Hole burning in well-defined noise fields: Motional narrowing

T. Kohmoto, Y. Fukuda, and M. Kunitomo
Department of Physics, Faculty of Science, Kobe University, Nada-ku, Kobe 657, Japan

K. Ishikawa
Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657, Japan

M. Tanigawa
Department of Physics, Faculty of Science, Kyoto Sangyo University, Kita-ku, Kyoto 603, Japan

K. Ebina
Division of Natural Environment and Physics, Faculty of Human Development, Kobe University, Nada-ku, Kobe 657, Japan

M. Kaburagi
Department of Informatics, Faculty of Cross-Cultural Studies, Kobe University, Nada-ku, Kobe 657, Japan
(Received 18 November 1993)

Hole burning in the proton NMR line in water was observed in well-defined noise fields. The hole shape was measured in two-state and Gaussian noise fields. The jumping-time dependences of the hole shape were well explained by the theory of motional narrowing and the conventional stochastic theory of relaxation. This approach is very useful for the experimental test of relaxation theories.

Relaxation phenomena in spectroscopy give much useful information on various physical systems, which include atoms, molecules, and condensed matter, through the interaction between the two-level system and the electromagnetic field. The relaxation phenomena commonly appear in experiments such as nuclear magnetic resonance (NMR), electron spin resonance (ESR), and optical or laser spectroscopy. Statistical and dynamical properties of the system can be derived from the analysis of the local field fluctuations. Many theories[1–5] of relaxation in the fluctuating local field have been considered for the investigation of various type of relaxation and used for the explanation of experimental results.

For the experimental test of relaxation theories and for the interpretation of experimental results which have no conventional theory to apply, an experimental study of relaxation phenomena in artificially generated noise fields, whose statistical properties are well known and can be controlled, is very useful. To carry out this experimental approach, the study of NMR relaxation phenomena in a two-level (spin-$\frac{1}{2}$) system interacting with a coherent rf field is suitable since the time evolution of the system can be fully monitored. This type of study has not been carried out so far. Recently, we studied phase relaxation both experimentally and theoretically in a two-state pulsed noise field.[6] The applicable condition of the conventional stochastic theory was made clear, and the importance of the statistics of fluctuation in the problem of relaxation was visualized. Noise field has been used, in a way different from our case, as an excitation field itself both in magnetic-resonance[7–9] and optical[10–12] experiments.

In the present paper, we observed *hole burning in the proton NMR line* in water. The hole shape was measured in well-defined fluctuating fields. The characteristic time of the fluctuation was changed, and *motional narrowing of the hole shape* was demonstrated clearly both in *a two-state noise field* and *a Gaussian noise field.* The experimental results were in good agreement with the theory of motional narrowing and the conventional stochastic theory. We show that the hole burning in well-defined noise fields is a powerful method for the experimental test of relaxation theories.

The hole-burning experiment is done by using a pulsed NMR spectrometer operating at 11 MHz. The longitudinal relaxation time of proton in water is 25 msec in our sample as determined by the concentration of copper-sulfate impurity. The width of resonance line is increased by an external inhomogeneous magnetic field. The hole is burned by a long-and-weak "write" pulse and is read out by a short-and-strong "read" pulse as a free-induction-decay (FID) signal. The pulse widths of the write and read pulses are 50 msec and 10 μsec, respectively, and the time separation between the end of the write pulse and the read pulse is 5 msec. The FID signals are phase-sensitively detected (PSD) and averaged by a signal averager. The hole spectrum is obtained from the Fourier transform of the FID signal.

The wave form of the noise field is synthesized by a personal computer using random numbers and fed into a digital-to-analog converter (20 MHz). A current proportional to the amplitude of the wave form is supplied to a coil which generates the controllable fluctuation of the magnetic field (noise field). The noise field is parallel to the static field (2.6 kOe) and gives a fluctuation in the Larmor frequency of the proton spins. The noise field is

0163-1829/94/49(21)/15352(4)/$06.00

supplied for the time interval from the start of the write pulse to the start of the read pulse.

The hole spectra obtained in *a two-state noise field* are shown in Fig. 1. The two-state noise here is a pulsed longitudinal fluctuation. The fluctuating field $\delta H_z(t)$ is described by random sudden jumps between two field values of magnitude h_z and time duration characterized by a lifetime τ. Then the frequency fluctuation $\delta w(t)$ is $\gamma \delta H_z(t)$, where γ is the gyromagnetic ratio. In Fig. 1 the frequency difference between the two states is fixed at $\Delta/2\pi = \gamma h_z/2\pi = 3.0$ kHz, and the jumping rate $W = 1/\tau$ is changed from $W = 5\times 10^2$ sec^{-1} to $W = 5\times 10^4$ sec^{-1}. 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 center of the resonance line. The FID signal is obtained by off-resonance excitation and detection. As is seen, the development of the line shape clearly shows the nature of motional narrowing; as the value of W is increased, the two holes are reformed to a single hole at the middle point of the two holes observed at small values of W, and then the width of the single hole becomes narrower.

The hole spectra obtained in *a Gaussian noise field* are shown in Fig. 2. Now the Larmor frequency value fluctuates over continuously distributed values instead of just two values. The distribution function of the frequency is a Gaussian with frequency width Δ ($\Delta^2 = \langle \delta\omega^2 \rangle$). In Fig. 2 the frequency width is fixed at $\Delta/2\pi = 2.0$ kHz, and the jumping rate $W = 1/\tau$ is changed from $W = 5\times 10^2$ sec^{-1} to $W = 1\times 10^5$ sec^{-1}. When the value of W is small, the hole width coincides with the frequency width Δ of the Gaussian fluctuation. As the value of W becomes larger than that of Δ, however, the hole width becomes narrower than Δ.

Next we consider theories for the explanation of the experimental results. The theory of motional narrowing in the two-state noise field was given by Anderson.[13,14] The relaxation function is calculated as

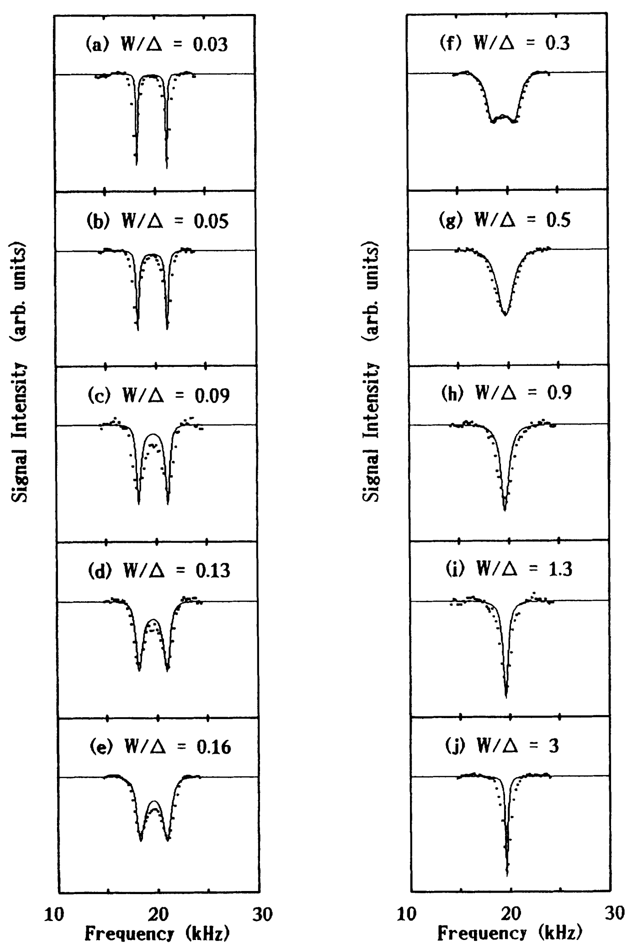

FIG. 1. Hole spectra obtained in a two-state noise field. The frequency difference between the two states is fixed at $\Delta/2\pi = 3.0$ kHz. The jumping rate W is changed from (a) $W = 5\times 10^2$ sec^{-1} to (j) $W = 5\times 10^4$ sec^{-1}. The solid lines are theoretical line shapes calculated from Eq. (2).

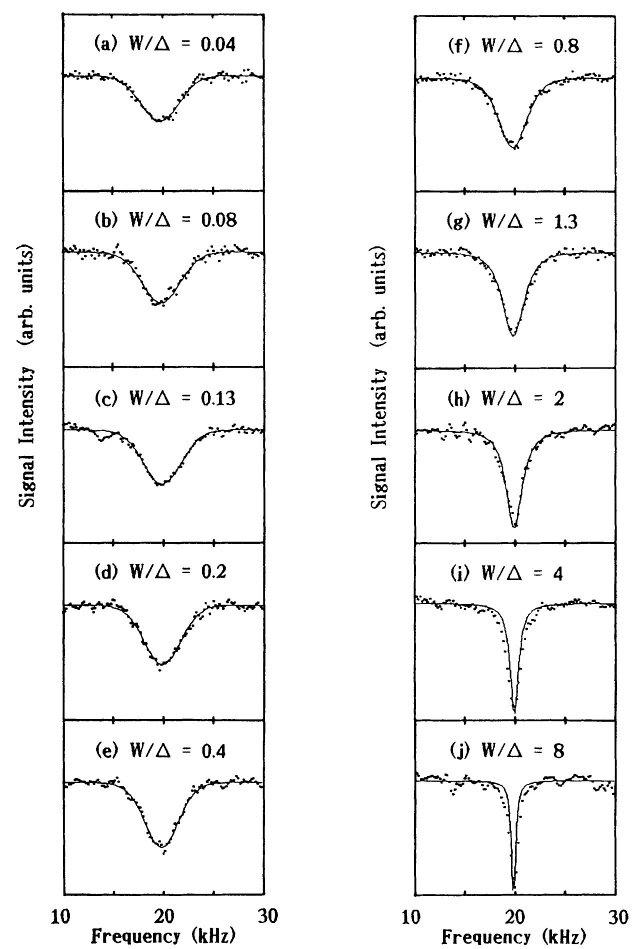

FIG. 2. Hole spectra obtained in a Gaussian noise field. The frequency width of the Gaussian fluctuation is fixed at $\Delta/2\pi = 2.0$ kHz. The jumping rate W is changed from (a) $W = 5\times 10^2$ sec^{-1} to (j) $W = 1\times 10^5$ sec^{-1}. The solid lines are theoretical line shapes obtained from the Fourier transform of Eq. (5).

$$\phi(t)=\left\langle \exp\left[i\int_0^t \delta\omega(s)ds \right]\right\rangle$$
$$=\frac{1}{2}\left[1+\frac{2W}{\sqrt{4W^2-\Delta^2}}\right]\exp[-(W-\tfrac{1}{2}\sqrt{4W^2-\Delta^2})t]+\frac{1}{2}\left[1-\frac{2W}{\sqrt{4W^2-\Delta^2}}\right]\exp[-(W+\tfrac{1}{2}\sqrt{4W^2-\Delta^2})t] \ . \quad (1)$$

The line shape $I(\omega)$ is obtained from the Fourier transform of the relaxation function and given by

$$I(\omega)=\frac{2W\Delta^2}{(\omega^2-\Delta^2/4)^2+4W^2\omega^2} \ . \quad (2)$$

The same result can be derived from the approach using the Bloch equations in the limit of long intrinsic transverse relaxation time T_2.[15–17] In the case of $W/\Delta \ll 1$ two peaks at $\omega=\pm\Delta/2$ are expected from Eq. (2), while in the case of $W/\Delta \gg 1$ one peak at $\omega=0$ is expected. The solid lines in Fig. 1 are theoretical line shapes calculated from Eq. (2). The behavior of the motional narrowing in the two-state noise field is well explained by the above theory. The linewidth of the experimental results is larger than that of the theoretical curve. This is because of the inhomogeneity of the noise field in the sample and of power broadening.

The theoretical line shape in the Gaussian noise field can be obtained from the conventional stochastic theory of relaxation.[18,19] The relaxation function in the Gaussian noise field is given by

$$\phi(t)=\left\langle \exp\left[i\int_0^t \delta\omega(s)ds \right]\right\rangle$$
$$=\exp\left[-\int_0^t (t-u)\langle \delta\omega(u)\delta\omega(0)\rangle du \right] \ . \quad (3)$$

In our case the correlation function is written as

$$\langle \delta\omega(t)\delta\omega(0)\rangle=\Delta^2\exp(-Wt) \ , \quad (4)$$

where $\Delta^2=\langle \delta\omega^2\rangle$ and $W=1/\tau$. The relaxation function can be calculated easily from Eqs. (3) and (4):

$$\phi(t)=\exp[-(\Delta/W)^2\{Wt-1+\exp(-Wt)\}] \ . \quad (5)$$

The line shape $I(\omega)$ is obtained from the Fourier transform of the relaxation function. In the case of $W/\Delta \ll 1$ the line shape is expected as a Gaussian with the width of Δ from Eq. (5), while in the case $W/\Delta \gg 1$ the line shape is expected as a Lorentzian with the width of Δ^2/W which is smaller than Δ by the factor of Δ/W. The solid lines in Fig. 2 are theoretical line shapes obtained from the Fourier transform of Eq. (5). As is seen, the motional narrowing of the resonance line in the Gaussian noise field is well explained by the conventional stochastic theory.

In conclusion we presented an experimental approach for the verification of the theory of relaxation. Hole burning in a proton NMR line was observed, and the hole shape was studied in the well-defined noise fields. We took up the phenomenon of motional narrowing to demonstrate the significance of our method. The characteristic time of the noise was changed, and the mechanism of the motional narrowing was clarified experimentally and theoretically.

It may be very interesting to study the power broadening of line shapes by using our experimental approach. Various theories have been proposed to explain the experimental results on optical free-induction decay observed by DeVoe and Brewer[20] in 1983 which violate the conventional optical Bloch equations in the saturation regime. However, those theories have not been verified sufficiently. We are planning to observe power broadening of the hole shape in the proton NMR line in well-defined noise fields and to study the problem of the violation of the Bloch equations experimentally and theoretically.

This work was supported by the Matsuo Foundation and the Hyogo Science and Technology Association.

[1]A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).

[2]R. Kubo, in *Fluctuations, Relaxation and Resonance in Magnetic Systems,* edited by D. ter Haar (Oliver and Boyd, Edinburgh, 1962).

[3]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[4]C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1989).

[5]R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II Nonequilibrium Statistical Mechanics* (Springer-Verlag, Berlin, 1991).

[6]T. Kohmoto, Y. Fukuda, M. Kunitomo, K. Ishikawa, M. Tanigawa, K. Ebina, and M. Kaburagi, Phys. Lett. A **181**, 97 (1993).

[7]R. R. Ernst, J. Magn. Reson. **3**, 10 (1970).

[8]R. Kaiser, J. Magn. Reson. **3**, 28 (1970).

[9]B. Blümich and R. Kasier, J. Magn. Reson. **54**, 486 (1983).

[10]M. H. Anderson, R. D. Jones, J. Cooper, S. J. Smith, D. S. Elliott, H. Ritsch, and P. Zoller, Phys. Rev. Lett. **64**, 1346 (1990).

[11]C. Chen, D. S. Elliott, and M. W. Hamilton, Phys. Rev. Lett. **68**, 3531 (1992).

[12]M. H. Anderson, G. Vermuri, J. Cooper, P. Zoller, and S. J. Smith, Phys. Rev. A **47**, 3202 (1993).

[13]P. W. Anderson, J. Phys. Soc. Jpn. **9**, 316 (1954).

[14]A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961), p. 447.

[15]C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1989), p. 592.

[16]H. S. Gutowsky, D. W. McCall, and C. P. Slichter, J. Chem. Phys. **21**, 279 (1953).

[17]H. S. Gutowsky and A. Saika, J. Chem. Phys. **21**, 1688 (1953).
[18]R. Kubo, in *Fluctuations, Relaxation and Resonance in Magnetic Systems,* edited by D. ter Haar (Oliver and Boyd, Edinburgh, 1962), p. 23.
[19]R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II Nonequilibrium Statistical Mechanics* (Springer-Verlag, Berlin, 1991), p. 40.
[20]R. G. DeVoe and R. G. Brewer, Phys. Rev. Lett. **50**, 1269 (1983).