Double-quantum nutations in a two-level spin system

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The transient oscillatory behavior of the nonlinear response of a two-level electron-spin system is experimentally investigated in a sample of glassy silica with E_1' centers ($S=\frac{1}{2}$) at microwave frequency at $T=4.2$ K. The transient regime, excited by an intense step-modulated radiation tuned to double-quantum (DQ) resonance, is monitored by revealing the second-harmonic (SH) wave radiated by the spins undergoing DQ transitions. Time- and frequency-domain results show that the emitted SH wave has two components: the former, which vanishes at the DQ resonance, exhibits an overdamped transient regime, the latter consists of damped oscillations at a frequency which depends on the intensity and the polarization of the input radiation but not on its detuning from the DQ resonance condition. Using a vectorial model of the DQ resonance in an $S=\frac{1}{2}$ spin system we relate the observed oscillatory behavior to the transient nutations induced by the DQ processes; the calculated DQ Rabi frequency and its dependence on the input radiation are found in quantitative agreement with the experimental results. Moreover, we calculate that the inhomogeneous broadening of the resonance line strongly affects the time dependence and the spectral content of the emitted radiation, and in particular it makes its oscillation frequency independent of the input radiation detuning, in agreement with the experimentally observed behavior. The relationship, with recent discussions on the suitability of Bloch equations to describe coherent effects in randomly diluted solids, is also examined.

I. INTRODUCTION

When the resonance condition between a two-level system and an external radiation is jumplike established, the response of the system may be oscillatory. These oscillations (Torrey wiggles[1] or transient nutations) occur because the interaction with the input radiation moves the system from its initial thermal equilibrium state in a coherent superposition state, where the (electric or magnetic) dipoles of the active centers are coherently driven from the ground to the upper level at a rate β (nutation frequency). The resulting oscillations of the population differences modulate at frequency β, the amplitude of the macroscopic response of the system. This free-atom behavior is counteracted by the relaxation interactions, which drive the system toward a new steady state, where the population difference is stationary and the response is no longer oscillatory.

Since the pioneering work by Torrey[1] in nuclear-spin systems at radio frequency, transient nutations have been observed in a variety of physical systems also at microwave and infrared frequencies.[2-8] As for other coherent regimes, the interest in this effect is twofold. On the one hand, the experimental detection of its decay properties yields real time rather than averaged information on the relaxation mechanisms effective in the system.[3,4,7] On the other hand, its experimental and theoretical study can be used to test the validity of phenomenological equations of motion in nonstationary conditions, especially in solid samples.[5,6,9]

In this paper we are concerned with the transient nutations induced by double-quantum (DQ) transitions and with their effect on the nonlinear response of the system. In particular, we consider a two-level electron-spin system with relatively long spin-spin (T_2) and spin-lattice (T_1) relaxation times. In our experiments, the DQ nutational regime is excited by suddenly switching on an intense and properly polarized[10,11] radiation at frequency $\omega=\frac{1}{2}\omega_0$ where $\hbar\omega_0$ is the energy-level distance. The ensuing transient regime is monitored by revealing the radiation emitted by the spins[12,13] in a narrow spectral region centered at the second-harmonic (SH) frequency 2ω ($\simeq\omega_0$). As described in a preliminary report,[14] at the DQ resonance the intensity of the SH wave exhibits damped oscillations after the onset of the input power. We report here a full set of experimental results on the time evolution and on the spectral content of the SH wave emitted during the transient and on their dependence on the intensity, the polarization, and the detuning of the input radiation.

According to our results, the emitted SH wave has two components out of phase by 90° from each other. The former (resonant, absorptionlike) has an oscillatory behavior with a frequency independent of the input radiation detuning; correspondingly sidebands appear in the emission spectrum. On the contrary, the latter (antiresonant, dispersionlike) is overdamped and reaches its steady-state value after a small overshoot.

The observed transient effects of the SH response can be related to the transient nutations of the DQ transitions by using a simplified vectorial model of the DQ resonance in an $S=\frac{1}{2}$ spin system. The time dependence and the spectral composition of the calculated SH response are shown to agree with the experimental results, provided that allowance is made for the inhomogeneous spread of the spin frequencies.

We recall that DQ nutations have been experimentally observed and theoretically analyzed in multilevel (atomic, molecular, and nuclear-spin) systems.[15–19] Unlike those experiments, where the DQ transitions between the ground and the excited state are enhanced by an intermediate level, the system considered here is a two-level system $S=\frac{1}{2}$. In this case the absence of resonant intermediate levels ensures that the observed effects are unaffected by the saturation or the power shift of the simultaneously excited one-photon resonances. Moreover, as previously noted,[14] a probe field[15,17,18] is not required in our case as the considered transition is as well one-photon allowed. Owing to this circumstance, these systems are particularly suitable for the experimental frequency-domain investigation of the DQ transient regimes.

In the next section we describe the experimental apparatus, and we report the experimental results. The comparison with the results of the vectorial model is carried out in Sec. III, where we also point out the effects of the inhomogeneous broadening, and we make a few remarks on recent nutation experiments carried out at the usual one-photon resonance.[5,6]

II. EXPERIMENTAL RESULTS

A. The apparatus

In our experimental apparatus the sample is located in a bimodal cavity resonating at $\omega=2\pi\times2.95$ GHz in a partially coaxial mode (excitation mode, $Q_\omega\simeq10^3$) and at $2\omega=2\pi\times5.90$ GHz in its TE_{102} mode (detection mode, $Q_{2\omega}=5\times10^3$). The sample is tuned to the frequency $\omega_0\simeq2\omega$ by the external field $\mathbf{H}_0$. The field geometry at the sample position is such that the ω- and 2ω-oscillating fields of the two modes are parallel to each other and make an angle α with respect to $\mathbf{H}_0$. α can be varied from 0° to +90° by rotating $\mathbf{H}_0$. To excite the transient regime the ω mode is fed by squared pulses of radiation at frequency ω, which create an oscillating magnetic field $\mathbf{h}(t)=2\mathbf{H}_1\cos(\omega t)$ at the sample position. We monitor the transient evolution of the system by revealing the time-dependent amplitude of the SH wave radiated by the spin system into the 2ω mode of the cavity.[14]

The input power pulses are obtained by pulse shaping the output signal of a cw low-power ($\simeq0$ dB m) source; high intensity is achieved by means of a traveling-wave tube with a maximum output power of 45 dB m. The resulting pulses have switching times <0.3 μs; their width w and repetition rate f are so regulated that the excitation can be considered as step modulated for our purposes, namely w is long enough ($w=0.1-1.0$ ms) to allow the detection of the entire transient regime, and f is low enough ($f=1$ Hz) to ensure complete thermal relaxation of the spin system between successive pulses.

The 2ω signal leaking out from the cavity is first filtered to isolate the spectral components around 2ω and amplified by a small-signal narrow-band amplifier (5.8–6.2 GHz); the output is then revealed by a logarithmic superheterodyne receiver (i.f.$=30$ MHz). The transient video signal is digitalized by a transient recorder. The signal-to-noise ratio is enhanced by averaging the transient signal over a number of pulses (usually 128); the average and also the control of repetitive acquisition is accomplished by a homemade microcomputer-based system. Finally, data are displayed on a cathode-ray tube and stored for further numerical processing. The whole receiver has a time resolution of 200 ns, a minimum detectable signal of -90 dB m, a dynamical range of 70 dB, and is calibrated with the accuracy of ±0.5 dB. Alternatively, the output signal of the microwave amplifier can be sent to a spectrum analyzer for frequency-domain analysis.

Owing to the residual parasitic coupling between the two modes of the cavity, a small H_0-independent SH signal is usually present at the output of the cavity. In some measurements, especially those taken at the exact DQ resonance, its interference with the SH signal emitted by the sample may cause significant distortions of the detected curves.[14] To minimize these effects a bridge system is occasionally used at the output of the cavity, where the parasitic signal is summed with an SH reference signal whose amplitude and phase are so regulated to reduce the field-independent signal. The stability of the bridge system is greatly improved by phase locking the cw low-power generator by a source-locking counter.

B. Results

We report here the results obtained in a sample of E'_1 centers in fused silica at liquid-helium temperature ($T=4.2$ K). E' centers were created by γ irradiating 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 nearly 10^{17} cm^{-3} on the basis of the total 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).[20] This system was chosen because of its long relaxation times: In our experimental conditions ($T=4.2$ K, $H_0=2$ kG) we measured $T_2=0.1$ ms and $T_1=0.1$ s in our sample.

Large-amplitude oscillations of the intensity of the SH wave emitted by the spins were observed when H_0 was adjusted to fulfill the DQ resonance condition $H_0=H_{0r}\equiv2\omega/\gamma$. We report in Fig. 1 the experimental curves of the SH intensity obtained at two different power levels and at $\alpha=45°$; this orientation is known[10,14] to maximize the DQ transition probability. The SH transient signal consists of a rapid increase at very short times after the onset of the input power and of damped oscillations toward a very low steady-state value (below noise level). The characteristic time τ_r of the initial rise is below the resolution of our receiver system ($\tau_r\lesssim0.2$ μs). The distance between successive maxima in the curves of Fig. 1 is constant in time except for the first two maxima whose distance is larger by nearly a factor 1.2. To interpret correctly the oscillations of Fig. 1, we note that, as our receiver measures the intensity rather than the amplitude of the SH wave, the period T_0 is twice the distance between successive maxima.

The oscillation period was measured as a function of the amplitude and of the polarization of the microwave

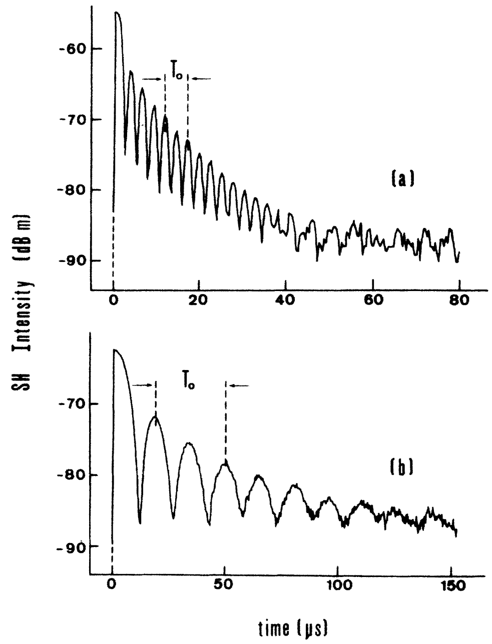

FIG. 1. Experimental curves of the SH transient signal at the DQ resonance ($H_0 = H_{0r}$) in a sample of E_1' centers in glassy silica at $T = 4.2$ K, at $\alpha = 45°$, at two different power levels: (a) $P = 30$ W ($H_1 = 12$ G), $T_0 = 5.3$ μs; (b) $P = 4.8$ W ($H_1 = 4.9$ G), $T_0 = 31.0$ μs.

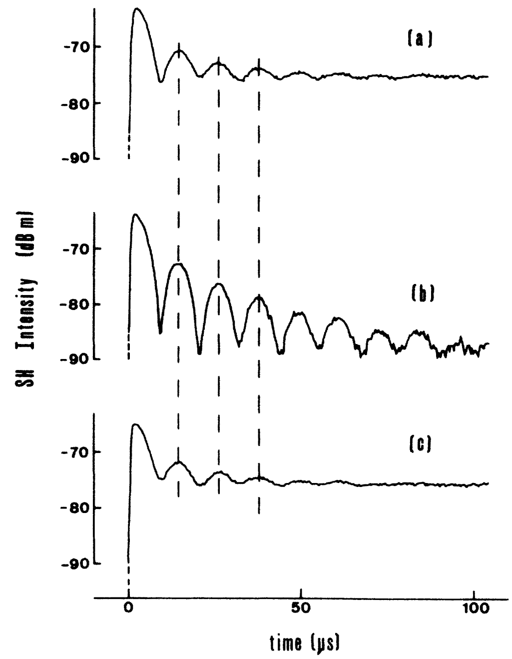

FIG. 2. Experimental curves of the SH transient signal at the DQ resonance: (a) at $\Delta H = +0.2$ G, (b) at $\Delta H = 0$, (c) at $\Delta H = -0.2$ G. Curves were taken at $\alpha = 45°$ and at $P = 6.6$ W ($H_1 = 5.6$ G, $T_0 = 24$ μs).

field $\mathbf{H}_1$. The experimental data were well fitted by a power law:

$$T_0 = \frac{K}{H_1^\eta},$$

with $\eta = 2.0 \pm 0.2$ and $K = (7.8 \pm 0.7) \times 10^{-4}$ s G^2 at $\alpha = 45°$. In these measurements H_1 was estimated by simultaneously revealing the saturation transient regime of a reference sample of dilute ruby.[21] As regards the dependence of T_0 on the angle α, T_0 was found[14] to be minimum at $\alpha = 45°$ and to increase toward $\alpha = 0°$ and $\alpha = 90°$ following a law $T_0 \propto [\sin(2\alpha)]^{-1}$.

The SH transient signals as experimentally detected at small detunings from the DQ resonance ($\Delta H = H_0 - H_{0r} = \pm 0.2$ G) are shown in Fig. 2 and compared with the resonant case. Whereas at $\Delta H = 0$ the SH wave is 100% amplitude modulated at a frequency $\chi = 2\pi/T_0$, at $\Delta H \neq 0$ the SH transient signal has two components; the former is not oscillatory, the latter oscillates at the same frequency as for $\Delta H = 0$. By using the bridge system we could verify that the two components are in quadrature with each other. Moreover, the period T_0 of the oscillations was measured to be independent of ΔH up to $\Delta H = \pm 1$ G (nearly the half-width of the resonance line) within the experimental uncertainty of $\pm 5\%$.

The different spectral composition of the SH signal at $\Delta H = 0$ and $\Delta H \neq 0$ is confirmed by the experimental spectra reported in Fig. 3. These spectra are detected by a spectrum analyzer with an i.f. bandwidth of 10 KHz and a sweep rate of 10 KHz/s low enough to minimize the noise caused by the low repetition rate of the input power

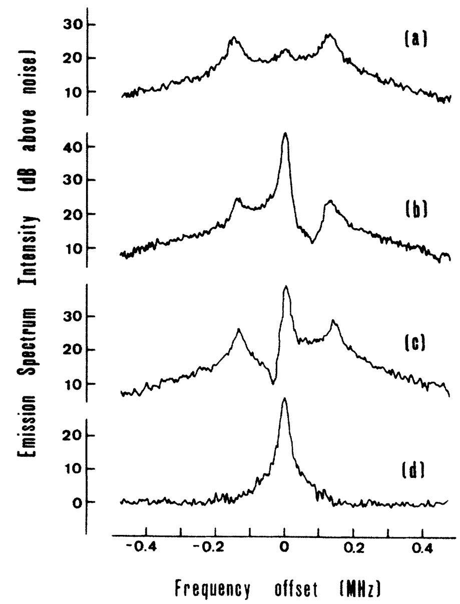

FIG. 3. Experimental spectra of the radiation emitted by the spin system (a) at the DQ resonance ($\Delta H = 0$), (b) at $\Delta H = -0.2$ G, (c) at $\Delta H = +0.2$ G, and (d) at $\Delta H = 5$ G. Spectra were recorded at $\alpha = 45°$ with an input power level of 22 W ($H_1 = 10$ G, $T_0 = 7.1$ μs) by a spectrum analyzer with i.f. bandwidth of 10 kHz and sweep rate of 10 kHz/s. Sidebands are centered at ± 140 kHz.

pulses. For the sake of comparison we also report in Fig. 3 the emission spectrum taken far from the line center ($\Delta H=5$ G). It is worth noting that the bandwidth of the 2ω mode of the cavity ($\simeq 1$ MHz) is large enough to allow the detection of the emission spectra without significant distortions. At the resonance $\Delta H=0$, the spectrum of the emitted radiation consists of two sidebands distant ± 140 kHz from the center; the small central structure is the residual parasitic signal aforementioned. The spectra taken at $\Delta H=\pm 0.2$ G exhibit a strong central component (at $\nu'=2\omega/2\pi$) and two sidebands which are essentially the same as at $\Delta H=0$. The central components of the spectra at $\Delta H=+0.2$ G and $\Delta H=-0.2$ G have a phase difference of π from each other, as expected for steady-state (nonoscillatory) dispersionlike signals; this can be inferred from the interference of their wings with the right and the left sideband, respectively.

Finally, we report that SH oscillatory signals with essentially similar features as described above were also observed in samples of diluted ruby (Al_2O_3:Cr^{3+}, with $[Cr^{3+}]\lesssim 0.01$ wt %) and of $CaWO_4$:Ce^{3+}. However, the detection of the coherent transition signals in these samples and especially their analysis are more difficult than in E_1' samples because of a much more rapid decay ($\simeq 10$ μs) perhaps caused by shorter relaxation times.

III. DISCUSSION

The aim of this section is to relate the SH oscillatory response to the transient nutations of the DQ transitions. This is accomplished by a simplified vectorial model of the DQ resonance in an $S=\frac{1}{2}$ spin system. In the following we disregard the relaxation interactions, as a detailed study of the decay properties of the SH transient regime is admittedly outside the scope of this paper. Instead, we take into account the inhomogeneous spread of the spin frequencies, which will prove of prime importance to interpret our experimental results.

A. The vectorial model

Firstly, we calculate the transient response of a homogeneous system of $S=\frac{1}{2}$ spin centers resonating at ω_0. We assume the field geometry of our experimental setup: In a laboratory reference frame (LRF) with the $\hat{\mathbf{z}}$ axis taken along $\mathbf{H}_0$, the oscillating field $\mathbf{h}_1(t)=2\mathbf{H}_1\cos(\omega t)$ has both a z and a transverse component: $h_z(t)=2H_1\cos\alpha\cos(\omega t)$ and $h_x(t)=2H_1\sin\alpha\cos(\omega t)$. For the sake of simplicity, in the following we retain only the rotating component

$$\mathbf{h}_r(t)=H_1\sin\alpha[\hat{\mathbf{x}}\cos(\omega t)+\hat{\mathbf{y}}\sin(\omega t)]$$

of the transverse field.[22]

A vectorial model of the DQ resonance of an $S=\frac{1}{2}$ system can be worked out in a rotating frame where the effective field is mainly static, namely with negligible time-dependent terms, so that the time evolution of the system can be described by Bloch-type equations in a constant field. The following sequence of rotations leads to a suitable doubly rotating reference frame (DDRF):

(a) Firstly, a time-dependent rotation around the $\hat{\mathbf{z}}$ axis by the angle ωt. In this new reference frame (RF) $(\hat{\mathbf{x}}_1,\hat{\mathbf{y}}_1,\hat{\mathbf{z}}_1)$ the effective field is

$$\gamma\mathbf{H}_{e1}=\hat{\mathbf{z}}_1[\omega_0-\omega+\omega_z\cos(\omega t)]+\hat{\mathbf{x}}_1\omega_r\ ,$$

where $\omega_z=2\gamma H_1\cos\alpha$ and $\omega_r=\gamma H_1\sin\alpha$.

(b) Secondly, a rotation around $\hat{\mathbf{y}}_1$ by the angle $\theta=\tan^{-1}[\omega_r/(\omega_0-\omega)]$. In this RF $(\hat{\mathbf{x}}_2,\hat{\mathbf{y}}_2,\hat{\mathbf{z}}_2)$ the effective field $\mathbf{H}_{e2}$ is given by

$$\begin{aligned}\gamma\mathbf{H}_{e2}=\hat{\mathbf{z}}_2\{&[\omega_0-\omega+\omega_z\cos(\omega t)]\cos\theta+\omega_r\sin\theta+O(2\omega)\}\\&+\hat{\mathbf{x}}_2\{-[\omega_0-\omega+\omega_z\cos(\omega t)]\sin\theta\\&\quad+\omega_r\cos\theta+O(2\omega)\}\ ,\end{aligned}$$

where $O(2\omega)$ stands for 2ω-oscillating nonresonant terms, which can be neglected for our purposes.

(c) Finally, a rotation about $\hat{\mathbf{z}}_2$ by the angle ωt. In this DRRF $(\hat{\mathbf{x}}_3,\hat{\mathbf{y}}_3,\hat{\mathbf{z}}_3)$ the effective field is

$$\gamma\mathbf{H}_{e3}=\hat{\mathbf{z}}_3\Delta+\hat{\mathbf{x}}_3\chi\ ,\tag{1}$$

where

$$\Delta=\omega_0-2\omega\ ,\tag{2}$$

$$\chi=\omega_r\omega_z/2\omega\ .\tag{3}$$

A resonance shift of the order of ω_r^2/ω, as well as ω- and 2ω-oscillating terms, were neglected in deriving Eqs. (1)–(3).

In DRRF the effective field is static within the approximations used to derive Eqs. (1)–(3); so the time evolution of the spin system is governed by a set of Bloch equations with time-independent coefficients:

$$\begin{aligned}\dot{\bar{u}}&=-\Delta\bar{v}\ ,\\ \dot{\bar{v}}&=\Delta\bar{u}+\chi\bar{w}\ ,\\ \dot{\bar{w}}&=-\chi\bar{v}\ ,\end{aligned}\tag{4}$$

where $\bar{u}=M_x/M_0$, $\bar{v}=M_y/M_0$, and $\bar{w}=M_z/M_0$ are the normalized components of the magnetization $\overline{\mathbf{M}}$ in DRRF. The transient solutions of this kind of equation have been extensively considered in literature[1–7,9] in connection with the transient regimes of the usual one-photon resonances. Within the approximations used to derive Eqs. (4), those solutions appear to be valid as well in our case of DQ resonances case, provided that the rotating frame, the resonance detuning Δ, and the Rabi frequency χ are redefined in a way suitable for the DQ resonance condition, namely as in Eqs. (2) and (3).

In particular, for a system initially at thermal equilibrium [$\bar{u}(0)=\bar{v}(0)=0$, $\bar{w}(0)=1$] and excited by a step-modulated radiation, the solutions are known:[1–7,9]

$$\begin{aligned}\bar{u}(\Delta,t)&=-(\Delta\chi/\beta^2)[1-\cos(\beta t)]\ ,\\ \bar{v}(\Delta,t)&=(\chi/\beta)\sin(\beta t)\ ,\\ \bar{w}(\Delta,t)&=\Delta^2/\beta^2+(\chi^2/\beta^2)\cos(\beta t)\ ,\end{aligned}\tag{5}$$

with $\beta^2=\chi^2+\Delta^2$. Note that the initial conditions in the DRRF should be written as $\bar{u}(0)=\sin\theta$, $\bar{v}(0)=0$, and $\bar{w}(0)=\cos\theta$; however, these differ from the LRF initial conditions only by negligible terms of the order of $\theta^2 \simeq (\omega_r^2/\omega^2)$.

Now we take into account the inhomogeneous broadening of the resonance line. We assume a Gaussian distribution of the spin frequencies ω_0' around the mean frequency ω_0:

$$g(\varepsilon) = (1/\sigma\sqrt{\pi})\exp(-\varepsilon^2/\sigma^2) ,$$

where $\varepsilon = \omega_0 - \omega_0'$. For a preselected detuning $\delta = \omega_0 - 2\omega$ of the input radiation from the DQ resonance, the macroscopic response of the system in DRRF is given by the convolution of the solutions in Eqs. (5) with $g(\varepsilon)$:

$$\bar{U}(t) = \int_{-\infty}^{+\infty} g(\varepsilon)\bar{u}(\varepsilon,t)d\varepsilon , \tag{6}$$

where $\bar{u}(\varepsilon,t)$ is the solution given in Eqs. (5) with $\Delta = \delta - \varepsilon$; similarly, we define $\bar{V}(t)$ and $\bar{W}(t)$.

The solutions $M_k(t)$ $(k = x,y,z)$ in LRF may be calculated by using the inverse transformation from DRRF to LRF. It can be easily shown that $M_k(t)$ $(k = x,y)$ solutions contain 2ω-oscillating resonant terms:

$$M_k^{2\omega}(t) = 2\,\mathrm{Re}\{M_k(2\omega,t)\exp(-2i\omega t)\} ,$$

with

$$\begin{aligned} M_x(2\omega,t) &= M_0[\bar{U}(t) - i\bar{V}(t)] , \\ M_y(2\omega,t) &= M_0[\bar{U}(t) + i\bar{V}(t)] . \end{aligned} \tag{7}$$

Equations (5)–(7) show that the time evolution of the spin system in DRRF, and in particular its DQ nutations, manifest in LRF as transient amplitude modulation of the 2ω-oscillating transverse magnetizations.

B. Comparison with experimental results

In our experimental setup, the spin system is coupled to a 2ω-resonating mode of the cavity, so that the 2ω-oscillating components of the transverse magnetizations radiate power into the cavity.[12] In particular, for our geometry only $M_x^{2\omega}(t)$ couples the revealing mode and we get from Eq. (7) the following expression of the intensity of the detected SH signal:

$$I_{\mathrm{SH}}(t) \propto [M_x(2\omega,t)]^2 = M_0^2\{[\bar{U}(t)]^2 + [\bar{V}(t)]^2\} . \tag{8}$$

Firstly, we consider the resonant case $\delta = 0$. In this case $\bar{U}(t)$ in Eq. (6) vanishes since $\bar{u}(\varepsilon,t)$ is an odd function of ε for $\delta = 0$. Analytical solutions of $\bar{V}(t)$ may be obtained[1,7,23,24] within the high-inhomogeneity approximation, namely for $\sigma \gg \chi$:

$$\bar{V}(t) \simeq \begin{cases} \chi t, \quad t \ll \sigma^{-1} & \text{(9a)} \\ \sqrt{\pi}(\chi/\sigma)J_0(\chi t), \quad t \gg \sigma^{-1} , & \text{(9b)} \end{cases}$$

where $J_0(\chi t)$ is the zeroth-order Bessel function. Note that the condition $\sigma \gg \chi$ is well satisfied in our experiments where $\sigma/\chi \simeq 40$ at the maximum available input power. According to Eqs. (9a) and (9b), the intensity I_{SH} of the SH wave is expected to have a very rapid leading edge and then to vary in time as $[J_0(\chi t)]^2$, in qualitative agreement with the experimental curves of Fig. 1. In particular, it is a property of $[J_0(\chi t)]^2$ that the distance between successive maxima, $\Delta t = \pi/\chi$, is constant in time, except for the first two maxima, whose distance is larger by a factor 1.19,[25] in agreement with our experimental results. Moreover, from Eq. (3) we calculate for $\omega = 2\pi \times 2.95$ GHz:

$$T_0 = (K/H_1^2)[1/\sin(2\alpha)] ,$$

with $K = 7.52 \times 10^{-4}$ s G^2, in quantitative agreement with the angular and the power dependence experimentally observed. Finally, we verified that the experimental curves of $I_{\mathrm{SH}}(t)$ decay more rapidly than $[J_0(\chi t)]^2$, as their damping is obviously affected by the relaxation interactions, which were not considered when deriving Eqs. (8). A thorough consideration of the decay properties of the nutational regime is admittedly outside the scope of the present paper. Here we limit ourselves to remark that the damping of $I_{\mathrm{SH}}(t)$ was found to depend on the amplitude of the input microwave field, being faster at higher power levels, as can be noted in Fig. 1 by comparing the two experimental curves.

For $\delta \neq 0$, $\bar{U}(t)$ no longer vanishes and for $|\delta| > \chi$ it yields the main contribution to $I_{\mathrm{SH}}(t)$. $\bar{U}(t)$ cannot be calculated analytically; moreover, the high-inhomogeneity approximation $(\sigma \gg \chi)$ used to calculate $\bar{V}(t)$ at $\delta = 0$ is unsuitable to yield valuable results off resonance. Therefore, numerical integration of the solutions $\bar{u}(\varepsilon,t)$ and $\bar{v}(\varepsilon,t)$ is required at $\delta \neq 0$. Typical results of the calculated $\bar{U}(t)$ at $\delta \neq 0$ are reported in Fig. 4. As shown, the dispersionlike component $\bar{U}(t)$ of the SH transient response does not oscillate for $\chi/\sigma < 0.1$ (inhomogeneous behavior); rather it exhibits only a small overshoot. A qualitative reason is that for a fixed detuning δ of the input power the resonant or near-resonant spins $(\varepsilon = \delta)$ do not contribute to $\bar{U}(t)$, which collects the contributions arising from distant packets; these nutate at progressively increasing frequencies $\beta(\varepsilon) = [\chi^2 + (\delta - \varepsilon)^2]^{1/2}$, so that the

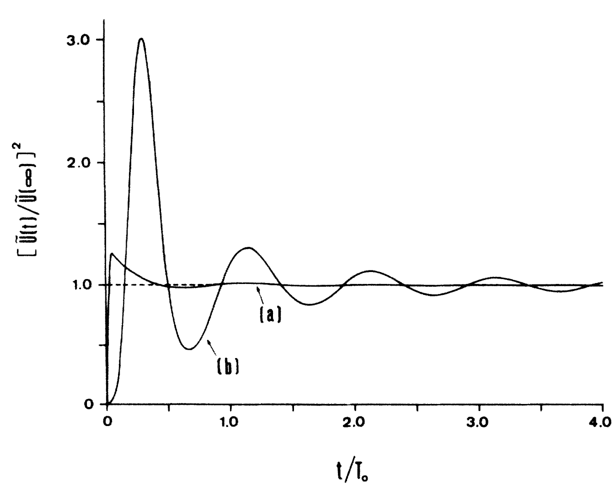

FIG. 4. Calculated $[\bar{U}(t)]^2$ at $\delta = \sigma$: (a) $\chi = 0.1\sigma$, (b) $\chi = \sigma$. $\bar{U}(t)$ is normalized to the steady-state value $\bar{U}(\infty)$. Time is expressed in units of $T_0 = 2\pi/\chi$.

superposition of their motion results in overdamped oscillations of the macroscopic response. For $\chi/\sigma > 0.1$ an oscillatory part appears in $\overline{U}(t)$, which progressively increases on increasing χ/σ, tending to the homogeneous behavior [100% amplitude modulation at frequency $\beta=(\chi^2+\delta^2)^{1/2}$].

On the other hand, even for $\delta\neq 0$, the main contribution to the absorptionlike component $\overline{V}(t)$ comes from the resonant or near-resonant packets that nutate nearly at χ. So $\overline{V}(t)$ is expected to keep its form and its period even for a nonresonant excitation in an inhomogeneous line. By numerically solving the integral of Eq. (6), we verified that $\overline{V}(t)$ is always oscillatory with a period independent of δ within 1% for $\chi/\sigma < 0.1$ and up to $\delta/\sigma \simeq 3.0$. The δ dependence of the oscillation frequency $\beta=(\chi^2+\delta^2)^{1/2}$ (homogeneous behavior) is restored in the opposite limit $\chi/\sigma > 3$. The intermediate case ($0.5 < \chi/\sigma < 3.0$) is rather complicated as the distance between successive maxima is no longer constant.

So, in our experimental conditions ($\chi/\sigma < 2.5\times 10^{-2}$) the SH intensity $I_{\mathrm{SH}}(t)$ [Eq. (8)] at $\delta\neq 0$ is expected to consist of two components in quadrature, the former nonoscillatory, the latter oscillating at a frequency χ independent of the detuning δ. This is in complete agreement with the behavior experimentally observed both in time and in frequency domains (Figs. 2 and 3).

C. A remark on one-photon transient-nutation experiments

As a final remark, we wish to comment on recent experimental investigations of transient nutations in dilute solid samples at the usual one-photon resonance.[5,7] According to our experimental and theoretical results, the inhomogeneous broadening of the resonance line affects the DQ transient-nutation regime as follows: (a) $\overline{V}(t)$ varies in time as $J_0(\chi t)$ rather than as $\sin(\beta t)$; (b) the oscillation frequency is χ at any δ rather than $\beta=(\chi^2+\delta^2)^{1/2}$; (c) $\overline{U}(t)$ does not oscillate.

It is worth noting that the aforementioned effects are not peculiar to the DQ resonance case. In fact, they originate in the integration [Eq. (6)] of the solution of Eqs. (4); so, the same results are expected to be valid as well for the one-photon resonances if the line is inhomogeneously broadened. Actually, a time dependence of the transient absorption signal, $J_0(\chi t)$, has been occasionally detected and correctly interpreted.[7,23,24] However, in other reports[5,6] the "cosine-like" rather than "sine-like" transient response of the absorption signal, the independence of its oscillation period on δ, and the nonoscillatory behavior of the transient dispersion signal were taken as experimental evidence of the failure of the Bloch equations to describe the coherent regimes in dilute solid samples. At variance we proved that these peculiarities are consistent with Bloch equations, provided that allowance is made for the inhomogeneity of the resonance line.

IV. CONCLUSIONS

We have reported experimental results on the oscillatory nonlinear response of a two-level spin system at DQ resonance. On the basis of the observed properties and of the theoretical results obtained by a simple vectorial model, we have pointed out the relationship between the SH transients regime and the transient nutations of the DQ transitions. The calculated time dependence and the spectral composition of the SH emitted wave and the dependence of the oscillation period on the properties of the input radiation have been found in quantitative agreement with the experimental results. The effect of the inhomogeneous broadening of the line has been examined in detail and our conclusions have been compared with recent experimental data on the transient nutations of the one-photon resonances.

For the sake of clearness, the model used here does not take into account the relaxation interactions, which determine the damping of the transient regime. Work is in progress in this direction, also in view of the possibility of testing the validity of modified Bloch equations, recently[9] proposed to describe the dephasing effects in randomly diluted solid samples.

Finally, we remark that the experimental procedure described here, based on DQ excitation and SH detection, may be proposed as a convenient method for the investigation of the coherent transient regimes, especially those occurring during the input power pulses. This kind of experiment can hardly be carried out by conventional techniques of absorption spectroscopy because of the simultaneous presence of the strong pump field. On the contrary, the method described here is based on the detection of the radiation emitted by the system at a frequency different from the input radiation. An instance of this convenience is the frequency-domain analysis of the transient response reported here.

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