of the order 10^{-5} Oe (0.01 A m^{-1}). Using contemporary laser tuning technology it has been shown theoretically[19,20,24] that the inverse Faraday effect is capable of selectively shifting and broadening NMR and ESR proton and other resonances by site selective magnetisation due to the conjugate product equation (28). This effect will occur in addition to that of section 2 with very intense lasers. Unlike the effect described earlier, inverse Faraday magnetisation can shift the NMR and ESR lines to higher as well as lower frequencies, to higher frequencies if π and the applied magnetic field, B, are in the same direction, and vice versa. Advantage can be taken, in principle, of both shifts, for example when attempting to increase the absolute frequency separation between complex NMR resonances, the laser's π is directed parallel to B of the spectrometer. If attempting to shift an ESR resonance down into the range of an NMR spectrometer, the laser's π is directed antiparallel to B of the spectrometer. Additionally, Landé coupling between Zeeman energy states due to B and π can occur,[20,24] further enriching the resonance spectrum. The mediating property in the case of resonance due to the inverse Faraday effect is the angular electronic polarisability,[25] which has the same T and P symmetries as the magnetic dipole moment.

Discussion

The hydrogen atom is of course a far cry from the complex resonances seen in contemporary NMR and two-dimensional NMR spectra of proteins in solution.[11-13] However, the principle of optical ESR and NMR remains the same in both cases. Additionally, it is possible, in principle, to prepare the complex sample in an excited electronic state using the laser, an excited state in which there is net electronic angular momentum (unpaired electrons), and in consequence a laser enriched ESR spectrum. Hyperfine couplings between the electron in this state and the nuclear spins will occur, leading to an enriched NMR and two-dimensional NMR protein spectrum. If this process of enrichment is site selective, *i.e.* give additional information on the various proton resonating sites[11–13] in a protein, it could prove to be of widespread analytical interest. There is also the possibility of tuning the applied laser to different electronic frequencies and therefore of producing a laser enhanced NMR spectrum which is characteristic of the tuning frequency, thereby producing further site selective information for analysis.

By varying the polarisation and intensity of the laser, further information is provided. For example, the polarisation can be varied from fully left polarised to fully right polarised, through a range of polarisation which includes linear polarisation (50% left and 50% right) as one of the full range of possibilities. Other examples include 25% left, 75% right; and so on. Section 2 has shown that in the simplest case, the splitting due to the laser depends on the state of polarisation.

When dealing with a complex protein system, finally, there may well be a dense array of extra resonances produced by the laser, which will appear to the

NMR spectrometer as a broadening, or diffusion of the resonance, in much the same way as some atomic lines appeared diffuse to early investigators.[4] This diffusion of the NMR lines is in itself a useful phenomenon, especially if site selective, and the manner and extent of diffusion will depend in general on the characteristics of the laser being used, the magnetic field strength, and of the sample under investigation.

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