Local-field-induced multiple-pulse free-induction decay

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(Received 9 August 1982)

We present recent experimental results on a three-level electron-spin system coupled via dipolar hyperfine interaction with nuclear moments. Anomalous multiple-pulse free-induction decay following rapid passage is observed to provide extremely precise frequency information. Measurements of electronic frequencies (10 GHz) to within multiples of the nuclear Larmor frequency (1 MHz) are made on a crystal with a one-photon inhomogeneous linewidth of 100 MHz in a single-shot experiment of 30 μs duration. The results are interpreted as a novel multilevel double-resonance phenomenon in which intrinsic oscillating nuclear moments, excited by electronic rapid passage, burn holes in the inhomogeneous electron-spin spectrum at multiples of the nuclear Larmor frequency.

Coherent transient-pulse techniques are widely recognized as a valuable probe of resonant systems with frequencies ranging from <1 MHz on into the optical domain. The complexities of the resonant response are sometimes not well understood if accessible states involve many levels or quantum substructure which arises from local field interactions between coupled systems.[1,2] This latter structure forms the basis for electron-nuclear double resonance[3] (ENDOR) (Ref. 3) and is known to be important for broadening and modulation in optical experiments[4–6] as well. In this paper we wish to report striking results obtained by employing coherent excitation of a paramagnetic three-level electron-spin system with intrinsic coupling to nuclear moments to generate local fields which induce correlations between electronic and nuclear precession. These correlations are reflected in subsequent radiation which appears surprisingly as a train of short pulses, spaced at the nuclear period, whose center frequency is defined by a sharp two-photon electron-spin transition. We present an approximate physical model in terms of a novel multilevel double-resonance effect.

Our experiments study $S=1$ Ni^{2+} ions doped at 0.01% concentration into a MgO single crystal containing ^{25}Mg nuclei at 10% natural abundance. The Hamiltonian describing this well-characterized system[7,8] in a strong Zeeman field $H_z\vec{z}$, excited by oscillatory fields $H_1\vec{x}$, and coupled by dipolar magnetic fields to one $I=\frac{5}{2}$ nucleus, can be written[3,9]

$$H_L=\omega S_z-\Delta(S_z^2-1)+\omega_1 S_x 2\cos\omega_0 t -\omega_n I_z+(AI_z+BI_x)S_z . \quad (1)$$

Here $\omega=g\mu_B H_z+\epsilon_L$ and Δ describe the electronic Zeeman and strain-induced splittings, $\omega_1=g\mu_B H_1$ is the Rabi frequency for driven resonant precession, and $\epsilon=\omega-\omega_0$ is the two-photon off-resonance parameter. Nuclei appear in the static Zeeman interaction $-\omega_n I_z$, and a couple to low-frequency electronic magnetic fields through constants A and B which are small compared to ω_n. The line shapes are symmetric distributions with half-widths $\bar{\epsilon}\approx 1$MHz and $\bar{\Delta}\approx 100$ MHz and we rank the terms in H_L as $A,B \ll \omega_n \approx \bar{\epsilon}_L \ll \bar{\Delta}$. The inhomogeneous line shapes, nuclear eigenstates for $\omega_1=0$, and the spectrum of H_L are indicated in Fig. 1.

We observe anomalous signals by employing rapid passage to invert Ni^{2+} spin systems near the broad inhomogeneous Δ line center. The sample is immersed in a liquid-helium—filled rectangular TE_{102} cavity resonant at 9.3 GHz and a large magnetic field is applied to tune the $\Delta m_s=1$ transitions to resonance. A pair of small coils generate sinusoidal magnetic-field pulses of variable amplitude and duration which sweep the spin systems about resonance. Intense microwave pulses are derived from a 2-kW traveling-wave tube (TWT) driven by a quartz-stabilized master oscillator. Free-induction decay and spin-echo signals are observed by amplifying radiation emitted from the cavity with gated low noise TWT's and detecting the intensity or amplitude and phase. Single-shot results are photographed from oscilloscope traces and multiple-shot data is collected with sampling head and boxcar averager.

A typical pulse sequence is shown in Fig. 2 where a sinusoidal magnetic-field pulse is initiated with no

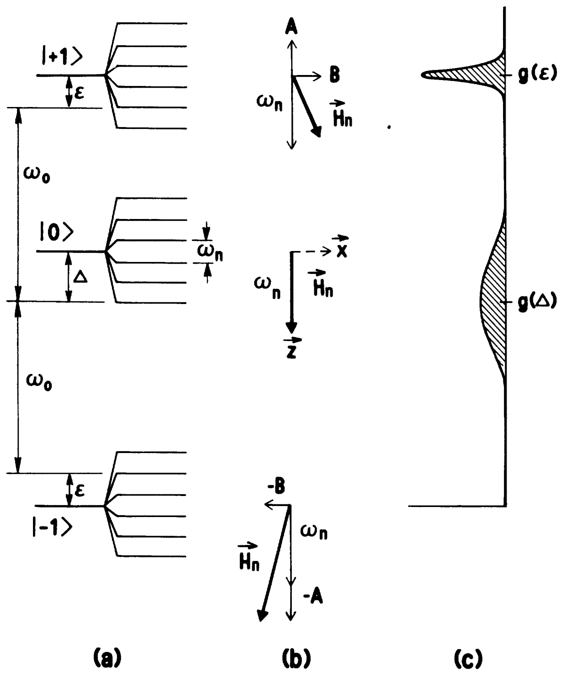

FIG. 1. (a) Energy levels of a weakly coupled $S=1$, $I=\frac{5}{2}$ composite electron-nuclear system. The m_s levels, inhomogeneous broadening parameters ϵ and Δ, and the nuclear substates and splittings are indicated schematically. (b) Effective fields at the nuclei which define the nuclear eigenbasis associated with each m_s level for $\omega_1=0$. (c) The inhomogeneous line-shape functions $g(\epsilon)$ and $g(\Delta)$ which describe the smearing of electronic energy levels by local fields and static-crystalline strains. The scales are exaggerated for clarity.

applied microwave power. At the peak of the field sweep a strong rectangular microwave pulse is applied and terminated 10 μs later when the magnetic field has swept to the opposite side of resonance. The field sweep spans nearly 100 G and $\omega_1 \approx 10$ MHz. When the magnetic field returns to its initial value a pair of short microwave pulses is applied to generate a spin-echo signal in order to monitor the inversion as shown in the lower trace. An unusual transient signal is observed 1.1 μs after the second pulse whose amplitude increases if the first short pulse is removed and vanishes if the passage pulses are absent.[10] The signal therefore represents the effects of the passage pulse which appears in subsequent free-induction decay. Optimizing the sweep field strength and duration and the intensity of the passage microwave pulse we obtain a series of five pulses in the free-induction decay as shown in Fig. 3. The pulse spacing is identical with the period of nearly sinusoidal modulation observed on spin-echo envelopes due to ^{25}Mg nuclei and the intensity is roughly 30 dB below a spin echo observed at 1.1 μs pulse spacing. If the master oscillator frequency is changed by 0.45 MHz the phase of the nth transient changes by $n\pi/2$ allowing the measurement of changes in the master oscillator frequency of <0.1 MHz between single-shot experiments of approximately 30 μs duration. In Fig. 4 we record the peak amplitude of the echo and the peak intensity of the anomalous transient as a function of the applied static magnetic field. The vanishing of dispersive components in the echo pinpoints two-photon reso-

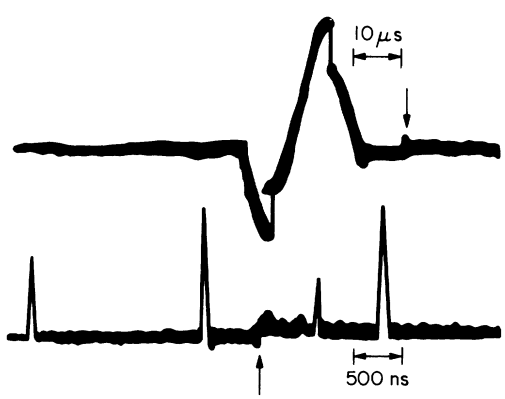

FIG. 2. Experimental pulse sequence. The upper trace represents the sum of the applied sinusoidal magnetic field sweep and the passage microwave pulse which is present between the extremal values of the sweep. The baseline discontinuity after the passage pulse arises from the gating detector. The lower trace shows pulses applied to generate an anomalous transient and a spin echo which appears following the detector gate pulse. These short pulses are not visible on the slower upper trace and the gate (arrow) establishes a common time origin.

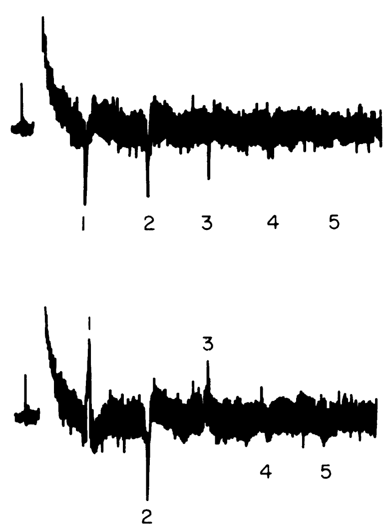

FIG. 3. Multiple free-induction pulses obtained by optimizing passage parameters as described in the text. The large initial transient represents the detector gate and five subsequent pulses are subsequently observed in these multiple-shot oscilloscope photographs.

nance and the narrow response of the transient suggests that multilevel processes are involved.[11]

Optimization of these transients requires correlated adjustments of all the parameters involved in the passage pulses. In brief we find a maximal response at full microwave power with the microwave pulse duration set at 15 μs. The amplitude of the field-sweep pulse is then adjusted to maximize the signals which vanish if this amplitude is altered by $\pm 25\%$. Maximal signals are always obtained by arranging the passage microwave pulse on and off times to coincide with the extrema of the field pulse but this adjustment is not critical. If the microwave power in the passage pulse is reduced from some initial value a smaller field-sweep amplitude is required. Our observations suggest that the important parameters for observing these transients are a substantial passage duration and a value of $\dot{\epsilon}/\omega_1^2 \approx 0.3$ where $\dot{\epsilon} = g\mu_B \dot{H}_z$ is proportional to the sweep-field slew rate. We presume that the constraints on passage duration arise from a compromise between a desirable long interaction time and damping due to relaxation processes but the constraint on $\dot{\epsilon}/\omega_1^2$ requires further consideration.

These observations narrow the range of possibilities which must be considered in identifying the mechanism for multiple-pulse generation. Evidently the precise frequency information displayed in the anomalous transients can reside only in the populations resulting from the passage and only in the spectral range near $\Delta = 0$ where three-level systems are equally spaced. Allowing for transitions between the nonorthogonal nuclear basis states it is immediately seen in Fig. 1(a) that a system with any $\epsilon(t)$ always has equal frequency transitions between $|+,m_I\rangle \leftrightarrow |0,m_I'\rangle \leftrightarrow |-,m_I\rangle$ states, provided that $\Delta = (m_I' - m_I)\omega_n$. If these particular Δ isochromates are saturated, then the inhomogeneous Δ line shape after inversion can be represented by a series of holes spaced at ω_n which should give a free-induction signal of the form observed. It is difficult to understand how such selective saturation can operate since we employ extremely high power pulses for which power broadening would ordinarily prohibit any sharp frequency structure.

We therefore consider the unusual limit where weak nuclear fields perturb eigenstates determined by a strong microwave field which sweeps through electron-spin resonance. We first transform into a rotating frame, with axes x_R and y_R precessing at ω_0 about $\hat{z}$ as shown in Fig. 5, where the microwave field appears static and, in terms of the operators in this frame,

$$H = \epsilon S_z - \Delta(S_z^2 - 1) + \omega_1 S_x - \omega_n I_z + (AI_z + BI_x)S_z . \quad (2)$$

To obtain a zero-order solution we first neglect nuclei and consider isochromats with $\Delta \approx 0$. In this limit $H_0 = \epsilon(t)S_z + \omega_1 S_z$ can be diagonalized with a

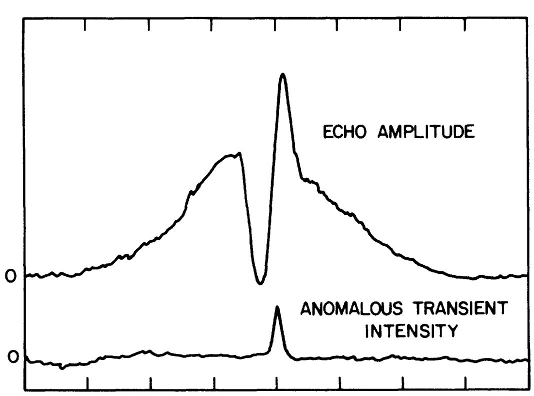

FIG. 4. Static magnetic field dependence of the spin-echo amplitude and the anomalous transient intensity in Fig. 3. The first pulse area and the applied pulse separation are chosen so that two observed transients are of comparable amplitude.

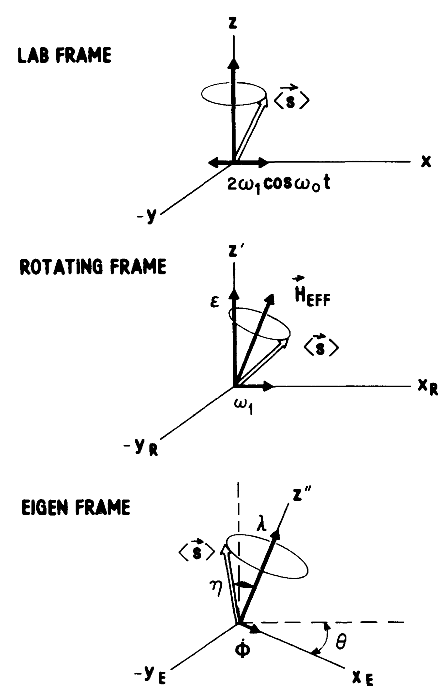

FIG. 5. Transformations employed in the text. Axes rotating at ω_0 about z are chosen to remove the oscillating time dependence of the microwave field and define the rotating frame. To remove the effect of the ϵ sweep a time varying rotation about the x_R axis is made so that H_0 appears stationary.

rotation by $\theta=\tan^{-1}(\omega_1/\epsilon)$ about $\vec{y}_R$. This eigenbasis follows the motion of H_0 during the frequency sweep through a coordinate rotation of x_E and z_E as in Fig. 5 and its density matrix $\tilde{\rho}$ satisfies

$$i\dot{\tilde{\rho}}\cong[\lambda S_z-\dot{\theta}S_y,\tilde{\rho}], \tag{3}$$

where $\lambda=(\epsilon^2+\omega_1^2)^{1/2}$ and $\dot{\theta}=\omega_1\dot{\epsilon}/(\omega_1^2+\epsilon^2)$. For $\dot{\theta}\ll\lambda$ spins adiabatically invert in laboratory and rotating frames but if $\dot{\theta}$ is increased spins partially process as their response time is limited by λ^{-1}. In the eigenbasis we find $\tilde{\rho}(t)=U\rho_0(0)U^{-1}$, with

$$U(t)=e^{-i\eta S_x}e^{-i\psi S_z}e^{i\eta S_x}, \tag{4}$$

describes the motion shown in Fig. 5. Here $\dot{\psi}=\lambda$ is the instantaneous precession frequency and the precession cone half-angle $\eta=\tan^{-1}(\dot{\theta}/\dot{\psi})$ is taken as a constant for simplicity. This model can be approximately corrected to account for the distinct frequencies which arise when Δ is small compared to ω_1 but large compared to ω_n. The secular equation obtained by including Δ in H_0 gives corrected eigenvalues $\lambda_\pm=\pm\lambda+(\Delta/2)\sin^2\theta$, $\lambda_0=\Delta\cos^2\theta$ which are important for a resonance phenomenon and appear in (4) through the replacement

$$\psi S_z\rightarrow\int_0^t\vec{\lambda}(t')dt'.$$

We neglect the small changes in other operators in $U(t)$ which do not alter the resonance frequency but do affect the signal intensity. The resulting expression

$$\tilde{\rho}_0(\Delta,t)=e^{i\eta S_x}e^{-i\Lambda}e^{-i\eta S_x}\rho_0(0)e^{i\eta S_x}e^{i\Lambda}e^{-i\eta S_x} \tag{5}$$

has matrix elements which contain several Fourier components as a consequence of the asymmetry for $\Delta\neq0$ and precession for $\eta\neq0$.

If the electron spin is inverted in a time which contains several nuclear periods we expect that local field changes will excite nuclear precession during passage. We remove this precession by transforming the electron-nuclear portion of H in (2) into a frame where nuclear basis states rotate at ω_n about z and electronic states are quantized along $\vec{H}_{\text{eff}}=\epsilon\hat{z}+\omega_1\hat{x}$ to find an interaction Hamiltonian H'_{en} representing oscillating magnetic fields which react on inverting electron spins:

$$H'_{en}=e^{+i\omega_n I_z t}(AI_z+BI_x)\times e^{-i\omega_n I_z t}(S_z\cos\theta+S_x\sin\theta). \tag{6}$$

The density matrix must now include nuclear indices and $\tilde{\rho}_0(m_I,m_I)$ is taken to be $\tilde{\rho}\delta m_I m_I$ by neglecting small nuclear population differences. Setting $\tilde{\rho}=\tilde{\rho}_0+\Delta\rho$ gives to first order

$$i\Delta\dot{\rho}-[\vec{\lambda},\Delta\rho]=[H'_{en},\tilde{\rho}_0]. \tag{7}$$

The structure of (7) describes three well-separated levels coupled to driving terms arising from H'_{en} and $\tilde{\rho}_0$. Simultaneous electron-nuclear excitation involves off-diagonal elements of H'_{en} which are maximal on resonance where $\epsilon=\theta=0$. As eigenvalues and matrix elements are both stationary here we restrict our attention to this portion of the sweep. A double resonance will appear in (7) for $\Delta\rho_{ij}$ provided $\lambda_i-\lambda_j$ matches a Fourier component in the driving term.[12] Substituting (5) and (6) into (7), isolating the time-dependent exponentials involving λ_i and ω_n, and considering the well-separated eigenvalues we find resonant coupling only if $(\lambda_+-\lambda_0)-(\lambda_0-\lambda_-)=\Delta=\pm\omega_n$ so that these two driven electronic transitions differ in frequency by the nuclear splitting. Isolating the appropriate term in (7) we find, for $\Delta=\omega_n$,

$$i\frac{d}{dt}(\Delta\rho_{+0}e^{-i(\lambda_+-\lambda_0)t})\approx\frac{B}{\sqrt{2}}I_+[S_x,e^{i\eta S_x}|0\rangle\langle0|e^{-i\eta S_x}\tilde{\rho}_0(0)e^{+i\eta S_x}|-\rangle\langle-|e^{-i\eta S_x}]_{+0}. \tag{8}$$

A similar result is obtained for $\Delta\rho_{0-}$ but $\Delta\dot{\rho}_{+-}=\Delta\dot{\rho}_{ii}=0$. Evidently, oscillating nuclear fields can selectively cross couple the unequally spaced levels and produce density matrix elements which are off-diagonal with respect to both I_z and S_z. The resonant coupling derives from a secular term which creates an off-diagonal $\Delta\rho$ through a combined electron-nuclear spin flip acting on resonant Fourier components of $(\tilde{\rho}(t))_{00}$ and $(\tilde{\rho}(t))_{+-}$. To obtain a crude numerical estimate we use (5), with $\eta<1$ and $\tilde{\rho}_0(0)=-S_z$, to estimate the driving term as $B\eta^2$.[13] For $\theta<\psi$ we find $\eta\approx\dot{\epsilon}/\omega_1^2$ which suggests that the precessing components generated for $\eta\neq0$ do account for experimentally observed relationships between optimal sweep amplitude and duration and microwave pulse power. Since the perturbation is weak we interpret (8) as a saturation term operating during inversion for specific isochromats within the Δ line shape.[14] If other terms in (6) are considered, then the $\Delta m_I=\pm1$ selection rule does not hold and saturation processes can burn holes for integral $|\Delta/\omega_n|<2I$. If the holes are of comparable depth one expects a train of pulses at the nuclear period, centered in frequency about $\epsilon=0$, and with individual durations equal to the inverse spectral range of excitation. The overall duration of the train reflects the inverse width of individual holes, roughly, $B\eta^2 \ll \omega_n$, and the sharp $\bar{\epsilon}_L$ distribution allows observation of the long-lived free-induction signals. Estimating the interaction time as a few nuclear periods and using the experimental value $\eta \approx 0.3$ we find the strength of saturation is roughly $0.1\ B/\omega_n$ for the $\Delta m_I = \pm 1$ transitions. If $B/\omega_n \approx 0.1$, which implies nominal 300 G electronic fields at the nuclei, then we expect narrow shallow holes which should yield signals about 40 dB below comparable spin-echo amplitudes. Although we do not understand the apparent strength of $|\Delta m_I| > 1$ transitions this model does justify the sharp magnetic field dependence, unusual procedures required to optimize signals, and the precise frequency information observed.

A physical insight into these results can be obtained by examining (5) and (7) in more familiar cases. If $\eta=0$ so that passage is completely adiabatic, then $\tilde{\rho}_0$ is static and the only possible resonance occurs when a frequency in H'_{en} matches an energy-level separation $\lambda_i - \lambda_j$. This case describes a normal rotary resonance.[3] If $\eta \neq 0$, but only two levels are considered, then $\tilde{\rho}_0$ has components which oscillate at $\lambda_1 - \lambda_2$; but these can only lead to secular terms in (7) if H'_{en} is static, thereby correctly implying that the system is off-resonance. The new feature of (7) for multilevel systems prepared as mixed states, $\eta \neq 0$, is that resonances can appear if frequencies in H'_{en} match the difference in frequency of electronic precession associated with pairs of levels. The special form of H'_{en} is not necessary for this to occur as nuclear variables need not be involved. This coupling is not a simple effect of the two-photon transition but the sharp ϵ_L distribution in our experimental system is necessary in order to observe the long free-induction signals which would otherwise be rapidly damped by inhomogeneous broadening, even if sharp structure in the Δ line shape is present. During the passage sequence the ϵ_L distribution is not important provided the sweep rate is constant, ϵ_L can then affect the time at which resonance is reached but not the final state of the populations.

These manifestations of coupled-system dynamics may be observable in other materials since most three-level systems with disparate transition frequencies and driving fields (ω_1) can be put in similar form if two near-resonant fields are used. Magnetic interactions are not specifically necessary as the results obtained here seem to require only a set of periodic sublevels which admix differently within individual three-level manifolds together with an excitation which can mix the Fourier responses of the manifolds. It then appears possible that similar techniques may be interesting in the optical range where Doppler-free techniques give sharp two-photon linewidths in gases. Alternatively one may employ two closely spaced states as termini of the two-photon transition with the intermediate state separated by an optical frequency. Indeed it might be useful to have magnetically tunable systems with which one can beat stable coherent lasers directly against nuclear precession to high precision.

The work at Berkeley was supported by the Division of Materials Research, National Science Foundation and was performed by one of us (R.J.W.) in partial fulfillment of the requirements for the Ph. D. degree at the University of California at Berkeley.

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[13]It should be noted that the special form of (5) is not essential. In fact neglected admixtures may enhance the response for $\Delta \neq 0$. The form of the eigenvalues near $\epsilon \neq 0$ is crucial and the parameter $\dot{\theta}$ must enter to generate electronic precession.

[14]This interpretation is rigorous if nuclear population differences are negligible within m_s manifolds. Since $\mathrm{Tr}(\Delta\rho\vec{S})=\mathrm{Tr}(\Delta\rho\vec{I})=0$, $\Delta\rho$ represents correlations which cannot radiate at either electronic or nuclear frequencies and therefore simulates saturation in our measurements.