Two-photon transient phenomena*

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(Received 14 March 1977)

The first observations of two-photon free-precession and driven transient coherence by Hatanaka *et al.* are extended by an experimental NMR verification of the Brewer-Hahn exact solutions for two-photon resonance.

From a set of Bloch-like equations for a three-level system, Brewer and Hahn[1(a)] (BH) have obtained exact resonant transient solutions for the interpretation of pulsed optical coherence experiments.[1(b)] Radio-frequency transient NMR studies provide superior experimental control of quantitative tests of the BH predictions. Three-level NMR experiments can display identical principles of two-photon dynamics which are applicable to optical studies, as long as propagation considerations are not important. We report here the first demonstrations of exact BH two-photon transient solutions at resonance, in terms of transient NMR. These solutions are applicable as well to a two-photon optical experiment which was reported[2] after NMR observations of two-photon coherence by Hatanaka *et al.*[3]

In a three-level system [see Fig. 1(a)] with forbidden single-photon transitions between levels 1 and 2, it is possible to excite two-photon transitions between levels 1 and 2 using the off-resonant level 3 as the intermediate state. Large enough pulse excitations during times short compared to the transverse damping time T_2 permit the observation of coherent effects. The three-level system is described by a density matrix which obeys the normal Liouville equation

$$i\hbar\dot{\rho} = [\mathcal{H}_0 + \mathcal{H}_1, \rho], \tag{1}$$

where $\mathcal{H}_0$ is the Hamiltonian in the absence of the time-dependent perturbation $\mathcal{H}_1 = -\vec{\mu}\cdot\vec{H}$. The applied time-dependent field is[4] $H = 2H_1\cos\omega t$, and μ is the dipole operator. The BH exact solution applies where the sum of the energies of the two photons is equal to the energy splitting between levels 1 and 2, namely $2\hbar\omega = \omega_{21}$ where $\omega_{ij} = (E_i - E_j)/\hbar$. Bloch-like solutions can be defined in terms of the following linear combinations of density matrix elements:

$$u_{ij} = \tilde{\rho}_{ij} + \tilde{\rho}_{ji},$$
$$iv_{ij} = \tilde{\rho}_{ij} - \tilde{\rho}_{ji}, \tag{2}$$
$$w_{ij} = \rho_{ii} - \rho_{jj}.$$

The i and j indices apply to states 1, 2, and 3. Here the $\tilde{\rho}_{ij}$ are components of the density matrix with the rapidly oscillating factors of the off-diagonal elements removed. Reference 1(a) gives solutions for w_{12}. The quantities measured in this experiment are w_{13}, w_{32}, the population differences between states 1 and 3, and 3 and 2, respectively. These quantities which can be derived algebraically using the solutions from Ref. 1(a), are

$$w_{13}(t) = \frac{\alpha^2\beta^2 w_{12}(0)}{\delta(\alpha^2+\beta^2)}\left\{\frac{\cos(\delta-\tfrac{1}{2}\Delta)t-1}{(\delta-\tfrac{1}{2}\Delta)} + \frac{\cos(\delta+\tfrac{1}{2}\Delta)t-1}{(\delta+\tfrac{1}{2}\Delta)}\right\} + \frac{K\epsilon(2\alpha^2+\beta^2)}{\alpha^2+\beta^2}(\cos\gamma t - 1) + w_{13}(0), \tag{3}$$

$$w_{32}(t) = \frac{\alpha^2\beta^2 w_{12}(0)}{\delta(\alpha^2+\beta^2)}\left\{\frac{\cos(\delta-\tfrac{1}{2}\Delta)t-1}{(\delta-\tfrac{1}{2}\Delta)} + \frac{\cos(\delta+\tfrac{1}{2}\delta)t-1}{(\delta+\tfrac{1}{2}\Delta)}\right\} - \frac{K\epsilon(2\beta^2+\alpha^2)}{\alpha^2+\beta^2}(\cos\gamma t - 1) + w_{32}(0), \tag{4}$$

with $\alpha = \mu_{13}H_1/\hbar$, and $\beta = \mu_{23}H_1/\hbar$. Here $\langle i|\mu|j\rangle = \mu_{ij}$ are the magnetic dipole matrix elements. Following Ref. 1(a), we have defined the following quantities:

$$\epsilon = 2(\alpha^2+\beta^2)^{1/2}, \quad \Delta = \omega - \omega_{31} = \omega_{23} - \omega$$
$$\delta = (\alpha^2+\beta^2+\Delta^2/4)^{1/2}, \quad \gamma = 2\delta,$$
$$K = \frac{2[\alpha^2 w_{13}(0) - \beta^2 w_{32}(0)]}{\epsilon\gamma^2}.$$

The physical significance of these solutions can be viewed as follows. The slowly varying components which involve $\cos(\delta - \frac{1}{2}\Delta)t$ pertain to the pure two-photon oscillations in the limit that $\alpha^2+\beta^2 \ll \Delta^2$. In this limit the two-photon rotating-frame radio frequency stands out as $\omega_{\text{eff}} = 2\alpha\beta/\Delta$. Smaller amplitude [to order $(\alpha^2+\beta^2)/\Delta^2 \ll 1$] and rapidly oscillating single-photon transitions (at frequency $\sim\Delta$ in the rotating frame) modulate the main two-photon oscillation amplitude. In the extreme condition of $\alpha^2+\beta^2 \ll \Delta^2$ the effect of one-photon oscillations may be neglected by setting $\dot{u}_{13} = \dot{u}_{32} = \dot{v}_{13} = \dot{v}_{32}$

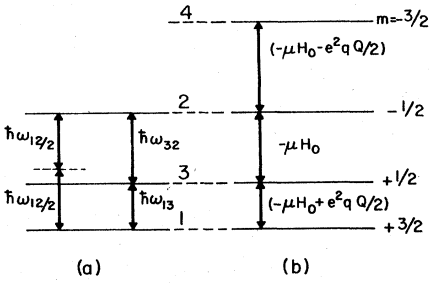

FIG. 1. (a) Energy-level diagram for theoretical treatment. (b) Energy-level diagram for Na^{23} nuclei. H_0 is the static magnetic field, and $\frac{1}{2}e^2qQ$ is the quadrupole splitting.

$=0$. If we assume as well a slight off-resonance two-photon condition $2\omega-\omega_{21}=\xi\ll\Delta$, a set of two-photon Bloch equations may be written as follows[5]:

$$\dot{u}_{12}-\left(\xi+\frac{\alpha^2-\beta^2}{\Delta}\right)v_{12}=0\,,$$

$$\dot{v}_{12}+\left(\xi+\frac{\alpha^2-\beta^2}{\Delta}\right)u_{12}-\frac{2\alpha\beta}{\Delta}w_{12}=0\,, \tag{5}$$

$$\dot{w}_{12}+\frac{2\alpha\beta}{\Delta}v_{12}=0\,.$$

These equations are unique in exposing the saturation-dependent off-resonance term $(\alpha^2-\beta^2)/\Delta$. This term identifies with the saturation dependent Stark shift $\Delta\nu=(\alpha^2-\beta^2)\Delta/(\Delta^2+1/T_2^2)$, obtained[1(a)] by BH when taken in the limit that the transverse damping time $T_2=\infty$, which we assume here. Note that the terms involving $\cos\gamma t$ in Eqs. (3) and (4) depend upon the finite difference $\alpha^2-\beta^2$ of transition rates between levels 1 ↔ 3 and 3 ↔ 2, just as does the saturation-dependent frequency shift. If α or β are zero, the $\cos\gamma t$ terms reduce to the normal off-resonant single-photon rate terms.

The transitions studied in this experiment are those of the Na^{23} nucleus ($I=\frac{3}{2}$) in a single crystal of $NaNO_3$ [see Fig. 1(b)]. All Na sites are identical, with an electric field gradient present at these sites. The symmetry axis of the field gradient is aligned along a 10-kG external magnetic field. For this crystal orientation the nucleus states will be pure eigenstates of the Zeeman Hamiltonian. The Zeeman splitting is about 11 MHz. The four levels are shifted by the quadrupole interaction ($e^2qQ=338$ kHz). Three angular transition frequencies therefore obtain, given by values of γH_0 and $\gamma H_0\pm\frac{1}{2}e^2Qq$. Each transition has a $1/e$ decay time of 280 μs, which corresponds to a linewidth of about 1 kHz. The central line has been reported by Andrews *et al.*[6] to have a linewidth of 1.2 kHz in a single crystal.

The $NaNO_3$ single crystal is placed inside the single coil of a pulsed NMR spectrometer. A low-Q coil allows all three transitions to be excited and examined without retuning of the coil or transmitter. The selectively excited levels $+\frac{3}{2}$, $+\frac{1}{2}$, and $-\frac{1}{2}$ of the sodium nucleus are labeled 1, 3, and 2, respectively, by our previous definitions. One can monitor the population differences w_{13} and w_{32} independently after a two-photon excitation at $\frac{1}{2}\hbar\omega_{12}$. The precise condition $\omega=\frac{1}{2}|\omega_{12}|$ is established from independent measurements of one-photon resonances at ω_{13} and ω_{32}, giving $\omega_{12}=\omega_{13}+\omega_{32}$. The population difference w_{42} can be monitored to make certain the $m=-\frac{3}{2}$ level is not excited and does not affect the results. Figure 2 depicts the pulse sequence used in the experiment. A pulse of frequency $\omega=\frac{1}{2}\omega_{12}$ is applied for a variable time. After a time t ($t\gg T_2$ to allow damping of the off-diagonal components) a $\frac{1}{2}\pi$ pulse is applied on-resonance for an allowed single-photon transition. The first pulse induces the transitions to be examined. The second pulse (of frequency ω_{ij}) monitors the population differences w_{ij}.

The results of the experiment for w_{32} are shown in Fig. 3. To obtain a value of H_1 accurate enough to test the theory, H_1 was determined from the

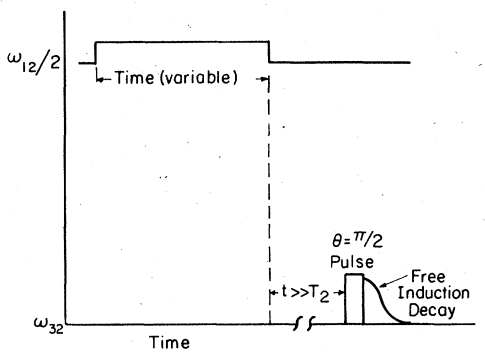

FIG. 2. Pulse sequence for the measurement of $w_{32}(t)$.

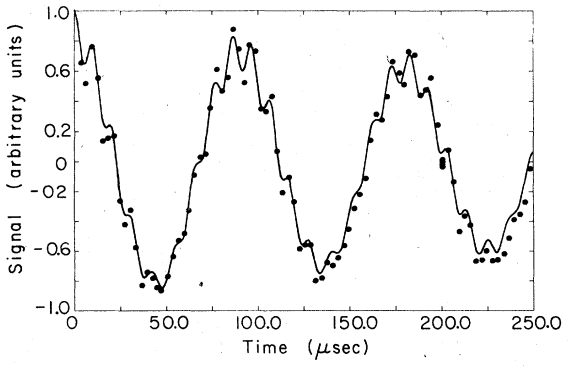

FIG. 3. Plotted experimental values of w_{32} (dots). The solid curve is the theoretical prediction for w_{32} [Eq. (4)] with damping added.

TABLE I. Fourier transformed data of Fig. 3 compared to the predictions of the theory for H_1 fitted to be 21.1 ± 0.4 G. Δ was measured independently to be 82.2 ± 0.2 Hz. The 2.3-kHz difference from $\frac{1}{4}e^2qQ$ results from the slight crystal misorientation mentioned in the text.

	Theoretical	Experimental
$\delta - \frac{1}{2}\Delta$ (kHz)	Fitted	11.1 ± 0.2
$\delta + \frac{1}{2}\Delta$ (kHz)	93.2	92.9 ± 0.9
γ (kHz)	104.2	103.3 ± 1.0
Amplitude of $\delta - \frac{1}{2}\Delta$ oscillation	0.887	0.898 ± 0.02
Amplitude of $\delta + \frac{1}{2}\Delta$ oscillation	0.105	0.084 ± 0.02
Amplitude of Δ oscillation	0.041	0.068 ± 0.02

frequency of the slow oscillation. Using only the oscillation peaks an experimentally measured value of $T_2 = 563$ μs was fitted to a decay envelope of the form e^{-t/T_2}. Examination of the data justifies this assumption for times to at least 1000 μs: four times larger than the 250 μs displayed in Fig. 3. However, for short times there is a small discrepancy which can be seen in the figure. The only other quantity (Δ) necessary to describe the system could be deduced from the measured level separation. Table I displays the theoretical values [Eq. (4)] and the values obtained from taking the cosine Fourier transform of the experimental data. Mixing effects due to a crystal misorientation of 6° affect the results negligibly. The rise time of the pulse envelope was about 2 μs. A slower rise time caused the single-photon oscillations to vanish due to adiabatic following by the single-photon off-resonant transition.[7] For a much faster rise time the fourth level would have been excited. Investigations of the w_{42} indicate that with the 2 μs rise time, the contributions from level 4 are negligible.

We have confirmed the particular BH solutions above which derive from a set of three-level Bloch equations[1] applicable to other types of experiments as well. A deuterium ($I = 1$) NMR chemical-shift measurement technique,[8] which was interpreted in terms of an operator method,[8] can be analyzed alternatively in terms of the macroscopic three-level BH Bloch equations. In a single crystal of $NaNO_3$ we have obtained additional two-photon effects of spin locking, adiabatic fast passage, rotary saturation, and rotary echoes which are amenable to analysis by the BH equations. A more systematic and detailed examination of these effects will be reported at a later date.

ACKNOWLEDGMENTS

We gratefully acknowledge illuminating discussions with Professor A. Pines and Dr. S. Vega. We also thank Dr. P. J. Herley and Dr. P. W. Levy from the solid-state group of the physics department at Brookhaven National Laboratory for supplying us a single crystal of sodium nitrate.

*Supported by the National Science Foundation through the Division of Materials Research.

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[4]The notation has been chosen to be the same as that of Ref. 1(a), with the following exception appropriate to NMR. In NMR notation it is conventional to define the linear time-dependent field $H = 2H\cos\omega t$. In Ref. 1(a) the analogous quantity is $E_x = \frac{1}{2}E_0 e^{i(\omega t - kz)} + \text{c.c.}$ If $2H_1$ is substituted for E_0, all results will be compatible.

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[7]For pulse rise times that are adiabatic with respect to the single-photon resonances the vector model of Grischkowsky, Loy, and Liao (see Ref. 5) will be valid. The vector model predicts only the slowly varying large amplitude oscillation will be present.

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