Hole burning in a well-characterized noise field: Nonadherence to the Bloch equations

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Applicability of the Bloch equations for describing relaxation in the saturation regime is studied experimentally and theoretically. Hole burning in the proton NMR line of water was observed, and the shape and width of the hole were investigated in a well-characterized noise field. The behavior of power broadening is remarkably different from that expected from the Bloch equations and strongly depends on the correlation time of the noise field. The hole shape is not a single Lorentzian. The experimental results are well explained by a stochastic theory of power broadening. We show that the hole burning in well-characterized noise fields is very useful for the experimental test of power-broadening theories.

I. INTRODUCTION

Spectroscopic studies concerned with the interaction between a quantum system and the electromagnetic field have played an important role in science. One of the most useful approaches in spectroscopy is the study of relaxation phenomena in fluctuating fields. These appear in nuclear magnetic resonance (NMR), electron spin resonance (ESR), optical or laser spectroscopy, and others.

For the test of relaxation theories, an experimental study of the relaxation in an artificially generated noise field, whose statistical properties are known and can be controlled, is significant. Since the time evolution of the spin system can be fully monitored, the study of NMR relaxation in a two-level (spin-$\frac{1}{2}$) system interacting with a coherent rf field best serves as such an experiment. Recently, we reported experiments on phase relaxation in time domain[1] and motional narrowing in frequency domain,[2] and showed that these experimental approaches could be used to verify relaxation theories. In NMR,[3–5] ESR,[6] and optical[7–9] experiments, the noise field has been used as an excitation field. In our experiments, the noise of the magnetic field (frequency) is applied as an external fluctuation, while the excitation field is a coherent one. This is different from earlier experiments, in some of which the relaxation phenomena were examined.

In the present paper, an NMR spectral hole-burning experiment is reported. Power broadening of the hole shape was observed in a well-characterized noise field. The line shape and the linewidth from the hole-burning experiment were compared with those expected from the Bloch equations.

In 1983, DeVoe and Brewer[10] studied the power dependence of optical free induction decay in Pr^{3+}:LaF_3, which cannot be explained by the conventional optical Bloch equations in the saturation regime. Since then, various theories have been proposed to explain the experimental results.[11–20] However, only a few experimental tests have been reported,[21] and those theories have not been verified sufficiently. The saturation is a universal problem, which appears in the interaction between any quantum system and the electromagnetic field. Here, we report the power broadening of the hole shape in NMR spectroscopy, and study the applicability of the Bloch equations and how important the details of the dephasing perturbations are. We show that the hole-burning in well-characterized noise fields is a powerful method for the experimental test of power-broadening theories.

The line shape $I(\omega)$ from the stationary solution of the Bloch equations is Lorentzian;[22,23]

$$I(\omega)=\frac{\chi^2 T_1/T_2}{\omega^2+T_2^{-2}+\chi^2 T_1/T_2} \ . \tag{1}$$

The linewidth $\delta\nu$ (half width at half maximum, HWHM) is given by

$$2\pi\delta\nu=\sqrt{(1/T_2)^2+(T_1/T_2)\chi^2} \ , \tag{2}$$

where T_1, T_2, and χ represent the longitudinal relaxation time, the transverse relaxation time, and the Rabi frequency, respectively. In NMR, the Rabi frequency is equal to γH_1, where γ is the gyromagnetic ratio and H_1 is the amplitude of the rf field. The width given by Eq. (2) is determined by T_1 and T_2 only. It does not depend on the statistical properties of the fluctuations. It is interesting to examine whether the line shape and width are the same in cases with the same T_1 and T_2 but with different correlation times of the fluctuations. To clarify this, we studied hole shapes for different values of the correlation time. The shape and width of the hole are discussed experimentally and theoretically.

II. EXPERIMENT

Hole burning in the proton NMR line of water was observed at room temperature. A pulsed NMR spectrometer operating at 11 MHz was employed. The width of the resonance line is increased by an external inhomogeneous magnetic field. The hole is burned by a long-and-weak "write" pulse and is monitored by a short-and-strong "read" pulse as a free-induction-decay (FID) signal. The widths of the write and read pulses are 50 msec and 12 μsec, respectively. The delay between the end of the write pulse and the start of the read pulse is 5 msec. The value of $\chi/2\pi$ for the write pulse is varied from 20 Hz to 7 kHz, while that for the read pulse is fixed at 20 kHz. The FID signals are phase sensitively detected (PSD) and averaged. The hole spectrum is the Fourier transform of the FID signal.

The wave form of the noise field is synthesized by a computer using random numbers and fed into a digital-to-analog converter (20 MSa/sec). A current proportional to the amplitude of the wave form is supplied to a coil, which generates a controllable fluctuation of the magnetic field (noise field). The noise field is parallel to the static field ($\sim$ 0.26 T) and consequently creates a fluctuation in the Larmor frequency of the proton spins. The noise field is supplied during the time interval from the start of the write pulse to the start of the read pulse (55 msec).

The hole-burning experiment is performed in a Gaussian noise field, whose wave form is prepared by the transformation method[24] of random numbers. Here "Gaussian" means that the distribution function of the fluctuating field has a Gaussian shape. The noise field is a pulsed longitudinal fluctuating field $\delta H_z(t)$, which is described by random sudden jumps among different field values and time duration, which is characterized by a lifetime τ_c. The frequency fluctuation $\delta\omega(t)$ is $\gamma\delta H_z(t)$. The Larmor frequency fluctuates over a range of values. The width Δ_G of this Gaussian frequency distribution is defined as $\Delta_G^2 = \langle \delta\omega^2 \rangle$.

In our experiment, the values of T_1 and T_2 were 25 msec and 1.0 msec, respectively. The value of T_1, which was measured by saturation recovery, was determined by the concentration of copper sulfate. The value of T_2, which was measured by Hahn spin-echo decay, was set at 1.0 msec by adjusting the Δ_G for different values of the correlation time. The decay curves were exponential in all experiments.

III. RESULTS

The observed hole spectrum in a Gaussian noise field for $\chi/2\pi = 0.44$ kHz and $\tau_c = 200$ μsec ($\chi\tau_c = 0.6$) is shown in

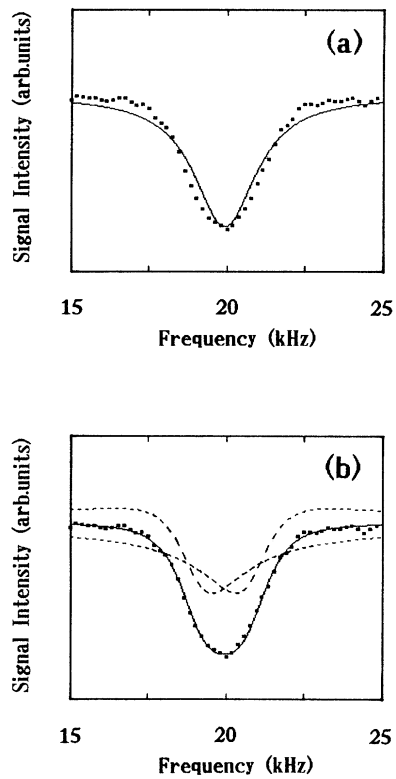

FIG. 1. Hole spectrum in a Gaussian noise field for $\chi/2\pi = 0.44$ kHz and $\tau_c = 200$ μsec ($\chi\tau_c = 0.6$). (a) Single Lorentzian fit. (b) Fit with Eq. (7). The broken lines show the contributions from the two terms in Eq. (7).

Fig. 1, where the center frequency is shifted by 20 kHz because the frequency of the read pulse and PSD is shifted by 20 kHz from that of the write pulse at the exact resonance. The FID signal is obtained by off-resonance excitation and detection. As is seen in Fig. 1(a), a single Lorentzian does not fit the experimental line. In Fig. 2 Rabi-frequency ($\chi = \gamma H_1$) dependences of the hole spectrum are shown, where the results for two different correlation times (τ_c is the inverse of the jumping rate) are shown. It is apparent that the power broadening for $\tau_c = 200$ μsec is smaller than for $\tau_c = 20$ μsec. These results are not predicted by the Bloch equations.

Rabi-frequency dependences of the HWHM linewidth for $\tau_c = 20$, 40, 80, and 200 μsec are shown in Fig. 3. The broken line in Fig. 3 is calculated from Eq. (2). The observed power broadening depends strongly on correlation time. The linewidth for large values of χ is much smaller than that expected from the Bloch equations.

IV. DISCUSSION

A. Stochastic theory of power broadening

We consider a stochastic theory of power broadening employing the stochastic theory of coherent transients by Hanamura,[11,12] which is valid for $T_1, T_2 \gg \tau_c, 1/\chi$. We derived the shape and width of the hole in terms of the dressed

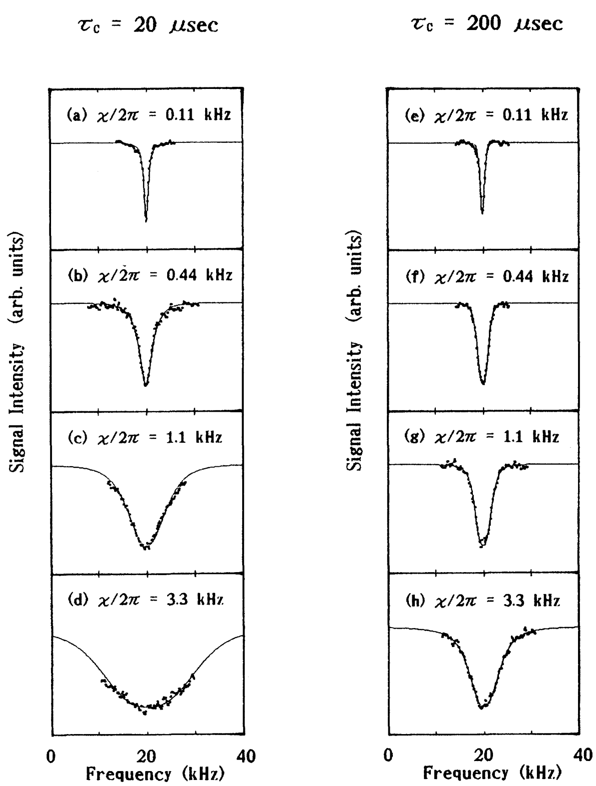

FIG. 2. Rabi-frequency ($\chi=\gamma H_1$) dependences of the hole spectrum in a Gaussian noise field for the two values of the correlation time ($\tau_c=20$ and 200 μsec). The solid lines are fitting curves with Eq. (7).

atom picture following the above theory.[11,12] Equations of motion for the density operators of a two-level system (lower level a and upper level b) are considered under the coherent field action (frequency ω_0) and the Gaussian-Markoffian frequency modulation. The density matrix elements in a rotating frame, which rotates with the off-resonant Rabi frequency Ω, are derived by the following transformation [Eqs. (5) in Ref. 12]:

$$|1\rangle=\cos\theta|b\rangle+\sin\theta|a\rangle,$$
$$|2\rangle=-\sin\theta|b\rangle+\cos\theta|a\rangle, \tag{3}$$

where $\tan2\theta=-\chi/\Delta$, $\Delta=\omega_{ba}-\omega_0$, and $\Omega=\sqrt{\Delta^2+\chi^2}$. Here, we start from the stationary solution in this rotating frame [Eqs. (9) in Ref. 12];

$$\rho_{12}=\rho_{21}=0,$$
$$\rho_{11}-\rho_{22}=\frac{-2\Gamma\cos2\theta}{\Gamma(1+\cos^2 2\theta)+\Gamma''\sin^2 2\theta}\ , \tag{4}$$

where $\Gamma''=\Gamma'/(1+\Omega^2\tau_c^2)$, 2Γ is the longitudinal relaxation rate ($1/T_1=2\Gamma$), and Γ' is the phase relaxation rate due to the frequency fluctuation ($1/T_2=\Gamma+\Gamma'$).

The hole shape is obtained from $\rho_{bb}-\rho_{aa}$, while the decay curves of coherent transients is from ρ_{ab}, as shown in Refs. 11 and 12. The stationary solution of $\rho_{bb}-\rho_{aa}$ is derived using the stationary solution Eqs. (4) and the inverse transformation of Eqs. (3) as

$$\rho_{bb}-\rho_{aa}=\frac{-\Delta^2}{\Delta^2+\chi^2(\Gamma+\Gamma'')/2\Gamma}\ . \tag{5}$$

The line shape $I(\omega)$ is given by

$$\begin{aligned}I(\omega)&=\rho_{bb}-\rho_{aa}+1\\&=\frac{\chi^2(\Gamma+\Gamma'')}{2\Gamma\omega^2+\chi^2(\Gamma+\Gamma'')}\\&=\frac{\chi^2\omega^2+\chi^4+(2T_1/T_2+1)\chi^2/\tau_c^2}{2\omega^4+(3\chi^2+2/\tau_c^2)\omega^2+\chi^4+(2T_1/T_2+1)\chi^2/\tau_c^2}\ ,\end{aligned} \tag{6}$$

where Δ is replaced by ω.

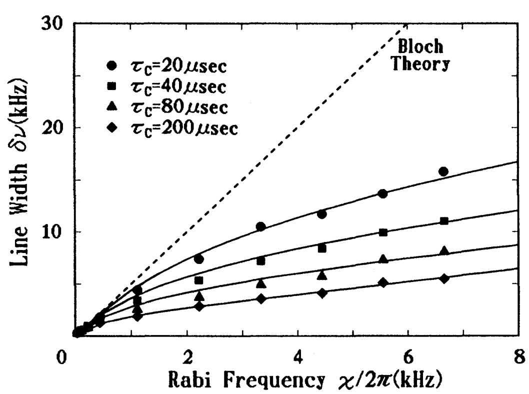

FIG. 3. Rabi-frequency ($\chi=\gamma H_1$) dependences of the linewidth (HWHM) for $\tau_c=20$, 40, 80, and 200 μsec. The values of T_1 and T_2 are 25 msec and 1.0 msec, respectively, in all cases. The broken and solid lines are theoretical curves calculated from Eqs. (2) and (9), respectively.

B. Line shape

In general, the line shape by Eq. (6) is the sum of two Lorentzians; the cases of weak and strong fields differ, however. For the case of $\chi\tau_c<x_0$ (weak field), where $x_0=\sqrt{4T_1/T_2}+\sqrt{4T_1/T_2-2}\simeq4\sqrt{T_1/T_2}$ ($T_1\gg T_2$) and $x_0\simeq20$ in our case, the line shape becomes

$$I(\omega)=\frac{c\ \omega+d}{(\omega+\beta)^2+\alpha^2}+\frac{-c\ \omega+d}{(\omega-\beta)^2+\alpha^2}\ , \tag{7}$$

where $\alpha^2\tau_c^2=xy/4+(3x^2+2)/8$, $\beta^2\tau_c^2=xy/4-(3x^2+2)/8$, $c\tau_c=x(y-x)/8\beta\tau_c$, $d\tau_c^2=xy/4$, $y^2=2(x^2+2T_1/T_2+1)$, and $x=\chi\tau_c$. This line shape is the sum of two Lorentzians whose linewidths are the same but whose center frequencies are shifted by $\pm\beta$.

The solid line in Fig. 1(b) is the theoretical line shape calculated from Eq. (7). The broken lines show the contributions from the two terms in $I(\omega)$. The non-Lorentzian line shape observed in the experiment is well explained by Eq. (7). The solid lines in Fig. 2 are fitting curves with Eq. (7).

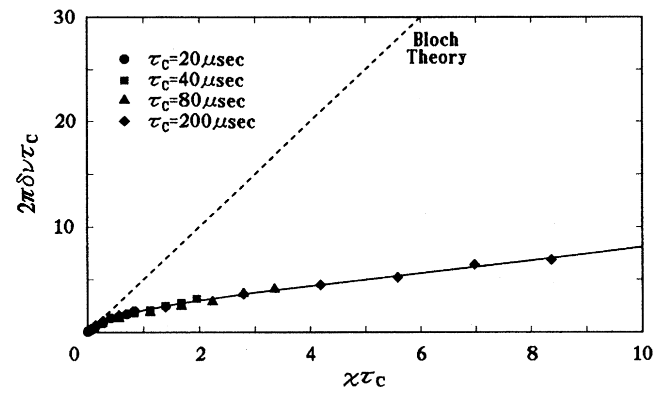

FIG. 4. Normalized plot of the linewidth. The linewidth and the Rabi frequency in Fig. 3 are normalized by the correlation time τ_c. The broken and solid lines are theoretical curves calculated from Eqs. (2) and (9), respectively.

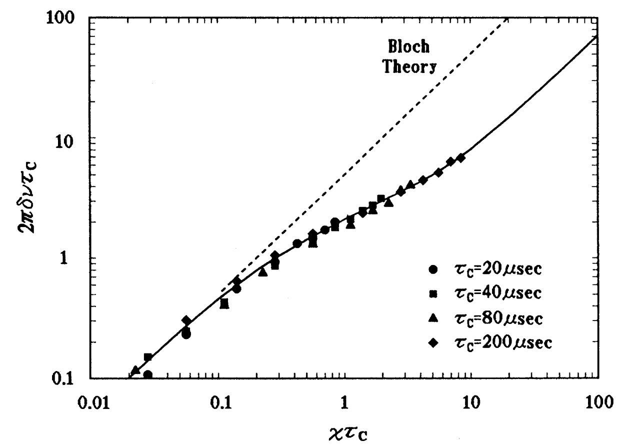

FIG. 5. Logarithmic plot of Fig. 4. The broken and solid lines are theoretical curves calculated from Eqs. (2) and (9), respectively.

For the case of $\chi\tau_c > x_0$ (strong field), on the other hand, the line shape is given by

$$I(\omega)=\frac{e_+}{\omega^2+\gamma_+^2}+\frac{e_-}{\omega^2+\gamma_-^2}\ , \tag{8}$$

where $\gamma_\pm^2\tau_c^2=(3x^2+2)/4\pm\frac{1}{4}\sqrt{(x^2+2)^2-16(T_1/T_2)x^2}$, $e_\pm\tau_c^2=\mp x^2(x^2+2T_1/T_2+1-\gamma_\pm^2\tau_c^2)/2(\gamma_+^2-\gamma_-^2)\tau_c^2$, and $x=\chi\tau_c$. The line shape is again the sum of two Lorentzians. In this situation the center frequencies are the same, but the linewidths are different. In the limiting case of $\chi\tau_c \gg x_0$, Eq. (8) becomes $I(\omega)=(\chi^2/2)/(\omega^2+\chi^2/2)$, a single Lorentzian with a linewidth $(1/\sqrt{2})\ \chi$. In our experiment, unfortunately, all data were taken in weak fields because of the instrumental limitation. For this reason this limit has no experimental test.

C. Linewidth

Next we consider the linewidth. The HWHM linewidth $\delta\nu$ from Eq. (6) is

$$2\pi\delta\nu\tau_c=\tfrac{1}{2}\sqrt{\sqrt{(3x^2+2)^2+16(T_1/T_2)x^2}-(x^2+2)}\ , \tag{9}$$

where $x=\chi\tau_c$. This expression is applicable both for weak and strong fields. When $\chi\tau_c \gg 1$, Eq. (9) becomes $2\pi\delta\nu=(1/\sqrt{2})\ \chi$, while the Bloch linewidth is $\sqrt{T_1/T_2}\ \chi$. Similar results to Eq. (9) can be derived from Refs. 14 and 17–19 in the limit of $T_1, T_2 \gg \tau_c, 1/\chi$. A plot of the linewidth is shown in Fig. 4, where the linewidth and the Rabi frequency in Fig. 3 are normalized by the correlation time τ_c. The experimental data for different τ_c are on the same curve. A logarithmic plot of Fig. 4 is shown in Fig. 5. The observed values of the linewidth strongly deviate from that expected from the Bloch equations for $\chi\tau_c \gtrsim 1$. The solid lines in Figs. 3, 4, and 5 are the theoretical curves calculated from Eq. (9). They fit the experimental results very well.

Our experiments correspond to the case of $T_2 \gg \tau_c$ and are explained well by the above stochastic theory of power broadening. The optical experiment by DeVoe and Brewer,[10] on the other hand, may correspond to the case of $T_2 \approx \tau_c$. It is very interesting to test theories of power broadening for that case. However, it should be noted that the decay curve of the transverse relaxation is expected to be nonexponential,[25] in which case the Bloch equations are not applicable even for $\chi\tau_c < 1$.

V. SUMMARY

An experimental approach for the verification of power-broadening theories is presented. Hole burning in a proton NMR line was observed, and power broadening of the hole shape was studied experimentally and theoretically. In the case of $\chi\tau_c \gtrsim 1$, the observed linewidth deviates from that predicted by the Bloch equations, and the line shape is not a single Lorentzian. The experimental results are explained by a stochastic theory in which the effect of the correlation time of the fluctuation is taken into consideration.

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