Observations of Bistability Effects in Electron Paramagnetic Resonance Experiments

M. Giordano, M. Martinelli, and L. Pardi
Dipartimento di Fisica dell'Università, Gruppo Nazionale e Centro Interuniversitario di Struttura della Materia, Pisa, Italy

and

S. Santucci
Dipartimento di Fisica dell'Università, Gruppo Nazionale e Centro Interuniversitario di Struttura della Materia, Perugia, Italy
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Bistability effects have been observed in electron-paramagnetic-resonance spectroscopy. When the sample amounts are varied, different instability regimes are detected. The homogeneous profile of the cavity resonator assumes a characteristic double-well pattern when a proper number of paramagnetic centers is put inside the cavity under magnetic resonance conditions. Saturation is not a requirement for the observation of the effect. Hysteresis loops arise from concurrence of this cavity profile and feedback effects of the spectrometer circuitry. Numerical calculations account well for the observed phenomena.

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A growing interest has arisen in bistability effects since their first observation,[1] subsequent to the theoretical predictions of this phenomenon.[2,3] Particular applications are optical digital computing and switching, and in a basic physics context, instabilities and chaos.[4] Since these effects deal with radiation-induced nonlinear behavior of dispersion or absorption in different materials, most of the pertinent literature concerns the optical field, where powerful sources are available. Far less attention has been paid to effects at radio frequency or microwave wavelengths.[5] Only a few papers have been devoted to bistability in the presence of magnetic resonance,[6] and these report self-induced laser activities in a solid with strongly polarized nuclear spins.

In this paper we report the first observation, to our knowledge, of bistability effects in electron-paramagnetic-resonance (EPR) experiments. The peculiar observed behavior arises from the generation of a spectral hole in the homogeneous cavity profile. The double-well pattern observed under proper conditions does not require saturation of the sample. Some preliminary theoretical predictions are also reported that account for the physical effect causing bistability phenomena.

The measurements were performed by means of a standard spectrometer, Bruker model ER200 D. Experiments were carried out with different amounts of the same paramagnetic sample (the electrolytically produced polypyrrole radical[7]). This is equivalent to having different filling-factor values in the resonant cavity.[8] The microwave irradiation power P_i was set in order to avoid any saturation effect in the spectra.

Figure 1 shows the results of such measurements. It is worth noting, that, while with small sample amounts (i.e., for the small values of the filling factor η) the signal is just the one expected in EPR spectroscopy, with a larger number of active paramagnetic centers (i.e., higher values of η), a characteristic signal appears. The peculiarities of this signal are the following: (i) There is evidence of discontinuities in the system response. (ii) Hysteresis phenomena are observed by sweeping of the magnetic field back and forth across the resonance. The hysteresis loop is always obtained when the number of paramagnetic centers used in measurements is varied in

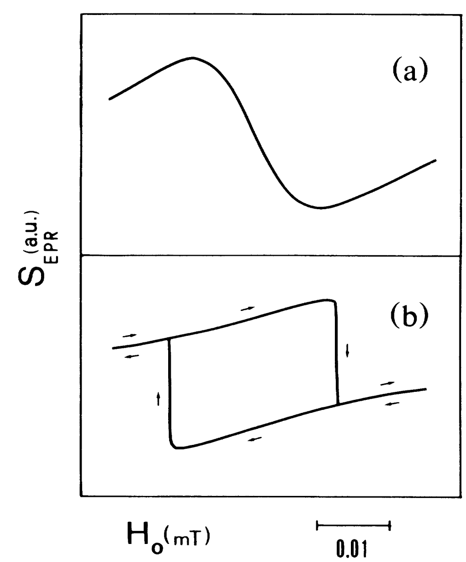

FIG. 1. EPR signal S_{EPR} (arbitrary units) obtained with samples containing different quantities of paramagnetic centers: (a) 5×10^{15} spins, (b) 10^{18} spins. The sample is the electrolytical radical of polypyrrole. Spectra are obtained by sweeping of the magnetic field H_0 back and forth across the resonance. The irradiating power P_i is 2×10^{-6} W.

a wide range; however, the width of the hysteresis loop changes according to the η value. (iii) Saturation of the sample is not required in order to observe the phenomenon.

Figure 2 shows the values of the irradiating frequency ω_s versus the magnetic field. It is important to notice that this measurement corresponds to determination of the resonant frequency of the sample cavity, since in EPR spectrometers the microwave oscillator is locked to the cavity resonance by an electronic automatic frequency-control system.[9] The frequencies have been measured by a microwave frequency counter, Systron Donner model 6054B, during the EPR experiments corresponding to the results of Fig. 1.

While the pattern is not reported for the case of the sample with a smaller number of paramagnetic centers, where the cavity frequency is essentially unaffected by the sample resonance, remarkable variations are measured in the case of the sample with a high number of spins. These variations follow the pattern of the EPR signal for the same sample.

In standard EPR experiments, the cavity containing the sample is part of a reflection microwave bridge. The microwave power reaching the detector is obtained from the power-reflection coefficient

$$\mathcal{R}(\omega) = P_r/P_i,$$

where P_i is the power incident on the cavity and P_r is the amount reflected back from the cavity to the detector. The resonance signal is obtained just by the change of $\mathcal{R}(\omega)$ when the static field H_0 is varied across the resonant values.

A better insight into the phenomenon is obtained when the field-swept experiments of Figs. 1 and 2 are combined with frequency-swept measurements. Figure 3 shows the pattern of the cavity power-reflection coefficient $\mathcal{R}(\omega)$ as a function of the frequency. In this experiment the microwave source, no longer locked to the cavity, performs a precise frequency sweep close to the cavity resonance, driven by a Hewlett-Packard synchronizer model 5344A. The magnetic field in each experiment assumes fixed values in order to give Larmor frequencies ω_0 nearly coincident with the resonance frequency of the cavity. These values are measured by a nuclear magnetic resonance gaussmeter, Bruker model ER035M. The quantity $\mathcal{R}(\omega)$ is accurately measured by a power meter, Marconi model 6960, equipped with a sensor, model 6920. Also in this case, $\mathcal{R}(\omega)$ has the expected pattern only when the small sample is studied [Fig. 3(a)]. In the other two cases where the sample with a larger number of spins is used, the cavity, besides the usual minimum, shows an additional dip whose position depends on the value of the selected Larmor frequency. In particular we notice that when $\omega_0 = \omega_c$, the two peaks are symmetrically distributed with respect to ω_c.

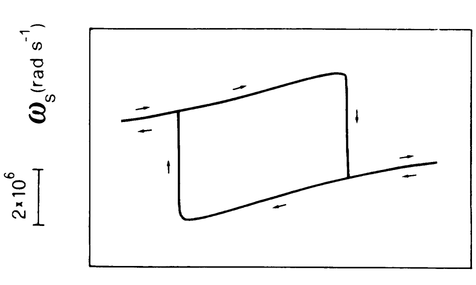

FIG. 2. Variations of the frequency ω_s of the microwave oscillator locked to the resonance of the cavity, measured during a paramagnetic resonance experiment. The experimental conditions are the same as in Fig. 1(b).

The explanation of the above-described phenomena requires a detailed consideration of the overall response of the resonator when strongly coupled to the sample under magnetic resonance conditions; the details and complete results of this study will appear elsewhere. Here we show some results that, although preliminary, are, however, sufficient to realize the phenomenon and to explain the establishment of the bistability regime.

In our experimental conditions, the function $\mathcal{R}(\omega)$ can be calculated by consideration of the cavity as a quadrupole and by use of the scattering-matrix formalism.[10]

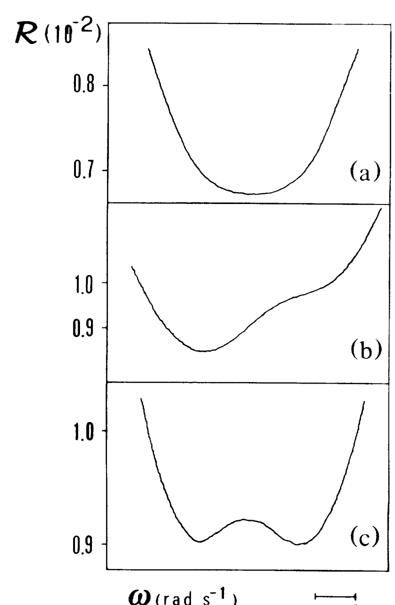

FIG. 3. Measurements of the cavity power reflection coefficient $\mathcal{R}$ variations vs the frequency, near the cavity resonance frequency. The cavity contains different quantities of polypyrrole radicals under magnetic resonance conditions: (a) 5×10^{15} spins and $\omega_0=\omega_c$, (b) 10^{18} spins and $\omega_0-\omega_c=8.1\times10^5$ rad s^{-1}, (c) 10^{18} spins and $\omega_0=\omega_c$. In all cases $P_i=2\times10^{-6}$ W.

The result of this calculation gives

$$\mathcal{R}(\omega)=(a^2-2a)/(1+b^2)+1,$$

with

$$a=\frac{1}{1+Q_0\eta\chi''},\quad b=\frac{2Q_0[\omega(1+\chi'\eta/2)-\omega_c]}{\omega_c(1+Q_0\eta\chi'')}.$$

Here ω is the instantaneous microwave angular frequency; ω_c and Q_0 are the cavity resonant frequency and quality factor, respectively, when the sample is out of resonance; χ' and χ'' are the real and imaginary parts, respectively, of the complex susceptibility of the spin system. Since we look for the effects of the coupling between spin system and cavity, we can consider a new parameter A that accounts for the quantities that contribute to this coupling, and rewrite the expressions for a and b as

$$a=[1+Q_0Af(\omega)]^{-1},$$

$$b=\frac{2Q_0\{\omega[1+(\omega-\omega_0)T_2Af(\omega)/2]-\omega_0\}}{\omega_c[1+Q_0Af(\omega)]},$$

where

$$f(\omega)=[1+(\omega-\omega_0)^2T_2^2+S]^{-1}.$$

Here ω_0 is the Larmor frequency; $S=g\mu_\mathrm{B}H_1^2T_1T_2$ is the saturation factor with g the magnetogyric factor, μ_B the Bohr magneton, H_1 the magnetic field intensity of the irradiating wave in the rotating frame, and T_1 and T_2 the longitudinal and transverse relaxation times of the spin system, respectively. A detailed numerical computation of $\mathcal{R}(\omega)$ shows the existence of a critical threshold A_c for the parameter A. In fact, if we consider $\omega_0=\omega_c$, for $A<A_c$, the function $\mathcal{R}(\omega)$ presents the usual minimum occurring at $\omega=\omega_c$; if, on the contrary, $A>A_c$, the function $\mathcal{R}(\omega)$ presents two minima symmetrically positioned with respect to the frequency $\omega=\omega_c$ where a relative maximum is now located. The separation between the two minima increases with A values.

In the same way, when $\omega_0\neq\omega_c$ and $A>A_c$, the two relative minima are no longer symmetric and are located near ω_c and ω_0, respectively.

These theoretical conclusions throw light on the experimental results of Fig. 3. These are indeed well understood by asserting that the sample used for the case of Fig. 3(a) corresponds to values of the parameter $A<A_c$; in the other two cases we have, on the contrary, $A>A_c$.

The mechanism which we have described generates a spectral hole that is tuned by the magnetic field through the homogeneous profile of the cavity. A similar effect has been observed in a homogeneously broadened optical-absorption line[11] and in homogeneously broadened laser-gain profiles where it is connected to intabilities and multifrequency emission.[12] In these cases, however, and generally in instability effects observed up to now, the phenomenon is driven by the coupling between a resonator and the nonlinear absorption or dispersion of a medium submitted to a strong resonant irradiation. In our case the physical origin of the phenomenon is different since the double-well cavity profile is observed, when a proper amount of resonating system is present, even in the low-saturation limit for the sample. The physical basis of the effect which we have observed seems to be rather the nonlinear behavior of the sample-cavity coupling.

As regards the observed hysteresis effects, they are interpreted by our taking into account the feedback effects of the automatic frequency-control system that locks the microwave oscillator to the cavity resonance frequency. The locking point, as a rule, is the minimum of the reflection coefficient $\mathcal{R}(\omega)$. If, however, the experimental conditions give values $A>A_c$, a single minimum is no longer found and, according to the shape, position, and intensity of the second minimum, an instability regime is established in the whole cavity-electronic feedback apparatus. Excess noise is then expected and jumps between the minimum near ω_c and the one near ω_0 are predicted each time the motion of these minima, according to the variations of the magnetic field, produces a flex point in the cavity profile. These jumps account for the results of Fig. 2 and they, in turn, explain the pattern of the EPR signal reported in Fig. 1(b). The alternation of the minimum where the oscillator is initially locked when the back-and-forth field sweep is applied gives rise to the hysteresis phenomena.

If the sample undergoes saturation effects, and these affect the shape of the minimum driven by the magnetic field, the resultant hysteresis loop is modified and its width decreases with increasing saturation of the paramagnetic system.

In summary, we have observed for the first time a peculiar effect, where the homogeneous profile of a microwave resonator is affected by a spectral hole when it is coupled with a sufficiently large number of resonating spin systems. This effect does not require any saturation of the sample, is quite general, and can be encountered each time two resonating elements are strongly coupled. The concurrence of this effect and the feedback circuitry of spectrometers gives rise to instability and hysteresis phenomena.

Further investigations are in progress about the influence of magnetic resonance conditions on this new effect and the noise effects on switching characteristics. Applications to optical spectroscopy and laser stability fields are also being evaluated.

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