Observation of Spin-Torsional Spectrum through Nuclear Magnetization Time Evolution in the Rotating Frame

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A new experimental technique is introduced by which tunneling splittings of ground torsional-oscillator states in solids can be obtained directly. Rotating-frame time evolution of the spin-torsional system, monitored by the proton spin magnetization, is presented for NH_4I and CH_3CD_2I, along with the frequency spectra. The resolution of the spectral lines is an order of magnitude better than the magnetization-loss spectra.

In a recent paper[1] experiments were described in which the nuclear spin system in the rotating frame is resonantly coupled to the set of lattice states produced by the tunneling splitting of the ground torsional-oscillator state of the NH_4^+ ion in NH_4I. During a long field pulse of a spin-locking pulse sequence,[2] the torsional system, initially at the lattice temperature, T_L, and the spin system, initially at a temperature $T_S=(H_1/H_0)T_L$ (H_1 and H_0 are the rotating-frame and laboratory-frame fields, respectively), come to a state of semiequilibrium describable by a common temperature. The resulting state is characterized by a loss of Zeeman polarization (heating) and a corresponding cooling of the torsional system. In this Letter we report preliminary experiments on the time evolution of the spin-torsional system towards a state of semiequilibrium.

The approach to semiequilibrium of the isolated nuclear Zeeman and dipolar spin systems in the rotating frame in a solid has been studied theoretically[3] and experimentally.[4] It is characterized by oscillations at the frequency $2\omega_1=2\gamma H_1$, damped on a time scale on the order of T_2. The oscillations result from the different initial temperatures of the Zeeman and dipolar reservoirs. They are brought about by the coherent exchange of energy between the two systems, induced by the nonsecular part of the rotating-frame dipolar interaction $\mathcal{H}_D^{(\pm 2)}$, which connects states whose Zeeman quantum numbers M differ by ± 2. The frequency $2\omega_1$ is the energy separation between such states. The present experiment is analogous, with the addition of a third system comprised of the torsional levels.

The time evolution of the nuclear Zeeman system is monitored by measuring $M_x(t)$, the magnitude of the free-induction decay signal following a spin-locking pulse sequence, as a function of the field-pulse duration t. The results of such an experiment, with the field-pulse amplitude $H_1 = 14$ G, are shown in Fig. 1 for NH_4I, which is known[5] to have a tunneling splitting of about 20 G. The magnetization decays on a time scale of the order of T_2, but the time dependence, while oscillatory in appearance, cannot be described with a single frequency $2\omega_1$. The corresponding spectrum, Fig. 2, is the Fourier transform of $M_x(t)$, and shows that there is a relatively complex spectrum of frequencies contributing to the time evolution. This result is explained by the presence of a set of tunneling-split torsional-oscillator

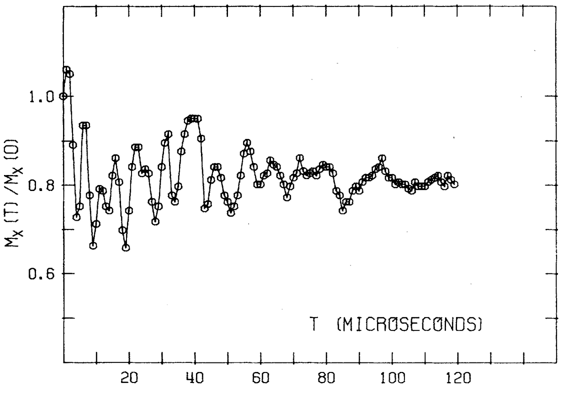

FIG. 1. Time evolution of $M_x(t)$ in NH_4I. $H_1 = 14$ G and the temperature is 16 K.

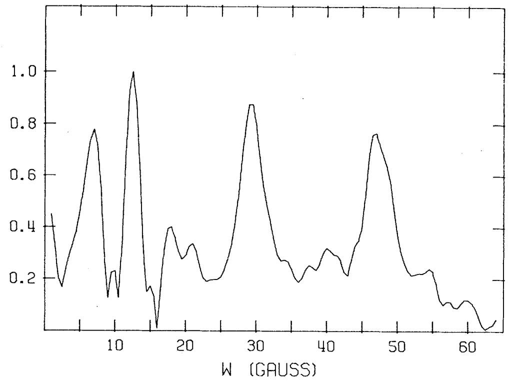

FIG. 2. Spectrum of NH_4I for $H_1 = 14$ G and $T = 16$ K.

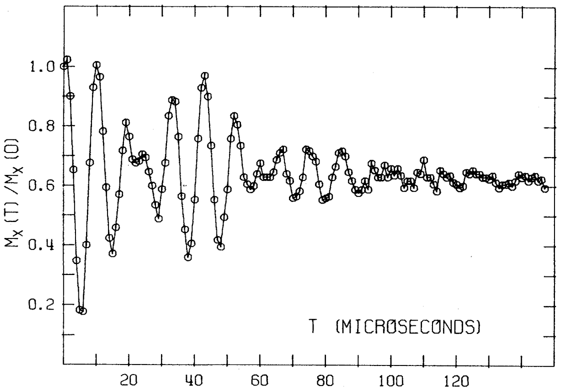

FIG. 3. Time evolution of $M_x(t)$ in CH_3CD_2I. $H_1 = 12$ G and the temperature is 66 K.

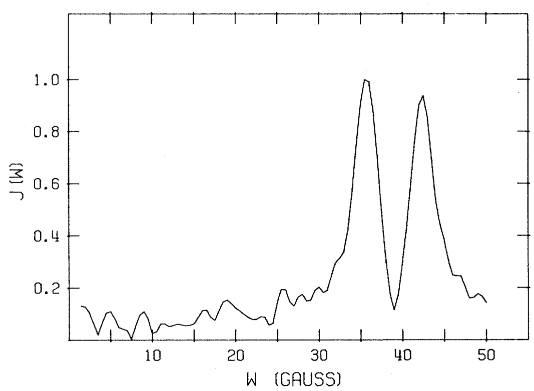

FIG. 5. Spectrum of CH_3CD_2I for $H_1 = 19$ G at $T = 66$ K.

levels in which the characteristic splittings are close to the Zeeman splittings in the rotating frame. The terms $\mathcal{H}_D^{(\pm 2)}$ of the dipolar interaction connect states whose magnetic quantum numbers differ by ±2, as in the usual (nontunneling) case. The energy separations between such states which belong to different torsional levels are $|2\omega_1 + \Delta_i|$ and $|2\omega_1 - \Delta_i|$, where Δ_i are the tunneling splittings. Consequently, these frequencies appear in the time evolution of the spin-torsional system as it evolves from an initial nonequilibrium state to a state of semiequilibrium. The results of further experimental work now in progress, which allow the assignment of each of the spectral lines in NH_4I, will be reported later.

The explanation of the time evolution in NH_4I is substantiated by a similar experiment on CH_3CD_2I. The CH_3-group hindered rotor in this material is known[6] to have a torsional ground-state A-to-E splitting of about 5 G. Unlike the four-spin tetrahedron of NH_4I, in which (according to the symmetry of the crystal field) the ground torsional state may be split into a maximum five levels, the CH_3 rotator has a simple torsional spectrum with only one tunneling splitting. Consequently, it is to be expected that two frequencies will appear in the time evolution of the spin torsional system, corresponding to the changes ±2 in the magnetic quantum number. The time evolution data for $H_1 = 12$ G, Fig. 3, indicate the beating of two signals of different frequencies. The corresponding frequency spectrum, Fig. 4, shows two well-resolved lines, at $2H_1 + 3.3$ G and $2H_1 - 3.3$ G. The spectrum at $H_1 = 19$ G, Fig. 5, also exhibits two peaks at $2H_1 \pm 3.3$ G demonstrating the $2H_1$ dependence discussed above. It should be noted that the reported 5 G is the low-temperature limit of the splitting, which decreases with increasing

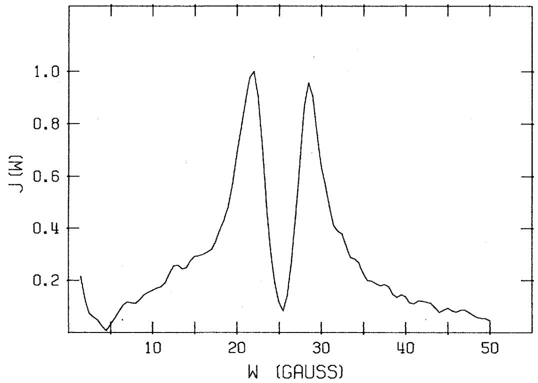

FIG. 4. Spectrum of CH_3CD_2I for $H_1 = 12$ G and $T = 66$ K.

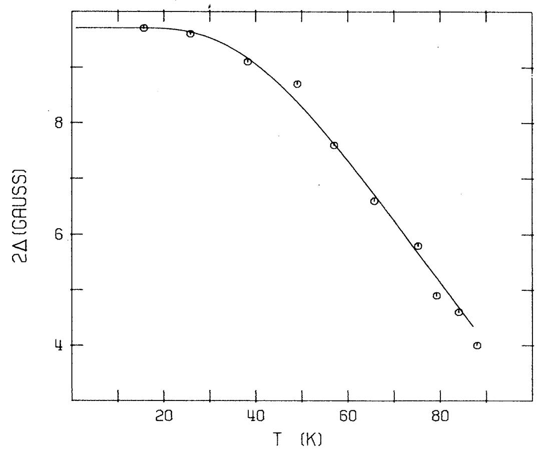

FIG. 6. Temperature dependence of the tunneling splitting of CH_3 rotor in CH_3CD_2I.

temperature.[7] The spectra in Figs. 4 and 5 were taken at 66 K. The resolution and signal-to-noise ratio obtained with this method are remarkably better than obtained from the NMR line shape or by the magnetization-loss technique.

The temperature dependence of the splitting, 2Δ, of the two lines in the spectrum of CH_3CD_2I has been measured and is shown in Fig. 6. It is qualitatively the same as that obtained by NMR line-shape analysis,[7,8] displaying a low-temperature asymptote of 4.8 G, and giving a good fit to the form

$$\langle\Delta\rangle=\Delta_0[1-\exp(-E_{10}/kT]+\Delta_1\exp(-E_{10}/kT). \tag{1}$$

Here $\langle\Delta\rangle$ is the observed splitting, and Δ_0 and Δ_i are, respectively, the splittings of the ground and first excited torsional levels, which are separated in energy by E_{10}. The values of E_{10} and Δ_1 are found from the slope and the intercept of the plot of $\ln(\Delta_0-\langle\Delta\rangle)$ vs 1000/T to be 310 ± 30 cal/mol and -11 ± 4 G, respectively. The solid line is generated from Eq. (1) using these values. The negative value of Δ_1 indicates the well-known inversion of the level scheme in the first excited state relative to the ground state, with the A level having higher energy than the E levels. The present numbers are not in agreement with the reported values of 700 cal/mol and -1075 G, respectively, which were arrived at by the NMR line-shape analysis.[7]

A second-order perturbation calculation has been carried out[9] which shows that the time evolution of the spin-torsional system is characterized by coherent energy exchanges among the Zeeman, torsional, and dipolar energy reservoirs. The time dependence of the Zeeman energy is given, for example, by

$$\langle\mathcal{H}_z(t)\rangle=A_0+A_2(t), \tag{2}$$

where

$$A_0=\alpha\mathrm{Tr}(\mathcal{H}_z{}^2), \tag{3}$$

and

$$A_2(t)=\alpha\sum_{TM}\sum_{T'M'}\frac{(\omega_M-\omega_{M'})^2}{(\omega_{TM}-\omega_{T'M'})^2}|\langle TM|\mathcal{H}_D{}^{(2)}+\mathcal{H}_D{}^{(-2)}|T'M'\rangle|^2\{1-\cos[(\omega_{TM}-\omega_{T'M'})t]\}, \tag{4}$$

with

$$\omega_M=-M\omega_1,\quad \omega_T=\Delta_T/\hbar,\quad \omega_{TM}=\omega_M+\omega_T,\quad \alpha=\mathrm{const.}$$

The basis states $|TM\rangle$ are simultaneous eigenstates of the torsional and spin Hamiltonians. The frequencies present in the time evolution are equal to the differences in energy between states connected by $\mathcal{H}_D{}^{(\pm 2)}$, and this gives rise to the selection rule $|\omega_M-\omega_{M'}|=2\omega_1$. The details of the calculation, together with complete experimental data on NH_4I and $(NH_4)_2BeF_4$, will be presented elsewhere.

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