other contexts in excitable media such as autowave diffraction (*16*).

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$$\partial e/\partial t = \nabla^2 e - f(e) - g$$
$$\partial g/\partial t = \varepsilon(e)(ke - g) \qquad (1)$$

with $f(e) = C_1 * e$ when $e < e_1$; $f(e) = -C_2 * e + a$ when $e_1 \le e \le e_2$; $f(e) = C_3 * (e - 1)$ when $e > e_2$; and $\epsilon(e) = \epsilon_1$ when $e < e_1$; $\epsilon(e) = \epsilon_2$ when $e_1 \le e \le e_2$; $\epsilon(e) = \epsilon_3$ when $e > e_2$. The parameters determining the shape of the function $f(e)$ are $e_1 = 0.0065$, $e_2 = 0.841$, $\epsilon_1 = 0.14$, $\epsilon_2 = 0.059$, $\epsilon_3 = 2.5$, $C_1 = 20$, $C_2 = 3$, $C_3 = 15$, $a = 0.15$, and $k = 3$. With these parameter values, the function $f(e)$ is continuous. To integrate Eq. 1, we used the explicit Euler method with time step $ht = 0.01$ and space step $hx = 0.3$, which gives less than 4% error for the velocity of plane wave propagation and 7% error for the period of the spiral rotation, about 15.5 time units. Neumann boundary conditions were used. A rectangular inexcitable obstacle was made using Neumann boundary conditions at its edges. External high-frequency stimulation was applied at one edge of the excitable medium with stimuli having amplitude four times the threshold value.

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High-Resolution Nuclear Magnetic Resonance Spectroscopy in a Circularly Polarized Laser Beam

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Nuclei in a fluid subjected to a continuous wave circularly polarized light beam are predicted to experience a static magnetic field proportional to $\mathbf{E}^{\pm} \times \dot{\mathbf{E}}^{\pm}$, where $\mathbf{E}^{\pm}$ is the electric vector of the right or left circularly polarized wave and the dot denotes a time derivative. The field strongly depends on the local electronic structure and is present in all atoms. For an intensity of 10 watts per square centimeter propagating in the direction of the field of a magnetic resonance spectrometer, the general theory presented here predicts shifts of $\pm 4 \times 10^{-8}$ hertz for protons and $\pm 10^{-5}$ hertz for fluorine-19. Larger shifts are predicted if the laser frequency is near an optical absorption.

Recently, there has been interest in laser-enhanced nuclear magnetic resonance (NMR) spectroscopy (*1–3*). Evans (*1*) predicted that a circularly polarized laser beam could raise NMR frequencies dramatically. Warren *et al.* (*2*) studied solutions of the chiral molecule *p*-methoxyphenyliminocamphor in linearly polarized as well as left and right circularly polarized light of wavelength 514 nm; they observed bulk high-field shifts on the order of 0.01 part per million and smaller differential shifts. Harris and Tinoco (*3*) estimated the change in the chemical shift of a nucleus induced by a polarized laser beam and concluded it was far too small to be measured.

Evans believes that a circularly polarized beam has an associated static magnetic field parallel to the direction of propagation and proportional to the square root of the intensity (*4, 5*), but this would lead to huge NMR shifts and would violate charge conjugation symmetry (*6*). Evans (*5*) also considers a second-order interaction of the laser with the molecular antisymmetric polarizability $\alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha}$, but he apparently failed to appreciate that in NMR spectroscopy, it is the antisymmetric polarizability induced by the nuclear magnetic moment that is relevant, just as it is the antisymmetric polarizability induced by the magnetostatic field that is responsible for the Faraday effect (*7*).

We show that the NMR shift may be expressed in terms of $\alpha'_{\alpha\beta}$ perturbed by the nuclear magnetic moment. Warren *et al.* (*2, 8*) suggest that the polarization proportional to the electric field of the light wave could produce a magnetic field at a nucleus, but presumably this field would be oscillating at the optical frequency and therefore would have no first-order effect on the spectrum. Harris and Tinoco (*3, 9*) consider nonchiral changes in energy proportional to the product $I_0 B_z^{(0)}$, where I_0 is the intensity of the laser beam and $B_z^{(0)}$ the magnetic field of the NMR spectrometer; they also consider small, chirally sensitive shifts proportional to I_0 and $I_0 B_z^{(0)}$.

In this report, we show that the electrons of any molecule in a circularly polarized light beam acquire a mean time-independent current density proportional to $\mathbf{E}^{\pm} \times \dot{\mathbf{E}}^{\pm}$, where $\mathbf{E}^{\pm}$ is the electric field associated with a right (+) or left (−) circularly polarized light wave and the dot denotes differentiation with respect to time. This current produces a magnetic moment [this is known as the inverse Faraday effect (*10*)] as well as a magnetic field at each nucleus. A steady molecular current induced by an optical field must be an even function of the field strength $|\mathbf{E}|$ in order that it be time-independent and an odd function of $\dot{\mathbf{E}}$ in a diamagnetic molecule in order that it should have the temporal properties of a current.

The electric field of a circularly polarized plane wave propagating in the direction of the unit vector $\mathbf{k}$, the z direction, is

$$\mathbf{E}^{\pm} = \frac{1}{\sqrt{2}} E^{(0)} \left[\mathbf{i} \cos \omega\left(t - \frac{nz}{c}\right) \mp \mathbf{j} \sin \omega\left(t - \frac{nz}{c}\right)\right] \qquad (1)$$

where $\mathbf{i}$ and $\mathbf{j}$ are unit vectors in the x and y directions, n is the refractive index, c the velocity of light in vacuo, and ω the angular frequency. The intensity of the beam is

$$I_0 = \frac{1}{2} \varepsilon_0 [E^{(0)}]^2 c \qquad (2)$$

where ε_0 is the permittivity of free space and I_0 is the power per unit area of a parallel beam of light; if $I_0 = 1$ W/cm², $E^{(0)} = 27.4$ V/cm.

From Eq. 1, the time derivative of $\mathbf{E}^{\pm}$ is

$$\dot{\mathbf{E}}^{\pm} \equiv \frac{\partial \mathbf{E}^{\pm}}{\partial t} = -\frac{\omega}{\sqrt{2}} E^{(0)} \left[\mathbf{i} \sin \omega\left(t - \frac{nz}{c}\right) \pm \mathbf{j} \cos \omega\left(t - \frac{nz}{c}\right)\right] \qquad (3)$$

The vector product $\mathbf{E}^{\pm} \times \dot{\mathbf{E}}^{\pm} = \mp(\omega/2)[E^{(0)}]^2\mathbf{k}$ is time-independent and behaves under the operations of parity P (that is, inversion of the coordinates of all particles through the origin, including the sources of the applied fields) and time reversal T (that

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Table 1. Behavior of various molecular properties and external fields under the symmetry operations of parity *P* and time reversal *T*.

Property or field	*P*	*T*
$\mathbf{E}$ (electric field)	−	+
$\dot{\mathbf{E}}$ (time derivative of $\mathbf{E}$)	−	−
$\mathbf{E} \times \dot{\mathbf{E}}$	+	−
μ (electric dipole moment)	−	+
$\mathbf{B}$ (magnetic field)	+	−
$\dot{\mathbf{B}}$ (time derivative of $\mathbf{B}$)	+	+
$\mathbf{m}$ (magnetic moment)	+	−
$\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$ (symmetric polarizability)	+	+
$\alpha'_{\alpha\beta} = -\alpha'_{\beta\alpha}$ (antisymmetric polarizability)	+	−
$\alpha'_{\alpha\beta\gamma} = \partial\alpha'_{\alpha\beta}/\partial B_\gamma$	+	+
$\chi_{\alpha\beta} = \chi_{\beta\alpha}$ (magnetizability)	+	+
$\sigma^{(I)}_{\alpha\beta}$ (nuclear magnetic shielding)	+	+
$G'_{\alpha\beta} = \omega^{-1}\partial\mu_\alpha/\partial\dot{B}_\beta = -\omega^{-1}\partial m_\beta/\partial\dot{E}_\alpha$	−	+

is, reversal of all momenta and spins) as a magnetostatic field (*11*) (however, $\mathbf{E}^\pm \times \dot{\mathbf{E}}^\pm$ is even under charge conjugation C, whereas a magnetic field is odd). Table 1 shows the effect of *P* and *T* on various properties and fields.

If the isotropic part of a property tensor is even under *P* and *T* (for example, $\alpha = \tfrac{1}{3}\alpha_{\beta\beta}$, magnetizability $\chi = \tfrac{1}{3}\chi_{\beta\beta}$, and $\alpha'(\mathbf{B}) = \tfrac{1}{6}\varepsilon_{\alpha\beta\gamma}\alpha'_{\alpha\beta\gamma}$), then the corresponding bulk property is exhibited by all matter (for example, refractive index, magnetic susceptibility, and the Faraday effect). If the isotropic part is even under *T* but odd under *P* (for example, $G' = \tfrac{1}{3}G'_{\beta\beta}$), then the bulk property (for example, optical activity) is only exhibited by chiral species.

The inverse Faraday effect (*10*) describes the magnetic moment m_z induced in a molecule by a circularly polarized light beam propagating in the z direction through an isotropic medium

$$m_z = \omega^{-1}\xi(\mathbf{E}^\pm \times \dot{\mathbf{E}}^\pm)_z = \mp\frac{1}{2}\,\xi[E^{(0)}]^2 \tag{4}$$

The bulk property $N\omega\xi$, where N is the molecular number density, is proportional to the Verdet constant, which gives the optical rotation induced by a magnetostatic field $B_z^{(0)}$ (*10*). This equivalence can be seen by considering the energy of interaction of an isotropically tumbling molecule with the external fields $\mathbf{E}^\pm$ and $\mathbf{B}^{(0)}$ (*12*)

$$\begin{aligned} \text{energy} &= -\langle m_\alpha\rangle B_\alpha^{(0)} = -\omega^{-1}\langle\xi_{\alpha\beta\gamma}\rangle \\ &\quad E_\beta^\pm\dot{E}_\gamma^\pm B_\alpha^{(0)} = -\omega^{-1}\xi(\mathbf{E}^\pm \times \dot{\mathbf{E}}^\pm)\cdot\mathbf{B}^{(0)} \\ \text{energy} &= -\langle\mu_\alpha\rangle E_\alpha^\pm = -\omega^{-1}\langle\alpha'_{\alpha\beta\gamma}\rangle \\ &\dot{E}_\beta^\pm B_\gamma^{(0)}E_\alpha^\pm = -\omega^{-1}[\alpha'(\mathbf{B})]\,(\mathbf{E}^\pm \times \dot{\mathbf{E}}^\pm)\cdot\mathbf{B}^{(0)} \end{aligned} \tag{5}$$

where $\boldsymbol{\mu}$ is the electric dipole moment and the angular brackets ⟨ ⟩ denote an isotropic average. It follows that $\xi = \alpha'(\mathbf{B})$.

The inverse Faraday effect will produce a bulk magnetic moment and hence induce a net magnetic field in the sample as a whole. This could give rise to bulk shifts in the NMR spectrum, but these are exceedingly small.

We are now in a position to describe the magnetic field $B_z^{(I)}$ induced at nucleus I in a tumbling molecule by a circularly polarized light beam. This field is of the same symmetry as, although independent of, the magnetic moment of the inverse Faraday effect. The induced magnetic field at the nucleus bears a similar relation to the inverse Faraday effect as the nuclear magnetic shielding constant $\boldsymbol{\sigma}^{(I)}$ bears to the magnetizability χ

$$B_z^{(I)} = \omega^{-1}\langle b_{z\beta\gamma}^{(I)}\rangle E_\beta^\pm\dot{E}_\gamma^\pm = \omega^{-1}b^{(I)}\,(\mathbf{E}^\pm \times \dot{\mathbf{E}}^\pm)_z \tag{6}$$

where the scalar $b^{(I)} = \tfrac{1}{6}\varepsilon_{\alpha\beta\gamma}b_{\alpha\beta\gamma}^{(I)}$ is even under *P* and *T* and is therefore a property of all nuclear sites in all molecules; it is not chirally sensitive. Its order of magnitude can be estimated from the experimental value of the Verdet constant through the approximation $b^{(I)} \sim \sigma_p^{(I)}\,\alpha'(\mathbf{B})/\chi_p$, where $\sigma_p^{(I)}$ and χ_p are the paramagnetic contributions to the nuclear magnetic shielding and the magnetizability. The energy of interaction of a nuclear magnetic moment $\mathbf{m}^{(I)}$ with this induced field is

$$\begin{aligned} \text{energy} &= -\,\mathbf{m}^{(I)}\cdot\mathbf{B}^{(I)} \\ &= -\omega^{-1}b^{(I)}\,(\mathbf{E}^\pm \times \dot{\mathbf{E}}^\pm)\cdot\mathbf{m}^{(I)} \end{aligned} \tag{7}$$

This energy can also be expressed in terms of the energy of the electric dipole moment induced in the molecule by the field $\omega^{-1}\dot{\mathbf{E}}^\pm$ in the presence of the distortion of the electronic structure by $\mathbf{m}^{(I)}$

$$\begin{aligned} \text{energy} &= -\langle\mu_\alpha\rangle E_\alpha^\pm = -\omega^{-1}\langle\alpha'_{\alpha\beta\gamma}[\mathbf{m}^{(I)}]\rangle \\ &\quad E_\alpha^\pm\,\dot{E}_\beta^\pm m_\gamma^{(I)} = -\omega^{-1}\alpha'[\mathbf{m}^{(I)}] \\ &\quad (\mathbf{E}^\pm\,\dot{\mathbf{E}}^\pm)\cdot\mathbf{m}^{(I)} \end{aligned} \tag{8}$$

Comparison of Eqs. 7 and 8 shows that $b^{(I)} = \alpha'[\mathbf{m}^{(I)}]$ {the more general equation $b_{\alpha\beta\gamma}^{(I)} = \alpha'_{\alpha\beta\gamma}[\mathbf{m}^{(I)}]$ also holds}.

To obtain a quantum mechanical formula for $b^{(I)}$, one need only replace the magnetic moment operator

$$\hat{\mathbf{m}} = -\frac{e\hbar}{2m_e}\sum_i \mathbf{l}_i$$

in the expression for $\alpha'(\mathbf{B})$ (*7*) by the magnetic field operator

$$\hat{\mathbf{B}}^{(I)} = 2\frac{\mu_0}{4\pi}\frac{e\hbar}{2m_e}\sum_i \frac{\mathbf{l}_i}{r_i^3}$$

where $-e$ is the charge on an electron, $\hbar$ is Planck's constant divided by 2π, m_e is the mass of an electron, $\hbar\mathbf{l}_i$ is the orbital angular momentum, and r_i the distance of electron i relative to nucleus I. The symmetry under *P*, *T*, and C of $b^{(I)}$ is identical to that of $\alpha'(\mathbf{B})$ (they are odd under C). The order of magnitude of $B_z^{(I)}$ in a right circularly polarized laser beam of 10 W/cm² may be estimated assuming 1 debye for the electric dipole matrix elements and $\langle r^{-3}\rangle$ for the $\Sigma_i l_i r_i^{-3}$ matrix element, where $\langle r^{-3}\rangle$ is obtained through the Bohr-Sommerfeld theory (*13*). We find $B_z^{(I)}$ to be of the order of $\pm 10^{-11}$ G for protons, giving a shift $\pm 4 \times 10^{-8}$ Hz. For ^{19}F, the shifts will be on the order of $\pm 10^{-5}$ Hz.

If the laser is tuned to an optical resonance frequency, the enhanced shift can be estimated from the expression for $b^{(I)}$ obtained with the use of the Wigner-Weisskopf lineshape function (*7*). Assuming a half-width of 1000 cm^{-1}, an enhancement of the shift by a factor of ~500 is obtained. If the half-width were 10 cm^{-1}, a resonance enhancement of ~10^6 would be expected.

Because of the magnetization induced in the sample, there will be a mean magnetic field $\mu_0 N\omega^{-1}\xi(\mathbf{E}^\pm \times \dot{\mathbf{E}}^\pm)$, and this will cause a shift of all NMR lines by the same amount. This field strength is estimated to be $\pm 10^{-16}$ G in beams of 10 W/cm² and is far too small to account for the general shift of about 2 Hz shown in figure 2 of (*2*) (10^{-16} G would produce a shift of 4×10^{-13} Hz).

Finally, we provide a physical mechanism that explains the magnetization and magnetic field induced by circularly polarized light. Consider a spherical atom in the electric field $\mathbf{E}^+$ or $\mathbf{E}^-$ of Eq. 1. The electron distribution is distorted at $t = 0$, leading to an induced dipole moment in the x direction. It is simultaneously distorted by the field $\omega^{-1}\dot{E}_y$, which induces a magnetic moment $m_z = -\omega^{-1}G'_{yz}\dot{E}_y$ (*12*); this magnetic moment may be attributed to the differential displacement in the y direction of electrons at $\pm x$ because of their polarization by E_x. This induced atomic magnetic moment retains its magnitude and sign as the phase of $\mathbf{E}^\pm$ changes. It leads in the case of left circularly polarized light to a mean positive electronic angular momentum in the z direction. The associated steady current produces the magnetic moment that comprises the inverse Faraday effect and the effect described here of a local magnetic field at all nuclei.

The shifts caused by the circularly polarized light are small, but they are reversed by a change in the handedness of the light and depend on the optical frequency. Like the familiar chemical shift, they are strongly dependent on the local electronic structure. In addition to the shifts described here, there will be laser-induced structural changes in the fluid of the type that give the optical Kerr effect (*14*); however, in the weak field of a continuous-wave laser, these effects will generally be small compared with those that can be achieved by applying a static electric field.

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Multiplex Spectroscopy: Determining the Transition Moments and Absolute Concentrations of Molecular Species

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A procedure is described that uses two spectroscopic techniques, absorption and infrared degenerate four-wave mixing, in tandem (multiplex) to measure the transition dipole moments and absolute concentrations of molecular species in situ. The method is demonstrated by the measurement of the relative transition moments and concentrations of two dissimilar sample gas components, hydrogen chloride and nitrogen dioxide, but is applicable to a wide variety of molecules and, thus, can provide new information for transient molecular species. Further, difficulties in obtaining quantitative information through techniques such as laser-induced fluorescence, coherent anti-Stokes Raman scattering, and degenerate four-wave mixing spectroscopies can be overcome when a multiplex approach is used.

The direct measurement of the absolute concentrations of transient molecular species has long eluded the scientific community. Numerous laser-based diagnostic techniques [laser-induced fluorescence (LIF), coherent anti-Stokes Raman scattering (CARS), multiphoton ionization (MPI), degenerate four-wave mixing (DFWM), and absorption spectroscopy] have been developed to measure the temperatures, velocities, and spatial and temporal profiles of a number of molecular species. None of these techniques can give us information on the absolute number density of molecular species if the line strengths of the probed transitions cannot be determined separately. Absorption spectroscopy is the only technique commonly used to measure molecular transition line strengths, but its usefulness is limited to stable molecular species that can be held at known pressure in a sample cell. Absorption spectroscopy cannot be used to deduce molecular transition line strengths of transient molecular species for which the absolute concentration cannot be determined. Some coherent optical transient methods, such as transient nutation and photon echoes (*1, 2*), can be used to deduce molecular transition dipole matrix elements, but only if the absolute intensity profile of the probe laser is well known. This inability of the current set of diagnostic probe techniques limits the degree to which chemical systems involving transient species can be understood. Without direct knowledge of the concentrations of transient or free-radical species (which can play pivotal roles in the kinetics and evolution of the chemical system) there is no way to confirm the accuracy of the reaction rates and kinetic models used to describe the chemical system.

The difficulty in measuring either a molecule's transition dipole moment, μ_{21} (or line strength, S_{21}, where $S_{21} \propto |\mu_{21}|^2$) or absolute number density, N, stems from the fact that spectroscopic probe methods generally require both μ_{21} and N in the equations that describe spectroscopic signal generation. In the case of absorption spectroscopy, the light intensity transmitted through an absorbing medium is given by

$$I_a = I_0 \exp\left(\frac{-\Delta N \ell |\mu_{21}|^2 \omega}{2\Gamma_{21} c \hbar \epsilon_0}\right) \tag{1}$$

at the spectral center of the molecular transition (*3*), where ΔN is the effective molecular number density (that is, the population difference between the quantum states connected in the molecular transition), I_0 is the applied laser intensity, Γ_{21} is the coherence decay rate, ω is the resonant field frequency, ℓ is the sample path length, ε_0 is the permittivity of vacuum, c is the speed of light, and $\hbar$ is Planck's constant (h) divided by 2π. Equation 1 involves both S_{21} (or $|\mu_{21}|^2$) and ΔN; consequently, we can never deduce these two quantities by making one measurement. In the case of DFWM spectroscopy (when the applied laser power is low compared to the optical saturation intensity, $I_0 \ll I_{sat}$), the intensity of the signal beam is given by

$$I_s = \left(\frac{2\omega}{\hbar^3 c^2 \epsilon_0{}^2}\right)^2 (\Delta N \ell_0)^2 \left(\frac{|\mu_{21}|^8}{\Gamma_0{}^2 \Gamma_{21}{}^4}\right) I_0{}^2 I_p \tag{2}$$

at line center (*3, 4*), where I_p is the intensity of the probe beam, Γ_0 is the quantum-state population decay rate, and ℓ_0 is the path length sampled by the DFWM process. Again, the spectroscopic signal depends on both μ_{21} and ΔN, and so we can never deduce these two quantities independently by making a single measurement.

It is possible to deduce the values of both μ_{21} and ΔN by implementing these two methods of spectroscopy in tandem (multiplex), either simultaneously or sequentially. The method relies on the fact that these two forms of spectroscopy involve the same quantities but have different functional dependences on the two variables of interest, μ_{21} and ΔN. In this case, Eqs. 1 and 2 can be treated as simultaneous equations and solved to determine both μ_{21} and ΔN separately. In the present work we measure the molecular transition dipole moment and absolute concentration of HCl by the simultaneous recording of infrared (IR) DFWM and absorption spectra. We include NO_2 in the gas sample mixture with HCl to serve as an in situ calibrant. We record the IR DFWM and absorption spectra of the HCl-NO_2 combined gas mixture and deduce the μ_{21} and ΔN values of HCl relative to those of NO_2. This method simplifies the experimental procedure, and Eqs. 1 and 2 give

$$|\mu_{21}|_{HCl} = \sqrt[4]{\frac{R_{DFWM}}{R_{abs}{}^2}} \, \frac{\Gamma_0{}^{HCl}}{\Gamma_0{}^{NO_2}} |\mu_{21}|_{NO_2} \tag{3}$$

and

$$\Delta N_{HCl} = \sqrt{\frac{R_{abs}{}^4}{R_{DFWM}}} \, \frac{\Gamma_0{}^{NO_2}}{\Gamma_0{}^{HCl}} \Delta N_{NO_2} \tag{4}$$

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