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Electron-spin double resonance by longitudinal detection: Line shape and many-quantum transitions

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A system of electronic spins in double-paramagnetic-resonance condition is examined. The impinging waves are both nearly resonant and with the magnetic field perpendicular to the static field. The nonlinearity of the sample induces a longitudinal magnetization oscillating at multiples of the difference of the frequencies of the two waves. The line shape shows only one peak for low-power levels and two for higher wave intensities. Measurements have been performed by an *ad hoc* built X-band spectrometer with remarkably high relative precision in the difference betwen the frequencies. Transitions involving up to 22 photons have been detected. Experimental and theoretical results are closely consistent.

I. INTRODUCTION

In the last few years, several interesting effects due to the nonlinear response of a spin system in magnetic resonance conditions have been shown. Characteristic nonlinear effects are resonance line saturation, harmonic generation,[1] multiple quantum transitions, spin decoupling,[2] intermodulation,[3] etc.

Recently, we have experimentally detected and explained[4] a new nonlinear effect which generates a dispersionlike line in the absorption spectrum of a nuclear spin system submitted to double irradiation. In order to detect this line, the frequency ω_s of one of the two irradiating waves has to be kept fixed and near to the resonance frequency ω_0 of the system. By varying the detecting frequency ω_r, the new resonance occurs when $\omega_r \simeq \omega_s$. If adequately intense waves are supplied, many-quantum transitions can occur; consequently, in transverse magnetization, oscillating terms appear at frequencies $n\omega_s + (n \pm 1)\omega_r$. Resonances are obtained when the condition $E_2 - E_1 = \hbar\omega_r \pm n\hbar(\omega_r - \omega_s)$ is satisfied, where E_1 and E_2 denote two energy levels of the spin system. We note that E_1 and E_2 depend on the static magnetic field and the wave intensities.

Because of the angular momentum invariance, the transverse terms of the magnetization $\vec{M}$ oscillate at the frequencies $\omega_r + n(\omega_r - \omega_s)$ and $\omega_s + m(\omega_r - \omega_s)$, while the longitudinal terms oscillate at $n(\omega_r - \omega_s)$. The latter terms resonate when condition $\omega_r \simeq \omega_s$ is satisfied.[4]

In an usual double-magnetic-resonance spectrometer, the signal is detected by observing the in-phase or in-quadrature terms of the transverse magnetization, which oscillate at the frequency of one of the two incident waves. Only one resonance line is expected for a two-level system. On the other hand, owing to spin-lattice relaxation and spin-radiation interaction, the various oscillations at harmonic frequencies of the magnetization components are coupled. The resonance at one harmonic therefore produces variation of all the harmonics.

In particular, the signal we have observed in NMR[4] for $\omega_r \simeq \omega_s$ is due to the interaction of the resonant terms of M_z oscillating at the frequency $n(\omega_r - \omega_s)$, with the term of M_y oscillating at the frequency ω_r.

In a further paper[5] we gave experimental evidence of the oscillation of the M_z component at the frequency $\omega_r - \omega_s$ under EPR conditions.

In the present paper we report detailed results concerning the line shape of various harmonics of $\omega_r - \omega_s$ for M_z. Particular care is required to perform this experiment, since the effect becomes detectable for $|\omega_r - \omega_s| \simeq 1/T_2$. Because of this, for a typical EPR system, the order of magnitude of $|\omega_r - \omega_s|$ is about 1 MHz. Since the effect we are studying is strongly nonlinear, fluctuations of $|\omega_r - \omega_s|$ produce high levels of noise. Therefore, we have phase-locked the frequencies of the two microwave sources with a relative stability of about 10^{-11}. With the experimental apparatus set up in our laboratory, up to eleven harmonics have been detected; such a process involves 22 photons.

II. THEORY

In Ref. 4, we have shown how to obtain the response of a spin-$\frac{1}{2}$ system submitted to double irradiation. In particular, we gave the expression of the absorption coefficient for one of the two waves. For the general treatment of the problem and notations we refer to Ref. 4. In the present paper, we develop a theory to include the oscillating terms of the longitudinal magnetization. We note that electronic spin systems are considered here, while nuclear spin systems were discussed in Ref. 4. Since protons and electrons have opposite magnetic moments, a straightforward correction of the formulas in Ref. 4 is required. In Ref. 6 the relaxation-dependent part of the statistical operator has been expanded in series of normal products of creation and annihilation operators for the photons of the two waves r and s; we have

$$D=\sum D_{m,n;p,q}\, a_r^{\dagger m} a_r^n a_s^{\dagger p} a_s^q \;, \tag{1}$$

the operator $D_{m,n;p,q}$ being a function of spin and of the other physical parameters.

The operators of interest are represented using a basis of the kind:

$$|m, n_r, n_s\rangle \;, \tag{2}$$

m being the spin quantum number and n_r and n_s are the occupation numbers for the two wave photons.

A set of states well suited to develop our theory is obtained by selecting among the states (2) the ones nearly degenerate in energy. As in Ref. 4, we order the states (2) in the succession

$$\cdots |+\tfrac{1}{2}, n_r+1, n_s-1\rangle \,,\; |-\tfrac{1}{2}, n_r+1, n_s\rangle \,,\; |+\tfrac{1}{2}, n_r, n_s\rangle \,,\; |-\tfrac{1}{2}, n_r, n_s+1\rangle \,,\; |+\tfrac{1}{2}, n_r-1, n_s+1\rangle \,,\; |-\tfrac{1}{2}, n_r-1, n_s+2\rangle \cdots , \tag{2$'$}$$

labeling them with ..., −2, −1, 0, 1, 2, 3, ... The number 0 corresponds to the state $|+\frac{1}{2}, n_r, n_s\rangle$. When a high number of photons is present,[6] the operator a can be substituted by the expectation value on the coherent state $|\alpha\rangle$.

In such a way we can exploit time dependence of a:

$$\alpha(t)=\alpha(0)e^{-i\omega t} \,. \tag{3}$$

Similar considerations apply to $a^\dagger$.

If we assume the photon occupation numbers to be good quantum numbers, the matrix elements of (1) between two states of the succession (2) are time independent. Thus, because of the high number of the photons, the radiation can be considered as coherent and expression (3) can be substituted in (1). In such a way, the time dependence of the oscillating terms is immediately obtained. We wish now to recall explicitly that the kth harmonic (with respect to ω) of the statistical average of an operator O is given in general by[6]

$$\langle O a^{\dagger k}\rangle/\alpha^k \,.$$

In our case two waves are present. Thus, in order to estimate the kth harmonic of M_z (with respect to $\omega_r-\omega_s$), we have to calculate $\frac{1}{2}\, g\mu_B \times\langle\sigma_z a_r^{\dagger k} a_s^k\rangle$. We note that other authors[7] have treated similar problems for the case where the intensity of one of the two waves is negligible.

A technique of numerical computation was developed in Ref. 4 to obtain the response of a spin system when the intensity of the two waves is of the same order of magnitude. In this case, because of the high number of photons, states $|m, n_r, n_s\rangle$ and $|m, n_r+1, n_s-1\rangle$ are equivalent. Thus the recurrence rule

$$D_{i,j}=D_{i+2,\,j+2} \tag{4}$$

is verified for the matrix elements $D_{i,j}$ of the statistical operator between any two states of the succession (2′). If we choose the states as in Ref. 4, whose notations we follow here, we get $\frac{1}{2}g\mu_B(D_{0,2}-D_{1,3})$ + c.c. for the first harmonic in $\omega_r-\omega_s$ in M_z, $\frac{1}{2}g\mu_B(D_{0,4}-D_{1,5})$ + c.c. for the second one, $\frac{1}{2}g\mu_B(D_{0,6}-D_{1,7})$ + c.c. for the third one, and so on.

We now use (4) and neglect processes involving more than a given number of photons; thus, we can solve the system of linear algebraic equations for the matrix elements $D_{i,j}$, which in turn give the different harmonics of M_z.

From expression (12) of Ref. 4, the equations for $D_{0,2}$ and $D_{1,3}$ are easily obtained:

$$(i/T_1)D_{0,2}=\lambda_r(D_{1,4}-D_{0,1})+\lambda_s(D_{1,2}-D_{0,3})+(\omega_r-\omega_s)D_{0,2}\,,$$
$$(i/T_1)D_{1,3}=\lambda_r(D_{0,1}-D_{1,4})+\lambda_s(D_{0,3}-D_{1,2})+(\omega_r-\omega_s)D_{1,3}\,. \tag{5}$$

In (5), T_1 is the longitudinal relaxation time and λ_r and λ_s are the matrix elements of the interaction of the spin system with the electromagnetic wave of frequency ω_r and ω_s, respectively. We sum the two equations (5) and get

$$(i/T_1)(D_{0,2}+D_{1,3})=(\omega_r-\omega_s)(D_{0,2}+D_{1,3})\,.$$

This equation is satisfied only if $D_{0,2}=-D_{1,3}$.

The same procedure applied to the terms related to the other harmonics gives

$$D_{0,2n}=-D_{1,2n+1}\,. \tag{6}$$

We now show that the result (6) can also be achieved with semiclassical considerations. In fact, the $D_{0,0}$ and $D_{1,1}$ terms represent the nonperiodic deviation from the thermodynamic equilibrium of the populations of the two levels. Because of the simultaneous presence of the two waves oscillations are produced on these populations. Condition (6) requires that the whole population variation from the thermodynamic equilibrium vanishes for each single harmonic. When both waves are very close in frequency to the resonance frequency ω_0, several many-quantum processes are excited. Therefore, so many elements $D_{i,j}$ should be considered that it becomes impossible to solve directly the system of linear equations. To overcome this difficulty, we wrote a computer program to build the system of equations and to get its numerical solution. We note explicitly that use of recurrence relation (4) allows us to consider only the unknown quantities $D_{0,i}$, $D_{1,j}$ $(i,j=1,2,\ldots)$.

Moreover, we can represent the Hamiltonian $\mathcal{H}_{\text{tot}}$ with a $(2k+3)\times(2k+3)$ matrix if the phenomenon we are considering can be explained by retaining processes involving at most $2k$ photons (k for r wave and k for s wave). Finally once the coefficients of the system in $D_{0,i}$, $D_{1,j}$ $(i \leq 2k$, $j \leq 2k)$ are obtained, a standard library subroutine directly gives amplitudes and phases of the different harmonics.

III. EXPERIMENT

In a previous paper[5] we observed the oscillating component of M_z in a spin-$\frac{1}{2}$ system under EPR conditions; in particular, only the oscillation at the frequency $\omega_r - \omega_s$ was detected. In fact the experimental apparatus used in Ref. 5 had some limitations.

(i) Since the sample was placed in a waveguide, the low intensity of the electromagnetic field did not allow the detection of higher harmonics and a detailed examination of the first harmonic saturation.

(ii) Because of rather high noise level, the phase-lock system was not completely reliable.

To overcome the foregoing difficulties, in the present experiment the sample was placed in a cavity excited by two electromagnetic waves, whose intensities allowed us to detect up to eleven harmonics in $\omega_r - \omega_s$. We used a rectangular cavity oscillating in the TE_{102} mode and with a loaded Q of about 4000. Because of this value of Q, we could obtain sufficient intensity of both the waves only if their frequency difference was not higher than a few hundred kHz. Thus particular care was required in the frequency phase-locking between the two waves and in the automatic frequency control of one wave to the resonant cavity frequency.

The microwave and electronic apparatus is reported in Fig. 1. Two klystrons (actually an X13 and a VA197W) simultaneously send electromagnetic power to the resonant cavity through a ferrite circulator. Decoupling between the two klystrons is performed by two isolators (not shown in the figure). The mixing of the two waves before entering the cavity is accomplished with the aid of matched hybrid tee. Parts of the two input signals are taken by two directional couplers and sent to a single-ended mixer. The low-frequency beat is phase-compared with the reference-oscillator frequency, and the error signal is sent to the repeller of one of the two klystrons. The other klystron is frequency stabilized on the resonant cavity. Since the oscillator we use as reference has a relative stability of 10^{-6} and its frequency is of the order of 10^5 Hz, the instability in the frequency difference is lower than 1 Hz. Such a low instability does not contribute appreciably to the noise of the detection system. The frequency synchronization system we have set up is actually a passive phase comparator, so that the ripple on the klystron repeller is minimum. The reference signal and the input signal produced from the beat of the two waves reach this comparator. For the best linearity of the phase comparator the input signal must be as amplitude constant as possible as the frequency varies. Since many effects may affect the amplitude of a beat signal on a diode, we have introduced an automatic gain control system in the input. Because of this, our system is independent of the type of the diode and, in a limited range, from the beat frequency. Moreover, it gives the same response for an input signal in the range 25 mV to 1 V. The frequency range is 10 kHz to 1 MHz. If necessary, the range can be easily extended by about two orders of magnitude. The synchronization system we have just described allows one to perform highly accurate sweeps at microwave frequencies. The accuracy attainable by our apparatus is very useful in usual spectroscopy for resolving complex structures as occur in electron-spin double-resonance spectroscopy.

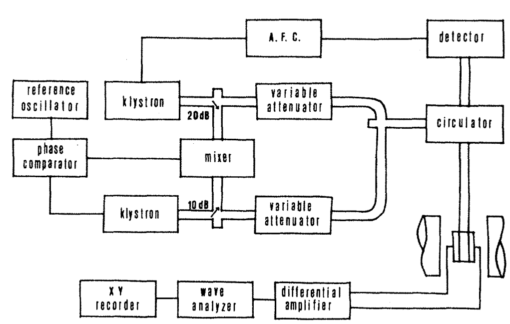

FIG. 1. Block diagram of electron-spin double-resonance spectrometer with longitudinal magnetization detection; ν_r and $\nu_s \simeq 9.5$ GHz.

We wish to emphasize that it is easy and very cheap to use the foregoing device to obtain a microwave frequency synthesizer, which can supply also high power at low noise levels. To this purpose, it is sufficient to get a microwave spectrum (with quartz-crystal stability) by means of an usual frequency multiplier; then we can phase lock to this spectrum an electronically tunable microwave source. The whole range of frequencies available from the microwave source can be continuously obtained by means of a low-frequency voltage-tunable oscillator giving the reference signal to the phase comparator.

We have frequency stabilized one klystron to the frequency of the cavity by an automatic frequency control system. Particular care is required, in order that the modulation index of the klystron is so low that a transfer of frequency modulation on the beat signal is negligible. A further difficulty arises since it is impossible to eliminate the signal due to the microwave reflection from the cavity to the stabilization crystal. The amplitude of the beat signal so produced is greater than the stabilization signal by some orders of magnitude. To overcome these two difficulties we used a low frequency of stabilization in order to separate as much as possible the two signals. The error signal for the frequency stabilization of the klystron was obtained with a lock-in amplifier Ithaco 391A, that has noticeable overload capabilities. To transfer the error signal from the low voltage to the high voltage of the repeller we used an optoelectronic device.[8] Thus, because of the high sensitivity of the stabilization system, the beat signal between the two klystrons was stable within 1 Hz.

The signal due to the longitudinal oscillating magnetization was detected by two coils with their axis parallel to the static magnetic field and placed in Helmoltz conditions on the walls of the cavity. We wish to emphasize the difference between this system and usual EPR spectrometers. In conventional spectrometers, the absorption signal is detected by a microwave diode (point-contact or Schottky-barrier diodes) which exhibits high noise levels for usual modulation frequencies. A better noise figure is obtained by the heterodyne detection method, which, however is not useful for power levels greater than some milliwatts. In our case, we have in the coils so low a noise level that we could detect signals up to few nanovolts without using phase detection techniques. The signal from the coils is amplified by a P.A.R. 114 preamplifier with the best noise contour at the coil impedance for the used frequencies.

The various harmonics of $\omega_r - \omega_s$ are selected and converted to the 10-kHz fixed frequency by a heterodyning system with about 0-dB gain. The output signal is observed by means of a General Radio 1900A wave analyzer.

IV. RESULTS AND DISCUSSION

In Fig. 2(a) we report experimental spectra relative to the oscillations of M_z at the frequency $\omega_r - \omega_s$. The spin system we used was that of oxipyrrol radical, obtained as described in Ref. 9. The frequencies ω_r and ω_s were fixed to give $(\omega_r - \omega_s)/2\pi = 100$ kHz while the magnetic field H_0 was varied. In Fig. 2(a) we show spectra obtained with different irradiation powers; for each spectrum, however, the same intensity of the magnetic fields of the two waves was fixed. We note that, for low power levels the signal has the usual absorption line shape. Increasing the microwave power produces a characteristic two-peak shape of the signal; a larger shift between the peaks is found for higher power levels.

In the actual experimental situation of Fig. 2(a), the intensity of the two waves was such that

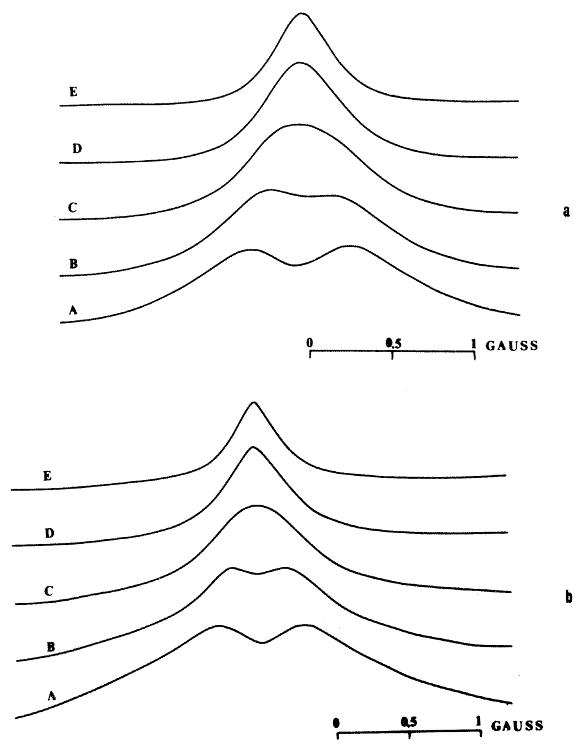

FIG. 2. Signal due to the longitudinal magnetization at $(\omega_r - \omega_s)/2\pi = 100$ kHz vs the magnetic static field, for all the spectra $\lambda_r = \lambda_s$. Different levels of irradiating power are used for each spectrum: (A) $\lambda_r/g\mu_B = 0.156$ G, (B) $\lambda_r/g\mu_B = 0.111$ G, (C) $\lambda_r/g\mu_B = 0.078$ G, (D) $\lambda_r/g\mu_B = 0.054$ G, (E) $\lambda_r/g\mu_B = 0.039$ G. Experimental spectra (a); theoretical spectra (b).

$\lambda_r/g\mu_B = 0.156$ G (A), 0.111 G (B), 0.078 G (C), 0.054 G (D), 0.039 G (E).

In Fig. 2(b) we report theoretical spectra, computed using the same parameters of Fig. 2(a). We have evaluated the relaxation times $T_1 = T_2 = 7.4 \times 10^{-7}$ sec, by means of a best-fit procedure. The theoretical spectra of Fig. 2(b) have been calculated as described in Sec. II; we have taken into account processes involving no more than 12 photons. Comparison between Figs. 2(a) and 2(b) shows a good agreement between experimental and theoretical results.

In Fig. 3 the intensity of first wave is constant to give $\lambda_s/g\mu_B = 0.156$ G, while the other changes according to the values of $\lambda_r/g\mu_B = 0.266$ G (A), 0.197 G (B), 0.156 G (C), 0.123 G (D), 0.093 G (E), 0.056 G (F).

The relevant features of Fig. 3 are as follows: (i) the two peaks shift as the intensity increases; (ii) because of the saturation effect, the signals decrease; (iii) a remarkable asymmetry between the two peaks is observed.

We wish to emphasize that the higher peak corresponds to the more intense wave, provided saturation effects are negligible. We also explicitly note that the shift between the peaks allows us to determine the contribution of each of the two waves to the whole signal. Obviously this is not possible if only one peak is detectable, as it is found, for low power levels. The theory of Sec. II gives a good agreement with the spectra of Fig. 3, but for simplicity we do not report here detailed theoretical results.

In a further series of experiments we have studied the signal due to the components of M_z oscillating at frequencies $n(\omega_r - \omega_s)$; in this series of spectra we have also varied the frequency $\omega_r - \omega_s$. Using a Hewlett-Packard wave analyzer 3590A, we have been able to detect signals involving up to 22 photons. Unfortunately we cannot quantitatively compare the experimental intensities with the theory, because of the strong nonlinear response of the detection system.

We can note, however, a remarkable qualitative agreement with the theory. In fact, the intensities of the harmonics decrease as n increases for low irradiation power. For high power, the harmonics corresponding to low-n values are more saturated. In Fig. 4, we report the signal for $n = 1, 2,$

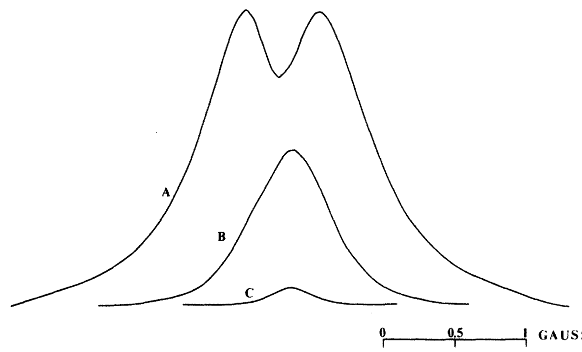

FIG. 4. Signal due to the longitudinal magnetization at frequencies $n(\omega_r - \omega_s)$, with $(\omega_r - \omega_s)/2\pi = 100$ kHz. (a) $n = 1$, (b) $n = 2$, (c) $n = 3$.

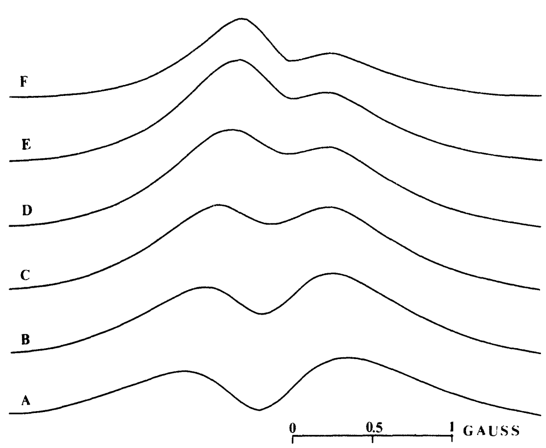

FIG. 3. Signal due to the longitudinal magnetization at $(\omega_r - \omega_s)/2\pi = 100$ kHz vs magnetic static field. All the spectra are taken for the same $\lambda_s/g\mu_B = 0.156$; λ_r varies so that: (A) $\lambda_r/g\mu_B = 0.266$ G, (B) $\lambda_r/g\mu_B = 0.197$ G, (C) $\lambda_r/g\mu_B = 0.156$ G, (D) $\lambda_r/g\mu_B = 0.123$ G, (E) $\lambda_r/g\mu_B = 0.093$ G, (F) $\lambda_r/g\mu_B = 0.056$ G.

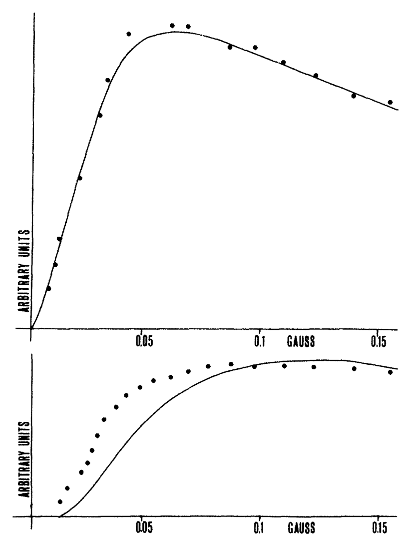

FIG. 5. Signal intensities in the center of the line for $n = 1$ and $n = 2$ vs $\lambda_r/g\mu_B$. Measures were taken with $(\omega_r - \omega_s)/2\pi = 100$ kHz and $\lambda_s = \lambda_r$.

3. Figure 4 clearly shows the different saturation effects on the line shape for $n=1$ and $n=2, 3$.

Anyhow, it has been observed that, for fixed incident power, while $\omega_r - \omega_s$ decreases, also the harmonics higher than $n=1$ get the characteristic two-peaked shape. In particular, for $(\omega_r - \omega_s)/2\pi = 44.5$ kHz, this effect was detected for the second and the third harmonic. In Fig. 5 we report the values of the signal intensities in the center of the line $n=1$ and $n=2$ vs $\lambda_s/g\mu_B = \lambda_r/g\mu_B$.

It is demonstrated that the saturation effect on the maximum of the two signals is different for the two harmonics. The theory fits satisfactorily both the curves for $n=1$ and $n=2$ of Fig. 5. However a direct comparison between the two curves of Fig. 5 it is not possible, due to the nonlinearity of the detection system. We note that the maximum of the curve for $n=1$ is found at smaller values of $\lambda_r/g\mu_B$ than the maximum of $n=2$, because of the different saturation effects on the two harmonics.

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