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Second-harmonic free-induction decay in a two-level spin system

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Two-photon free-induction decay (FID) was experimentally investigated in a two-level electron-spin system by revealing the second-harmonic wave emitted by the system. Oscillatory FID signals were detected for large-area pulses of the input power, analogously to recent observations by Kunitomo *et al.* for single-quantum resonances. Moreover, the measured decay time of the FID signal following a steady-state preparation was found to be larger than the theoretical value by a few orders of magnitude.

A free-induction decay (FID) emission occurs whenever the resonant interaction between a physical system and an external radiation is abruptly switched off at $t=t_0$, e.g., by turning off the radiation. The FID emission originates in the coherent superposition of the states of the system, induced by the resonant EM field during the preparative stage ($t < t_0$); at $t > t_0$, these coherences outlast the input radiation for a time of the order of the dephasing time T_2 and result in an oscillating macroscopic polarization which radiates at the atomic transition frequency. Since its first detection in nuclear-spin systems,[1] the FID effect has been extensively investigated in a large variety of physical systems in many regions of the EM spectrum.

Recent progress in the study of FID has led to the observation of two new effects. The former is the FID signal originating in the coherent states induced by two-photon (TP) absorption processes in multilevel systems.[2-5] The latter is the appearance of large-amplitude oscillations in the FID signal of an inhomogeneous system coherently prepared by a radiation pulse with duration $t_0 << T_2$; this effect was predicted by Schenzle, Wong, and Brewer[6] and has been observed very recently in the single-quantum transitions of nuclear-spin[7] and atomic[8] systems.

In this Communication we are concerned with the FID signals that arise from the coherent states induced by TP transitions and, in particular, with their oscillatory behavior. Unlike the TP-FID experiments aforementioned,[2-5] the system considered here is a two-level (pure $S=\frac{1}{2}$) electron-spin system resonating at microwave frequency. As discussed below, in this case the time decay of the TP coherences after switching off the input power may be measured by detecting the radiation that the system emits at $t > t_0$ at the second-harmonic (SH) frequency (hereafter this signal will be referred to as SH-FID). In the following we report experimental results on the SH-FID ensuing from (a) a coherent-pulse preparation ($t_0 \lesssim T_2$) and (b) a steady-state preparation ($t_0 >> T_2$). In the former case (a) we detected oscillatory SH-FID signals for input power pulses long enough; to our knowledge, oscillatory TP-FID signals have not been reported heretofore. In the latter case (b) our experimental curves of the SH-FID agree with the expected ones only qualitatively, because of an order-of-magnitude discrepancy between the experimental and the theoretical value of the decay time.

To outline our experiments, we recall that if a two-level system with energy separation $h\nu_0$ is driven by an EM field, TP transitions between the two levels can take place provided that the frequency ν and the polarization of the field fulfill the energy-conservation condition ($\nu_0=2\nu$) and the angular momentum selection rules.[9] In the case of a pure $S=\frac{1}{2}$ system with energy levels split by a static field $\vec{H}_0$, the latter condition requires that the microwave magnetic field $\vec{H}_1$ has both a longitudinal and a transverse component in a reference frame with $\hat{z} \parallel \vec{H}_0$. As known,[10,11] the TP transitions between the states $|m_s=\pm\frac{1}{2}\rangle$ induce a coherent superposition of the spin states eventually counteracted by the relaxation interactions; since the magnetic dipole moment has a nonvanishing matrix element between the two states, these coherences result in a macroscopic transverse magnetization $M_\perp^{2\omega}(t)$ oscillating at the SH frequency whose amplitude has a resonant maximum at $\nu_0=2\nu$. In the experiments described below the system is selectively coupled both to a ν mode and to a 2ν mode of the EM field by means of a bimodal cavity. The system is coherently prepared by a squared pulse ($0 < t < t_0$) of intense and properly polarized radiation tuned to the TP resonance; at $t > t_0$, the time evolution of the TP coherences is monitored by revealing the time-dependent intensity of the radiation that $M_\perp^{2\omega}(t)$ emits into the 2ν mode of the cavity.

The measurements reported here were taken in a system of E_1' centers in glassy silica,[12] obtained by γ-ray irradiation of a Suprasil quartz in a ^{60}Co source with a dose intensity of 5×10^5 R/h at room temperature. The concentration of E_1' defects was estimated to be about 10^{17} cm^{-3} on the basis of the total γ-ray dose of 10^3 Mrad. E_1' centers have $S=\frac{1}{2}$; in glassy silica they are characterized by a highly inhomogeneous line (with a peak-to-peak distance of 2 G in the electron-spin-resonance spectrum) and by very long spin-spin (T_2) and spin-lattice (T_1) relaxation times: we measured $T_2=37$ μsec and $T_1=0.1$ sec at 4.2 K and at $H_0=2$ kG in our sample.

In our experimental apparatus a bimodel cavity resonating both at $\nu=3.0$ GHz and at $2\nu=6.0$ GHz was used to excite and to detect the SH-FID signal. The sample was located in a point of the cavity where the magnetic fields of both modes are maxima. During the preparative stage, the ν mode was fed by a squared pulse of microwave power (typically $P\simeq10$ W) at 3.0 GHz lasting a time t_0, adjustable in the range 1.0 μsec to 10 msec; the distance between successive pulses was kept long enough (>2 sec) in order to allow complete thermal relaxation of the spin system. In order to get the input power pulse, the output signal of a cw low-power source was pulse shaped and then amplified by means of a travelling-wave tube; switching times shorter than 0.5 μsec were usually obtained. The SH radiation emitted by the sample into the harmonic mode of the cavity was detected by a superheterodyne receiver with the local oscillator tuned to $\nu_{LO}=2\nu \pm 30$ MHz; the receiver could be gated at $t > t_0$ in order to isolate the SH-FID signal. A home-built microprocessor-controlled signal averager was used to improve the signal-to-noise ratio and a microwave amplifier was occasionally inserted in the output line of the cavity. The sensitivity and accuracy of the overall receiver setup were estimated to be -100 dBm and ± 0.5 dB, respectively. We refer to Ref. 13 for further details of our transient SH spectrometer.

A SH signal at $t > t_0$ was detected when the field $\vec{H}_0$ was adjusted to fulfill the TP resonance condition $\nu_0 = 2\nu$, namely, $H_0 = 4\pi\nu/\gamma$, where γ is the gyromagnetic ratio. $\vec{H}_0$ was oriented at an angle $\alpha = 45°$ with respect to the direction of the input microwave field $\vec{H}_1$ at the sample position; as known, this orientation maximizes the TP transition probability $W_{TP} = T_2[\gamma H_1^2 \sin(2\alpha)/2H_0]^2$ for $S=\frac{1}{2}$ spin systems.[14] The appearance of a SH signal at $t > t_0$ only very near the resonance $\nu_0 = 2\nu$, its dependence on the angle α, and the switching time (< 0.5 μsec) of the input power pulse were carefully checked in order to rule out the possibility that the SH signal at $t > t_0$ could be caused by the trailing edge of the input pulse through a parasitic coupling between the two modes of the cavity. Moreover, we note that higher (even) harmonics of the magnetization can be expected to build up in the sample as a consequence of higher-order multiphoton processes which may occur at $\nu_0 = 2\nu$; however, these effects can be disregarded in our experimental conditions since they are far off resonance from the cavity modes and from the receiver system.

All the measurements reported here were taken at 4.2 K and at the center of the TP resonance line.

(a) Coherent-pulse preparation. Oscillatory behavior of the SH-FID signals was observed when the conditions $t_0 \lesssim T_2$ and $\theta > 2\pi$ were fulfilled; here θ is the (generalized) pulse area, defined as $\theta = 2\pi(t_0/T)$, where T is the nutational period of the TP resonance. In our experimental setup, T could be easily measured by monitoring the nutations of the SH intensity[15] emitted by the spin system during the exciting pulse ($0 < t < t_0$).

A typical experimental curve of the SH-FID signal following a coherent-pulse preparation is reported in Fig. 1(a): in particular, this curve was recorded at the maximum input power level ($P = 20$ W) and with a pulse duration $t_0 = 12.5$ μsec, corresponding to a pulse area $\theta = 5.0\pi$. As shown, the SH-FID signal starts at $t = t_0$ from a low value $I(t_0)$, rapidly increases to a maximum, and then decays passing through a few maxima and minima.

At the maximum available power level, oscillatory decay curves were observed for any value of t_0 within the range $5.0 < t_0 < 30$ μsec ($2\pi < \theta < 12\pi$). The disappearance of the oscillations for larger pulse areas is to be related to the breach of the coherent-excitation condition $t_0 << T_2$. The initial value $I(t_0)$ was observed to depend on θ, being maximum for $\theta = (n + \frac{1}{4})\pi$ ($n = 1, 2, \ldots$) and minimum for $\theta = (n - \frac{1}{4})\pi$ ($n = 2, 3, \ldots$). Moreover, for any value of θ, the SH-FID signal was found to last a time $t_{FID} \lesssim t_0$, in agreement with a general theorem on the coherent transients.[16]

On the basis of the above properties and analogously to the single-quantum case,[6-8] we may relate the oscillations of the SH-FID signal to the sidebands created by the TP nutations of the nonresonant packets of the inhomogeneous line. This interpretation is also supported by the comparison of our experimental curves with the corresponding

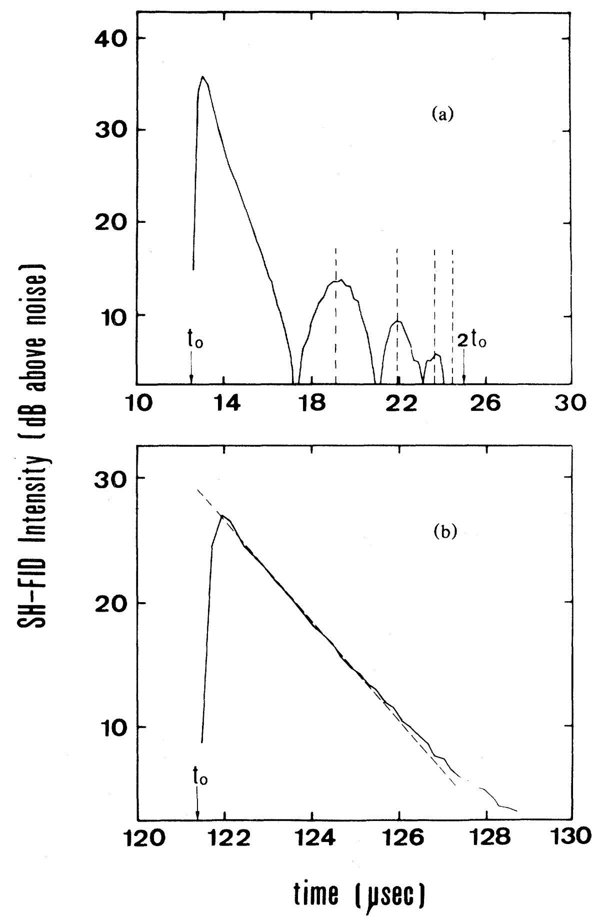

FIG. 1. Time dependence of the SH-FID signal detected at the center of the DQ (double quantum) resonance line after (a) a coherent-pulse preparation ($P = 20$ W, $t_0 = 12.5$ μsec, $T = 50$ μsec), and (b) a steady-state preparation ($P = 5.7$ W, $t_0 = 121.5$ μsec, $T = 17.4$ μsec). In (a) dashed lines show the expected positions of the maxima, and the instants $t = t_0$ and $t = 2t_0$ are also indicated. In (b) the dashed line is the exponential function with decay time $\tau_d = 2.2$ μsec, that best fits the experimental curve.

ones (equal pulse area) calculated for the single-quantum case.[6,7] In particular, in Fig. 1(a) dashed lines show the expected positions of the SH-FID maxima, as obtained by generalizing the curves of Refs. 6 and 7 to the TP resonance case and by allowing for our power (squared amplitude) detection. As shown, the agreement is fair for the observed maxima; the absence of the last maximum in the experimental curve may be ascribed to the signal-to-noise ratio and perhaps to the fact that the coherence condition $t_0 << T_2$ is only approximately fulfilled in our experimental conditions.

(b) Steady-state preparation. As the duration t_0 of the preparative stage was increased over T_2, the oscillations of Fig. 1(a) disappeared and the SH-FID signal was observed to decay by following a monotonic exponential law. For $t_0 \gtrsim 50$ μsec, the properties of the SH-FID signal were found to depend only on the power level of the input pulse and not on its length t_0, at least up to the maximum available pulse length $t_0 \simeq 10$ msec.

In Fig. 1(b) we report a typical experimental curve of the

SH-FID signal following a steady-state preparation of the system. This curve was recorded after a pulse of input power $P = 5.7$ W lasting a time $t = 121$ μsec; at this power level a nutational period $T = 17.4$ μsec was measured. As shown, the SH-FID signal starts from a very low value, reaches a maximum in a very short time τ_r ($\lesssim 0.2$ μsec), and then decays exponentially to zero with a characteristic time $\tau_d = 2.2$ μsec. Accurate measurements of τ_r were not possible owing to the limited time resolution of our receiver system. The decay time τ_d was measured to increase on decreasing the input power level.

The time dependence of the SH-FID signal in Fig. 1(b) is similar to the ones observed and analyzed theoretically, in connection with single-quantum transitions[6,17–20] and TP transitions in multilevel systems.[3,5] According to those works, the time evolution of the steady-state FID signal is affected to a large extent by the inhomogeneous nature of the resonance line, which enriches the FID signal with the contributions coming from the off-resonance packets; in particular, the initial fast rise and the presence of a maximum were shown to occur when the dispersion component dominates over the absorption one.[18]

According to the steady-state FID theories, carried out both for single-quantum and for TP transitions, τ_d is given by

$$\tau_d = T_2[1 + (1 + \beta^2 T_1 T_2)^{1/2}]^{-1} \quad , \tag{1}$$

where $\beta = 2\pi/T$ is the nutation frequency.[5,6,18–20] Here we wish to compare our experimental results on the power dependence of τ_d with Eq. (1). To this aim, τ_d and T were measured at various input power levels and the experimental points were arranged in the plot of Fig. 2, where the quantity $\eta = [(T_2/\tau_d - 1)^2 - 1]$ is plotted versus T. This kind of plot is convenient since, according to Eq. (1), η is expected to follow a simple power law: $\eta = K/T^2$ with $K = 4\pi^2 T_1 T_2$. As shown in Fig. 2, an inverse square law fits quite well the experimental points in the whole investigated range of the input power. However, the value of K that best fits the experimental points was determined to be $K_{\rm expt} = 7.5 \times 10^{-8}$ sec^2, to be compared with the value $K_{\rm theor} = 1.46 \times 10^{-4}$ sec^2 expected on the basis of Eq. (1) and the measured values of T_1 and T_2. The disagreement is striking; in fact, in our experimental conditions ($\beta^2 T_1 T_2 >> 1$), Eq. (1) predicts a decay time $\tau_d \simeq (T/2\pi)\sqrt{T_2/T_1} \simeq 3 \times 10^{-3} T$, which yields to $\tau_d \lesssim 10^{-8}$ sec, well below the time resolution of our experimental setup. So, the very fact that we detect a SH-FID signal in our experimental conditions is by itself in disagreement with Eq. (1). We have not yet found a satisfactory explanation of this point and here we limit ourselves to note that Eq. (1) was derived by using the steady-state solutions of the Bloch equations which are known to fail to describe the resonance dynamics for $T_2 << T_1$ in the high-power regime $\beta T_2 >> 1$. Further work in this direction is in progress.

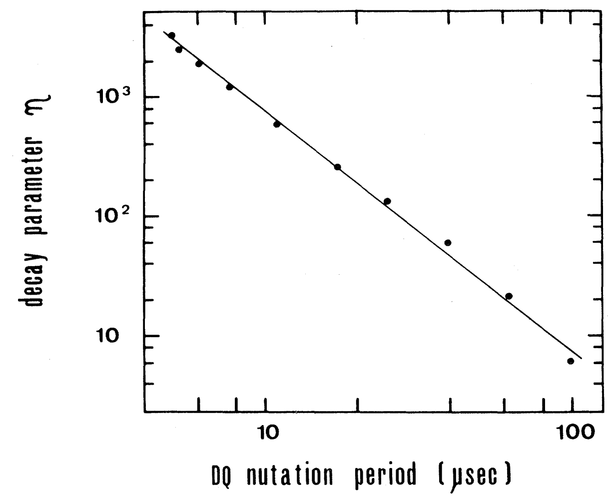

FIG. 2. Experimental values of the decay parameter $\eta = [(T_2/\tau_d - 1)^2 - 1]$ vs T. Data were taken at various input power levels, with $t_0 \sim 120$ μsec, at the center of the DQ resonance line. The continuous line is the function $\eta = K/T^2$ that best fits the experimental points ($K_{\rm expt} = 7.5 \times 10^{-8}$ sec^2).

In conclusion, the TP-FID effect in a two-level system has been investigated with use of the technique of the SH detection. By this method, we have detected large-amplitude oscillations in the TP-FID signal ensuing from a coherent-pulse preparation of the system. In the opposite limit of very long excitation pulses, we found an order-of-magnitude disagreement between the experimental and the theoretical values of the decay time.

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