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Optical NMR and ESR

M. W. EVANS[1]

433 Theory Center, Cornell University, Ithaca, New York 14853

The theory of optical NMR and ESR is developed 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 polarized 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 2D and enhancement techniques.

INTRODUCTION

Optical NMR and ESR are based on the ability of visible frequency circularly and linearly polarized 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 optically induced magnetic dipole moment. The intensity (in watts per square centimeter) of light is proportional to the number of light quanta (photons) per unit volume multiplied by its angular frequency ω (in rad sec^{-1}) and the reduced Planck constant $\hbar$. It follows that there is much more intensity per photon at visible frequency than at radiofrequency, because for the former ω is about 100 000 to 1 000 000 times bigger. The number of photons per unit volume is also increased by using more watts per square centimeter, i.e., by increasing the light intensity, which is proportional to light energy per unit volume. The latter is proportional to the square of the amplitude of the oscillating electric field strength (volts per centimeter) of the light beam. By both frequency and intensity being increased 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 radiofrequency beam.

The quantum theory of radiation (*1*) argues that the photon is handed, i.e., there can be right-handed and left-handed photons, characterized by a quantum number M. This is a consequence of the fact that circularly polarized 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 polarized visible radiation. The angular momentum of light in quantum theory is

$$|\mathbf{M}| = n_0 M \hbar \tag{1}$$

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[1] 1990/1991: Institute of Physical Chemistry, University of Zürich, Winterthurerstrasse 190, CH 8057 Zürich, Switzerland.

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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*)) $\hbar$. When a photon is absorbed by an atom or molecule, all its angular momentum is given to an electron. For a left circularly polarized laser, this transfer is described by a change of $+1$ in the magnetic quantum number M, and -1 for a right circularly polarized 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 polarized photon contributes either $+\hbar$ or $-\hbar$ 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

$$\Delta L = \pm 1; \qquad \Delta M = 0, \pm 1 \tag{2}$$

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, but the change $\Delta M = 0$ for photon to electron angular momentum transfer is not 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, called 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 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 are described in Section 1. The magnetic dipole moment ($\mathbf{m}$) per photon given to the electron of an atom or molecule during absorption of circularly polarized 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 $\mathbf{B}$ 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 polarized laser, and the two-dimensional NMR spectrum characterizes this site selective nature.

Section 2 estimates 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. Section 3 is a brief description of additional magnetization effects of circularly polarized light, such as the inverse Faraday effect (*4–6*), which may become important in very intense laser beams. Finally, a discussion is given of the likely uses of laser NMR and ESR.

I. THE LIGHT-INDUCED MAGNETIC DIPOLE MOMENT

A magnetic dipole moment is created by a loop of moving charge, a current, I (A), 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 electron 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

$$|\mathbf{m}| = \frac{e}{2m_e}|\mathbf{L}| \equiv -\gamma_e|\mathbf{L}|, \tag{3}$$

where $\mathbf{L}$ is the orbital angular momentum. The latter is written as $\hbar\hat{\mathbf{L}}$, where $\hat{\mathbf{L}}$ is the dimensionless angular momentum operator (*8*), and the quantity γ_e is the gyromagnetic ratio. The product $-\gamma_e\hbar$ is the Bohr magneton, the atomic unit of magnetic moment. The effect of an external magnetic field $\mathbf{B}$ 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 oriented at an angle θ to the direction of $\mathbf{B}$, a torque

$$|\mathbf{T}| = -|\mathbf{m}|\ |\mathbf{B}| \sin\theta = -|\mathbf{m}\times\mathbf{B}| \tag{4}$$

is set up between the field and the 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

$$\Delta w = \int |\mathbf{T}|\,d\theta = |\mathbf{m}|\ |\mathbf{B}|\cos\theta = \mathbf{m}\cdot\mathbf{B}. \tag{5}$$

It follows that a magnetic dipole moment in a magnetic field $\mathbf{B}$ has a potential energy which is the same in magnitude as the work done but opposite in sign:

$$\Delta E = -\Delta w = -\mathbf{m}\cdot\mathbf{B}. \tag{6}$$

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

$$\Delta E_L = -\gamma_e\mathbf{L}\cdot\mathbf{B}, \tag{7}$$

assuming that the orbit size is unaffected by $\mathbf{B}$.

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 and 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 (7) are detected with radiofrequency 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 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

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

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 2D 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 $\mathbf{B}$ (T).

The absolute frequency separation of proton resonances in a protein can be changed by changing the energy (7). This can be done in two ways: (1) by increasing $\mathbf{B}$ (using a stronger magnet); (2) by increasing the effective magnetic dipole moment $\mathbf{m}$ 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 $\mathbf{m}$ by optically injecting angular momentum into the sample using a visible frequency circularly polarized laser of up to a few hundred watts per square centimeter 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 $n_0\hbar\omega$, where n_0 is the number of photons per unit volume, and its angular momentum about the axis of propagation (Z) is $n_0 M\hbar$. 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

$$E_f - E_i = \hbar\omega \tag{9}$$

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 $+\hbar$ per photon for left circularly polarized laser radiation and $-\hbar$ for its right-handed counterpart.

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

$$|\mathbf{m}| = \gamma_e \hbar = -\mu_B \tag{10}$$

units of magnetic dipole moment, where μ_B is the Bohr magneton. It follows that Bohr magneton units of moment are created per photon. The greater the number of photons per unit volume, n_0, the greater the number of units of induced magnetic dipole moment in the sample. The more energy, $\hbar\omega$, per photon, the greater the difference (9); i.e., more energetic transitions become possible between higher L states (e.g., $L = 1$ to $L = 2$, p to d states). Such transitions are not possible with radiofrequency photons because there is not enough energy per photon. Electronic transitions are observed spectroscopically at radio-, infrared, visible, and ultraviolet frequencies, for example, the Lyman, Balmer, Paschen, Brackett, Pfund, and Humphreys series of atomic hydrogen. The Lyman series begins in the ultraviolet, the Balmer in the red (visible), the Brackett in the infrared, and the Humphreys series in the mid to low infrared range.

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

The total angular momentum of the laser is therefore more accurately (*15*) written as

$$|\mathbf{M}| = n_0^{L,M} M\hbar, \tag{11}$$

where $n_0^{L,M}$ is associated with quantum numbers L and M. The total laser angular momentum obeys the commutation relations (*15*)

$$[M_X, M_Y] = i\hbar M_Z$$

$$M_X^2 + M_Y^2 + M_Z^2 = \hbar^2 L(L+1) \tag{12}$$

so that its magnitude is proportional to $\sqrt{L(L+1)}$. 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 $\mathbf{M}$ of the laser carries with it the capability of imparting $n_0^{LM}\hbar\gamma_e$ units of magnetic dipole moment to the atom which absorbs the energetic visible frequency photon according to the selection rules on 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 $|\hbar\gamma_e|$, the magnitude of 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 changed frequencies, because the magnitude of the orbital electronic angular momentum, and therefore the magnetic dipole moment, is proportional to $\sqrt{L(L+1)}$, and there are more possible resonances, because threefold degeneracy has been replaced by fivefold degeneracy. In the presence of a field $\mathbf{B}$ 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.

2. ORDER OF MAGNITUDE ESTIMATES

The discussion of the effect of a circularly polarized laser starts with the hydrogen atom, in particular the first Lyman transition at 1215.67 Å in the ultraviolet. This is the Ly α 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 H atom is described by the quantum numbers

$$n = 1, l = 0, m_l = 0, s = \tfrac{1}{2}, m_s = \tfrac{1}{2}, -\tfrac{1}{2} \tag{13}$$

which, for one electron, follows from the rules (*3*)

$$l = 0, 1, \ldots, n - 1; \qquad m_l = -l, \ldots, l$$
$$s = \tfrac{1}{2}; \qquad m_s = -s, \ldots, s. \tag{14}$$

By tuning a laser in a vapor of H atoms to the frequency of the Ly α transition, a photon is absorbed and the electron is prepared in a higher-energy condition, governed by the selection rules of the H atom quantum numbers. Depending on the circular polarization of the laser, the condition of the electron is described as

$$n = 2, l = 1, m_l = +1, s = \tfrac{1}{2}, m_s = \tfrac{1}{2}, -\tfrac{1}{2} \tag{15}$$

for left circularly polarized radiation,

$$n = 2, l = 1, m_l = -1, s = \tfrac{1}{2}, m_s = \tfrac{1}{2}, -\tfrac{1}{2} \tag{16}$$

for right circularly polarized radiation, and

$$n = 2, l = 1, m_l = 0, s = \tfrac{1}{2}, m_s = \tfrac{1}{2}, -\tfrac{1}{2} \tag{17}$$

for linearly polarized radiation.

A transition from state (13) to any of the states (15), (16), and (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 1215.67 Å. In state (15), for example, produced by a left circularly polarized laser at this wavelength, note that $m_l = l = 1$, and it is no longer equiprobable that the electron occupy any of the states $m_l = -l, \ldots, l$. Similarly, after absorption of a right-handed photon from a right circularly polarized laser, the magnetic quantum number in the prepared state is confined to $m_l = -1$. In a linearly polarized laser, it is confined to $m_l = 0$.

Using a laser at a given frequency and specific polarization it is possible to prepare the electron of the H 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. The electron population having been prepared 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** 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

$$\Delta H = \hbar\omega = (g_{j1}m_{j1} - g_{j2}m_{j2})\mu_B B_Z, \tag{18}$$

where the total angular momentum quantum numbers j and m_j are defined through the Clebsch–Gordan series (*3*)

$$\left.\begin{aligned} j &= l + s, l + s - 1, \ldots, |l - s|, \\ m_j &= m_l + m_s, \end{aligned}\right] \tag{19}$$

and where the Landé factor is defined in general by

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}. \tag{20}$$

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 ($n = 1$, $l = 0$), which consists of the transition $m_j = -\frac{1}{2}$ to $m_j = +\frac{1}{2}$; $\Delta m_I = 0$, at 9185.5046 MHz for their applied magnetic flux density. Here Δm_I 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 9185.5046 MHz was arrived at by injecting microwave radiation at this frequency into the ground state H atom, whose electron absorbs photon energy, and undergoes a quantum transition from the lower-energy state ($m_j = -\frac{1}{2}$) to the higher-energy state ($m_j = \frac{1}{2}$), 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 microwave frequency, absorption of a photon occurs, as observed experimentally by a net lowering of the power level at the microwave detector. At 9185.5046 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

$$\begin{aligned} \hbar\omega_R &= (g_{1/2}m_{1/2} - g_{1/2}m_{-1/2})\mu_B B_Z; \\ \omega_R &= g_{1/2}(\mu_B B_Z/\hbar) = 2\mu_B B_Z/\hbar, \end{aligned} \tag{21}$$

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

$$j = l + \tfrac{1}{2}, \ldots, |l - \tfrac{1}{2}| = \tfrac{1}{2}; \tag{22}$$

the single observable resonance frequency is

$$\omega_R = 2(\mu_B B_Z/\hbar). \tag{23}$$

The H electron in one of the states (15) to (17) having been laser prepared, however, the ESR spectrum will consist of more than one line. This is easily seen by reference to Table I, which summarizes the allowed j and m_j states. Zeeman transitions between these states occur in the presence of the magnet according to the section rules (*3*)

$$\begin{aligned}
\Delta j &= 0; & \Delta m_j &= 1;\\
\Delta j &= 0; & \Delta m_j &= -1;\\
\Delta j &= 1; & \Delta m_j &= 1;\\
\Delta j &= 1; & \Delta m_j &= 0;\\
\Delta j &= 1; & \Delta m_j &= -1;\\
\Delta j &= -1; & \Delta m_j &= 1;\\
\Delta j &= -1; & \Delta m_j &= 0;\\
\Delta j &= -1; & \Delta m_j &= -1;
\end{aligned} \tag{24}$$

In the state prepared by the left circularly polarized laser (Table I) these selection rules allow three resonance frequencies from Eq. (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:

$$(1)\ (j = \tfrac{3}{2},\ m_j = \tfrac{3}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = \tfrac{1}{2}); \qquad \omega_R = \frac{4}{3}\frac{\mu_B B_Z}{\hbar};$$

TABLE I

Quantum Numbers of the Ground and Laser Prepared H Atom Electronic States. Lyman Alpha Line

	n	l	m_l	s	m_s	j	m_j
Ground	1	0	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	1	0	0	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
Prepared							
Left	2	1	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
	2	1	1	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
	2	1	1	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Right	2	1	-1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{1}{2}$
	2	1	-1	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{2}$	$-\frac{3}{2}$
	2	1	-1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$
Linear	2	1	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
	2	1	0	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{3}{2}$	$-\frac{1}{2}$
	2	1	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	2	1	0	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

$$(2)\ (j = \tfrac{3}{2},\ m_j = \tfrac{3}{2}) \leftarrow (j = \tfrac{1}{2},\ m_j = \tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = \frac{5}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(3)\ (j = \tfrac{3}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{1}{2},\ m_j = \tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = \frac{1}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar}.$$

The state prepared by the right circularly polarized laser allows the same pattern of lines at these frequencies, but originating in different transitions:

$$(4)\ (j = \tfrac{1}{2},\ m_j = -\tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = -\tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = \frac{1}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(5)\ (j = \tfrac{1}{2},\ m_j = -\tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = -\tfrac{3}{2}); \qquad \omega_{\mathrm{R}} = \frac{5}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(6)\ (j = \tfrac{3}{2},\ m_j = -\tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = -\tfrac{3}{2}); \qquad \omega_{\mathrm{R}} = \frac{4}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar}.$$

The state prepared by the linearly polarized laser allows four resonance frequencies:

$$(7)\ (j = \tfrac{3}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{1}{2},\ m_j = -\tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = 1.0\,\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(8)\ (j = \tfrac{3}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{1}{2},\ m_j = \tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = \frac{1}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(9)\ (j = \tfrac{3}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = -\tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = \frac{4}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(10)\ (j = \tfrac{1}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = -\tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = 1.0\,\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(11)\ (j = \tfrac{1}{2},\ m_j = -\tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = -\tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = \frac{1}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar};$$

$$(12)\ (j = \tfrac{1}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{1}{2},\ m_j = -\tfrac{1}{2}); \qquad \omega_{\mathrm{R}} = \frac{2}{3}\frac{\mu_{\mathrm{B}} B_Z}{\hbar}.$$

These correspond to six allowed transitions.

Significantly, the microwave resonance frequencies for the left and right circularly polarized lasers 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 polarized lasers. For the linearly polarized laser there are six possible transitions, generating four resonance lines in the microwave, because two of the transition energies coincide. Clearly, the splitting of the original single ground state resonance of atomic hydrogen by a laser tuned to the Ly α 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 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 H 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 Ly β line at 1025.72 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 6562.80 Å, the Landé factors become smaller, so that for the simple H 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. This is discussed further later in this section.

(b) In this analysis, no account has been taken of the interaction between the spins 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 9185.5046 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 multiphoton absorption. If the laser tuned to the Ly α line is intense enough to cause two-photon absorption, the selection rules are extended to

$$(l, m_l) \rightarrow (l + 1, m_l + 1) \rightarrow (l + 2, m_l + 2) \tag{25}$$

for left circular polarization, to

$$(l, m_l) \rightarrow (l + 1, m_l - 1) \rightarrow (l + 2, m_l - 2) \tag{26}$$

for right circular polarization, and to

$$(l, m_l) \rightarrow (l + 1, m_l) \rightarrow (l + 2, m_l) \tag{27}$$

for linear polarization (*17*). This gives rise to the possibility of more resonances in the microwave between multiphoton Zeeman states, resonances which are within range of an NMR or ESR spectrometer.

When the spin–orbit coupling is broken in favor 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 $n = 2$, $l = 1$, $m_l = -1, 0, +1$, $s = \frac{1}{2}$, $m_s = -\frac{1}{2}$ and $+\frac{1}{2}$, transitions can occur between the m_l and the m_s Zeeman levels, a total of five levels. The microwave resonance spectrum will therefore record these transitions.

The Lyman β Transition

The Lyman β transition is caused by tuning the laser to 1025.72 Å in the ultraviolet, and causes electronic transitions between the $n = 1$ and $n = 3$ principal quantum numbers of the electron of the hydrogen atom. The electronic term $n = 3$ is described in the absence of hyperfine interactions by the following set of quantum numbers. The selection rule $\Delta l = 1$ allows transitions between the $l = 0$, $n = 1$ condition and the $l = 1$, $n = 3$ condition. In the microwave region, transitions are observed therefore between the same Zeeman states as for the Lyman α line.

The Balmer α Transition

In this case the laser is tuned to the red part of the visible at the wavelength 6562.80 Å. Transitions occur between $n = 2$ and $n = 3$, assuming that there is a significant electronic population initially in the state $n = 2$. The l selection rule allows transitions between (1) the $n = 2$, $l = 0$ condition and the $n = 2$, $l = 1$ condition; and (2) the $n = 2$, $l = 1$ condition and the $n = 3$, $l = 2$ condition. Transitions between Zeeman states in the former condition are governed by $l = 1$, and therefore occur at the same frequencies in the microwave as those for the $l = 1$ condition reached by tuning the laser to Lyman α and Lyman β lines. However, in the condition $n = 3$, $l = 2$, a richer ESR and NMR spectrum will be observed, produced by microwave and radiofrequency transitions between the j and the m_j states described in Table II. The Landé factors governing these transitions are different from those for $l = 1$ transitions, because from Eq. (20), the Landé factor is governed by $l(l+1)$, $s(s+1)$, and $j(j+1)$.

From Table II, microwave and radio frequency/microwave transitions occur as summarized below for left and right circularly polarized and linearly polarized laser preparation from the $n = 2$ to $n = 3$ condition at the Balmer α wavelength in the red. The various ESR transitions include the following patterns of lines.

Triplet Type ($\Delta j = 1$; $\Delta m_j = 1$); *Left Circular Polarization*

$$(j = \tfrac{5}{2}, m_j = \tfrac{5}{2}) \leftarrow (j = \tfrac{3}{2}, m_j = \tfrac{3}{2}); \qquad \frac{1.8\mu_B B_Z}{\hbar};$$

$$(j = \tfrac{5}{2}, m_j = \tfrac{3}{2}) \leftarrow (j = \tfrac{3}{2}, m_j = \tfrac{1}{2}); \qquad \frac{1.4\mu_B B_Z}{\hbar};$$

$$(j = \tfrac{5}{2}, m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2}, m_j = -\tfrac{1}{2}); \qquad \frac{1.0\mu_B B_Z}{\hbar}.$$

Therefore there are three ESR lines from this type at three different frequencies.

First Singlet Type ($\Delta j = 0$; $\Delta m_j = 1$); *Left Circular Polarization*; $j = \frac{5}{2}$

$$(j = \tfrac{5}{2}, m_j = \tfrac{5}{2}) \leftarrow (j = \tfrac{5}{2}, m_j = \tfrac{3}{2}); \qquad \frac{1.2\mu_B B_Z}{\hbar};$$

$$(j = \tfrac{5}{2}, m_j = \tfrac{3}{2}) \leftarrow (j = \tfrac{5}{2}, m_j = \tfrac{1}{2}); \qquad \frac{1.2\mu_B B_Z}{\hbar};$$

$$(j = \tfrac{5}{2}, m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{5}{2}, m_j = -\tfrac{1}{2}); \qquad \frac{1.2\mu_B B_Z}{\hbar}.$$

TABLE II

Resonance Frequencies, Balmer Alpha Line (In Units of $\mu_B B_Z/\hbar$)

Transition	Left	Right	Linear
$j = \frac{5}{2}$; $\Delta j = 0$, $\Delta m_j = 1$	1.2; 1.2; 1.2	1.2; 1.2; 1.2	1.2; 1.2; 1.2
$j = \frac{3}{2}$; $\Delta j = 0$, $\Delta m_j = 1$	0.8; 0.8	0.8; 0.8	0.8; 0.8; 0.8
$\Delta j = 0$, $\Delta m_j = -1$	—	—	—
$\Delta j = 1$, $\Delta m_j = 0$	0.2; 0.6	0.2	0.2; 0.6
$\Delta j = 1$, $\Delta m_j = 1$	1.0; 1.4; 1.8	0.6; 1.0	0.6; 1.0; 1.4
$\Delta j = 1$, $\Delta m_j = -1$	—	—	—
$\Delta j = -1$, $\Delta m_j = 0$	0.2	0.2; 0.6	0.2; 0.6
$\Delta j = -1$, $\Delta m_j = 1$	0.2; 0.6; 1.0	0.4; 1.0	0.6; 1.0; 1.4
$\Delta j = -1$, $\Delta m_j = -1$	—	—	—

Three lines occur at the same frequency, so the observable is a line three times more intense than those of the triplet type.

Second Singlet Type ($\Delta j = 0$; $\Delta m_j = 1$); *Left Circular Polarization*; $j = \frac{3}{2}$

$$(j = \tfrac{3}{2},\ m_j = \tfrac{3}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = \tfrac{1}{2});\qquad \frac{0.8\mu_B B_Z}{\hbar};$$

$$(j = \tfrac{3}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = -\tfrac{1}{2});\qquad \frac{0.8\mu_B B_Z}{\hbar}.$$

Two lines occur at the same frequency; therefore, an ESR absorption is seen with twice the intensity of the triplet type.

Doublet Type ($\Delta j = 1$; $\Delta m_j = 0$); *Left Circular Polarization*

$$(j = \tfrac{5}{2},\ m_j = \tfrac{3}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = \tfrac{3}{2});\qquad \frac{0.6\mu_B B_Z}{\hbar}$$

$$(j = \tfrac{5}{2},\ m_j = \tfrac{1}{2}) \leftarrow (j = \tfrac{3}{2},\ m_j = \tfrac{1}{2});\qquad \frac{0.2\mu_B B_Z}{\hbar}.$$

Two lines are seen at two different frequencies.

Third Singlet Type ($\Delta j = -1$; $\Delta m_j = 0$); *Left Circular Polarization*

$$(j = \tfrac{3}{2},\ m_j = -\tfrac{1}{2}) \leftarrow (j = \tfrac{5}{2},\ m_j = -\tfrac{1}{2});\qquad \frac{0.2\mu_B B_Z}{\hbar}.$$

A single line is seen at the reduced frequency 0.2, which is the same as one of the doublet frequencies, thus doubling its intensity.

The overall effect of a left laser tuned to the Balmer α transition of H is therefore to promote a significant electron population in the $n = 3$, $l = 2$ condition, in which transitions between Zeeman states produce the final ESR spectrum. This has split the ground state line into seven observable lines, two of which have three times the intensity, and three of which have twice the intensity, of the other two. All seven lines are shifted from the GHz to the 100 MHz range, i.e., to within range of an NMR spectrometer. For the left circularly polarized laser there are a total of 14 transitions, for the right circularly polarized laser a total of 12 transitions, and for the linearly polarized laser a total of 16 transitions associated with tuning the laser to the Balmer α line. These transitions between Zeeman states cause resonance frequencies which are recorded in Table II in units of $\mu_B B_Z / \hbar$.

This process can be continued for a laser tuned to the first Paschen transition ($n = 3$ to $n = 4$ at 18 751.0 Å), for the first Brackett transition ($n = 4$ to $n = 5$ at 40 512.0 Å), for the first Pfund transition ($n = 5$ to $n = 6$ at 74 578.0 Å), for the first Humphreys transition ($n = 6$ to $n = 7$ at 123 680.0 Å); and so on. The laser ESR/NMR spectrum seen in the MHz/GHz range becomes progressively richer, and a computer program has been written to produce the results. For the first Paschen transition from $n = 3$, $l = 2$ to $n = 4$, $l = 3$, for example, the laser NMR/ESR spectra for left, right, and linearly polarized lasers tuned to 18 751.0 Å are already rich in detail.

The laser can also be tuned to the higher frequencies of the Lyman, Balmer, Paschen, Brackett, Pfund, and Humphreys series, giving a wide range of possible frequencies to match with available tunable laser frequencies such as those from tunable dye, excimer, and garnet lasers. The Balmer series is particularly useful for this purpose, because its frequencies occur in the visible range. All the lines of the Balmer series are generated by electronic transitions from $n = 2$ to higher integral positive n. For $n = 2$, the allowed values of l are 0 and 1, and the dipole selection rule $\Delta l = 1$ for the absorption of one photon by the H electron means that whatever the final n state, the final l states can only be 1 and 2. The $l = 1$ and $l = 2$ ESR/NMR resonances have been described already, and can be generated by tuning the laser to any one of the Balmer series, whose initial n state is always 2, and whose first few final n states correspond with the following wavelengths in angstroms: 6562.8 ($n = 2$ to $n = 3$); 4861.32 ($n = 2$ to $n = 4$); 4340.46 ($n = 2$ to $n = 5$); 4101.73 ($n = 2$ to $n = 6$); 3970.07 ($n = 2$ to $n = 7$); 3889.05 ($n = 2$ to $n = 8$); 3835.38 ($n = 2$ to $n = 9$); 3797.90 ($n = 2$ to $n = 10$); 3770.63 ($n = 2$ to $n = 11$); 3750.15 ($n = 2$ to $n = 12$). This series of wavelengths covers the visible range from the red through to the infinity value at 3646.0 Å in the violet, and many of its frequencies are therefore suitable for visible frequency tunable lasers. The thermal population of each n level is a Boltzmann distribution, and the effect of tuning the laser to the 3835.38 Å wavelength, for example, would be to populate the $n = 9$ level at the expense of the $n = 2$ level. The intensity, but not the frequency pattern, of the optical ESR/NMR spectrum depends on the relative electronic population of each n state. The electronic state for a laser tuned to 3835.38 Å would change from $n = 2$, $l = 0, 1$ to $n = 9$, $l = 1, 2$.

A similar procedure can be followed for the Lyman series, for example, but this appears of less practical importance because the Lyman series occurs in the ultraviolet, the initial n state being always 1. The first few Lyman wavelengths in angstroms are: 1215.67 ($n = 1$ to $n = 2$); 1025.72 ($n = 1$ to $n = 3$); 972.537 ($n = 1$ to $n = 4$); 949.743 ($n = 1$ to $n = 5$); 937.803 ($n = 1$ to $n = 6$); 930.748 ($n = 1$ to $n = 7$);

926.226 (n = 1 to n = 8); 923.150 (n = 1 to n = 9); 920.963 (n = 1 to n = 10); 919.352 (n = 1 to n = 11); 918.129 (n = 1 to n = 12). Tuning a laser to any one of these lines will produce photon absorption from the state $n = 1$, $l = 0$ to an upper n state with $l = 1$, giving the pattern of optical NMR/ESR lines already discussed.

The Paschen series of electronic transitions from an initial state $n = 3$ for H occurs in the near infrared to red range. The optical ESR/NMR spectrum in this case is richer in detail, because it encompasses transitions such as $n = 3$, $l = 0, 1, 2$ to higher n states with $l = 1, 2, 3$, satisfying the dipole selection rule $\Delta l = +1$ on the absorption by the H electron of a single photon. The first few Paschen transitions occur at the following wavelengths in angstroms: 18 751.0 (n = 3 to n = 4); 12 818.1 (n = 3 to n = 5); 10 938.1 (n = 3 to n = 6); 10 049.4 (n = 3 to n = 7); 9545.98 (n = 3 to n = 8); 9229.02 (n = 3 to n = 9); 9014.91 (n = 3 to n = 10); 8862.79 (n = 3 to n = 11); 8750.47 (n = 3 to n = 12).

The first Brackett transition (n = 4 to n = 5) occurs in the mid infrared (at a wavelength in angstroms of 40 512.0, about 2500 wavenumbers). The series continues up to the near infrared. The following few wavelengths of the Brackett series (in angstroms) are: 26 252.0 (n = 4 to n = 6); 21 655.8 (n = 4 to n = 7); 19 445.6 (n = 4 to n = 8); 18 174.1 (n = 4 to n = 9); 17 372.1 (n = 4 to n = 10); 16 806.5 (n = 4 to n = 11); 16 407.2 (n = 4 to n = 12). An infrared laser tuned to any of these wavelengths, and from which one photon is absorbed by the H electron, produces transitions from $n = 4$, $l = 0, 1, 2, 3$, to a higher n, $l = 1, 2, 3, 4$, governed by the dipole selection rule $\Delta l = +1$. This produces a very rich optical NMR/ESR spectrum, even for the simple H atom.

The first few wavelengths of the Pfund series occur in the mid infrared at about the carbon dioxide laser range. They are, in angstroms; 74 578 (about 1300 wavenumbers) (n = 5 to n = 6); 46 525 (n = 5 to n = 7); 37 395 (n = 5 to n = 8); 32 961 (n = 5 to n = 9); 30 384 (n = 5 to n = 10); 28 722 (n = 5 to n = 11); 27 575 (n = 5 to n = 12). Pumping any of these lines produces one-photon absorption accompanied by $n = 5$, $l = 0, 1, 2, 3, 4$ to higher n, $l = 1, 2, 3, 4, 5$.

The first few wavelengths, finally, of the Humphreys series occur in the far to mid infrared, again in the vicinity of the carbon dioxide laser wavelength. They are, in angstroms: 123 680 (n = 6 to n = 7); 75 005 (n = 6 to n = 8); 59 066 (n = 6 to n = 9); 51 273 (n = 6 to n = 10); 46 712 (n = 6 to n = 11); 43 753 (n = 6 to n = 12). A pump laser tuned to any of these wavelengths produces one-photon absorption governed by $n = 6$, $l = 0, 1, 2, 3, 4, 5$ to a higher n, $l = 1, 2, 3, 4, 5, 6$.

It is clear that for the simple H atom, a series of electronic transitions covering the far infrared to the ultraviolet is available for use in optical NMR/ESR, whose pattern becomes richer as the initial electronic state progresses from $n = 1$ (Lyman) to $n = 6$ (Humphreys). There are also other H electronic series with initial n state higher than 6, which occur in the far infrared, microwave, and radiofrequency range. Pumping one of these with, for example, a powerful microwave source such as a klystron, or tokamak plasma, would produce, in principle, a very rich optical NMR/ESR spectrum between Zeeman states. Zeeman transitions up to $n = 18$ have been computed. There is therefore a scope for utilization of optical NMR and ESR for applied and fundamental investigation with lasers, tokamak plasma, carcinotrons, masers, klystrons, and other radiative sources covering the electromagnetic range from the ultraviolet to the radiofrequency range. This occurs for the simple one-electron H atom, so that the possibilities for heavier atoms and molecules multiply.

Finally, 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.

3. THE INVERSE FARADAY EFFECT

It is appropriate in this section to include a nonlinear mechanism of magnetization by a circularly polarized laser which is proportional to the conjugate product

$$\mathbf{\Pi} = \mathbf{E}_L^+ \times \mathbf{E}_L^- = -\mathbf{E}_R^+ \times \mathbf{E}_R^- = 2E_0^2\mathbf{k}i. \tag{28}$$

Here **E** denotes the electric field strength (in V m^{-1}) of the laser, the subscripts R and L denote right and left circular polarization, and the superscripts + and − denote plus and minus conjugates of the electromagnetic plane wave (*18*). In Eq. (28) E_0 is the scalar electric field strength amplitude, **k** a unit vector in the Z axis of the laboratory frame, and i the square root of minus one. The conjugate product $\mathbf{\Pi}$ has the same negative motion reversal symmetry (T) and positive parity inversion symmetry (P) as magnetic flux density **B**, and a circularly polarized 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 circular polarized ruby laser radiation of 10^7 W per cm^2 produced bulk magnetization of the order 10^{-5} O (0.01 A per m). Using contemporary laser tuning technology it has been shown theoretically (*19, 24*) that the inverse Faraday effect is capable of selectively shifting and broadening NMR and ESR proton and other resonances by site-selective magnetization due to the conjugate product (28). This effect will occur in addition to that of Section 2 with very intense lasers. Unlike the effect described earlier, inverse Faraday magnetization can shift the NMR and ESR lines to higher as well as lower frequencies; to higher frequencies if $\mathbf{\Pi}$ 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 one attempts to increase the absolute frequency separation between complex NMR resonances, the laser's $\mathbf{\Pi}$ is directed parallel to the **B** of the spectrometer. If one attempts to shift an ESR resonance down into the range of an NMR spectrometer, the laser's $\mathbf{\Pi}$ is directed antiparallel to the **B** of the spectrometer. Additionally, Landé coupling between Zeeman energy states due to **B** and $\mathbf{\Pi}$ 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 polarizability (*25*), which has the same T and P symmetries as the magnetic dipole moment.

DISCUSSION

The H 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., gives 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 polarization and intensity of the laser, further information is provided. For example, the polarization can be varied from fully left polarized to fully right polarized, through a range of polarization which includes linear polarization (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 polarization.

When a complex protein system is being dealt with, 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 (*4*) to early investigators. 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 the characteristics of the sample under investigation.

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Note added in proof. The feasibility of the optical NMR experiment has been demonstrated by Professor W. S. Warren and co-workers at the Frick Chemical Laboratory, Princeton University, since this MS was submitted, and the first ONMR data have been presented at the 1991 St. Louis NMR Conference. Using only half a watt of laser power, shifts were observed in a chiral sample in the liquid state in methoxy and ring proton resonances. Since then methods have been developed by Warren and co-workers to remove heating effects and deuterium lock signal interference.

The mediating property tensors of optical NMR are the antisymmetric polarizability (alpha theory) and magnetic/electric/electric hyperpolarizability (beta theory), and in general, the effect is observable far from resonance. This was proven to satisfaction in the early stages of the Princeton experiment. In this respect, therefore, the lifetime of excited states does not enter into consideration. Further work since this MS was submitted has developed the Langevin function associated with ONMR, and also the rigorous quantum theory. This work will be reported in full elsewhere.

Experimental work is in progress in several directions, aimed at optimizing the ONMR spectrum under a given set of conditions.

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