Two dimensional Zeeman nuclear quadrupole resonance spectroscopy[a)]

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(Received 23 September 1983; accepted 10 October 1983)

We describe the first application of two-dimensional spectroscopy to the pure quadrupole regime. One- and two-pulse Zeeman perturbed experiments are outlined, and results of a one-pulse experiment on the two crystallographically nonequivalent ^{35}Cl sites in 2,4,6-trichloro-1,3,5-triazine ("cyanuric chloride") are presented. The results demonstrate that the overlapping Zeeman-perturbed resonances in a one-dimensional experiment are fully resolved in a two-dimensional experiment. The methods appear to have considerable utility for the determination of the quadrupole coupling constant e^2qQ/h and asymmetry parameter η for spin $I = 3/2$ nuclei in systems with several closely spaced pure nuclear quadrupole resonance lines.

INTRODUCTION

Nuclear quadrupole resonance (NQR) spectroscopy is a powerful technique for obtaining both static and dynamic information on molecules in the solid state. For a system of quadrupolar nuclei in zero field, the Hamiltonian is given by

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}\left[3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)\right] . \qquad (1)$$

The nuclear quadrupole coupling constant e^2qQ and the electric field gradient tensor asymmetry parameter η are extremely sensitive to the electron distribution around the quadrupolar nucleus, and hence are the parameters of interest in NQR.[1,2]

Due, however, to the $\pm m$ degeneracy in the absence of a magnetic field, pure nuclear quadrupole resonance (PNQR) studies for spin $I = 3/2$ nuclei are insufficient to determine either e^2qQ or η, since only a single quadrupole resonance frequency ν_Q given by

$$\nu_Q = \frac{1}{2}\left[\frac{e^2qQ}{h}\right]\left[1+\eta^2/3\right]^{1/2} \qquad (2)$$

is observed experimentally. However, the application of a static Zeeman field perturbation removes the degeneracy of the quadrupolar energy levels, and hence permits the observation of four transitions, from which the quadrupole parameters can be determined. Zeeman nuclear quadrupole resonance spectroscopy (ZNQRS) has been employed previously for both polycrystalline[3–9] and single crystal specimens.[10,11]

Morino and Toyama[3] developed the basic ZNQR line shape theory for polycrystalline specimens, for the case in which the static Zeeman field H_0 is aligned parallel to the radio frequency field H_1. The important feature of the line shape (Fig. 1) is that singularities occur at $\nu_Q \pm (1+\eta)\nu_0$ and $\nu_Q \pm (1-\eta)\nu_0$, where $\nu_0 = \gamma H_0$ is the Larmor frequency, and ν_Q is the pure NQR frequency. By measuring the splitting of the singularities, η can be evaluated. However, a severe limitation of the steady state powder method is associated with the maximum usable value of the Zeeman field strengths. Often, the signal to noise ratio of the ZNQR signal deteriorates even before the paired singularities can be well resolved, and such problems are exacerbated by the presence of multiple resonance lines. While it has been shown recently[9] that the Zeeman perturbed nuclear quadrupole spin-echo envelope modulations (ZSEEM) for spin $I = 3/2$ nuclei in polycrystalline specimens are sensitive to η, decoding the information content of the ZSEEM patterns for multiple sites appears to be a rather difficult task.

Even in methods based on single crystal ZNQR studies, when closely spaced resonance lines occur in the system under investigation, overlaps of the Zeeman-split NQR lines of the different sites are expected to occur, as has been reported in the case of a ^{35}Cl ZNQR study of $GeCl_4$,[12] and it is likely that such spectral overlaps may lead to ambiguities in the proper assignments of the NQR resonances.

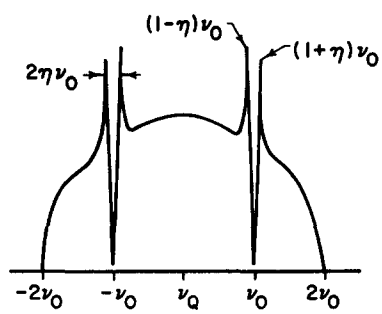

FIG. 1. Theoretical Zeeman NQR powder pattern (absorption line shape) for spin $I = 3/2$ and $\eta \neq 0$, with external static Zeeman field H_0 and radio frequency field H_1 applied parallel, neglecting the original pure NQR linewidth. The position of the unperturbed NQR line is ν_Q and ν_0 is the Larmor frequency of the nucleus in the external applied magnetic field H_0 [after Moroin and Toyama (Ref. 3)].

[a)] This work was supported in part by the National Science Foundation (grants PCM 81-17813, 83-02512, DMR 83-11339) and the National Institutes of Health (grant HL-19481), and has benefitted from facilities made available through the University of Illinois–National Science Foundation Regional NMR Instrumentation Facility (grant CHE 79-16100).

[b)] USPHS Research Career Development Awardee, 1979–1984 (grant CA-00595).

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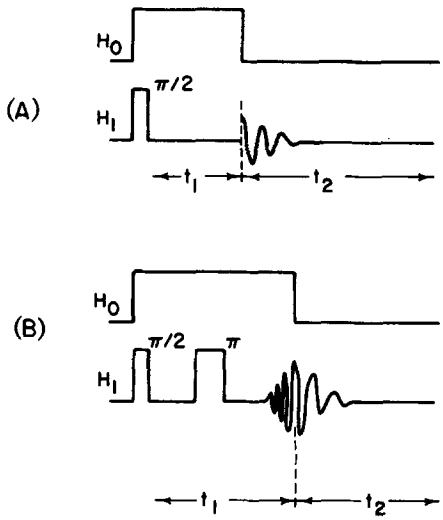

FIG. 2. Two-dimensional Zeeman NQR pulse sequences. (A) One pulse sequence. (B) $\pi/2-\tau-\pi$, two-pulse spin-echo sequence. The evolution and detection periods are t_1 and t_2, respectively.

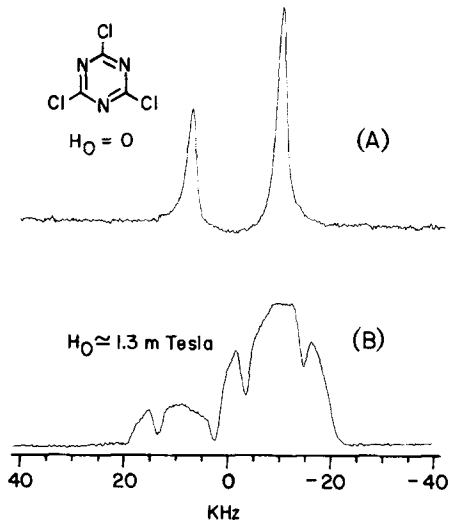

FIG. 3. Chlorine-35 NQR spectra of 2,4,6-trichloro-1,3,5-triazine ("cyanuric chloride") showing effect of a static Zeeman field. (A) ^{35}Cl FT PNQR spectrum at 23 °C, recorded at 36.3 MHz using a $\pi/2$ pulse width of 10 μs, 800 scans at a 300 ms recycle time. (B) ^{35}Cl FT ZNQR spectrum obtained with $H_0 \parallel H_1$, using a $\pi/2$ pulse width of 10 μs, 6400 scans at a 300 ms recycle time, and a Zeeman field strength of 1.3 mT.

In situations such as these, it thus appears that suitable application of two-dimensional spectroscopic techniques[13] should provide the resolution enhancements necessary for unequivocal data analysis. We propose in this paper the first schemes for obtaining site-resolved ZNQR spectra, and present preliminary results obtained with a polycrystalline specimen. The advantages of the methods proposed are that (i) the two-dimensional ZNQR schemes can be implemented for both single crystals as well as polycrystalline specimens, (ii) since spectra are obtained in *zero field*, the signal-to-noise ratio problems associated with the presence of static Zeeman fields are eliminated, and (iii) spectral overlaps due to Zeeman splittings are eliminated. In short, well-resolved Zeeman splittings in complex molecules in either single crystal or polycrystalline form may be readily obtained using the 2*D*-ZNQR methods described below.

2*D* ZNQR SCHEMES

We show in Fig. 2 two schemes for two-dimensional Zeeman perturbed NQR experiments. In scheme (1),

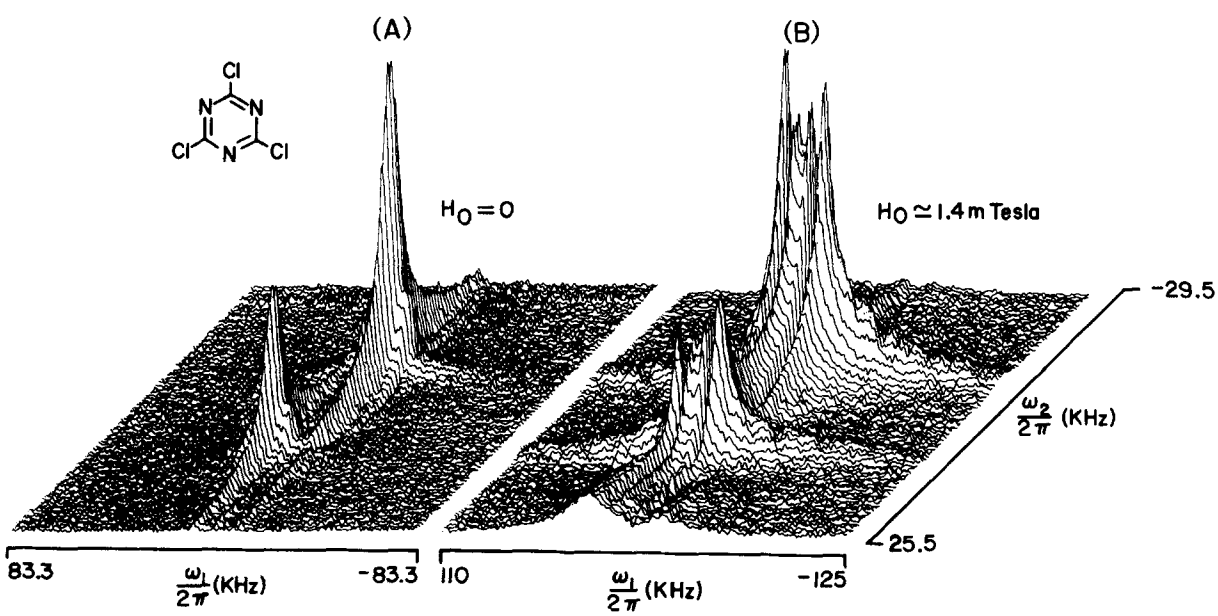

FIG. 4. Two-dimensional ^{35}Cl NQR spectra of cyanuric chloride at room temperature. The pulse sequence of Fig. 2(A) was employed, using 128 points in the t_1 domain and 1024 points in the t_2 domain. "Zero filling" in the t_1 domain was used to improve spectral appearance. The $\pi/2$ pulse width was 10 μs and the recycle time 300 ms. (A) at zero field with a t_1 increment of 6 μs and 400 scans per t_1 value. (B) at $H_0 \simeq 1.4$ mT ($H_0 \parallel H_1$) with a t_1 increment of 3 μs and 1200 scans per t_1 value.

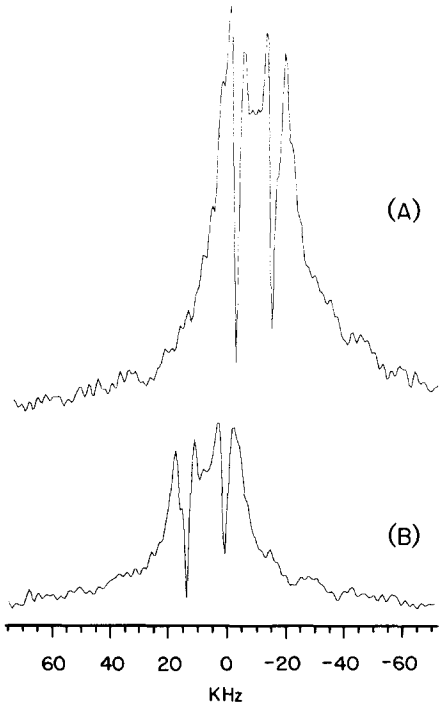

FIG. 5. Cross sections through the 2D ZNQR spectrum (parallel to the ω_1 axis) for the two chlorine sites in cyanuric chloride.

Fig. 2(A), transverse magnetization is prepared by applying a $\pi/2$ pulse to the spin system, and the magnetization is then allowed to evolve for a period t_1 in the presence of both Zeeman and quadrupole interactions. During the detection period t_2 the Zeeman field is switched off, and the magnetization evolves under the pure quadrupole interaction. By incrementing the t_1 values in suitable intervals, a two-dimensional data matrix $S(t_1, t_2)$ is created, and subjected to double Fourier transformation to yield the 2D spectrum $S(\omega_1, \omega_2)$. The projection of the 2D spectrum along the ω_2 axis results in PNQR lines arising from the nonequivalent sites in the crystal lattice—which we refer to as NQR "shifts." The 2D spectrum along the ω_1 axis exhibits both Zeeman structure and the NQR shift features. By taking cross sections parallel to the ω_1 axis, the Zeeman NQR powder pattern-multiplet structure for the individual sites can be conveniently obtained.

In scheme 2, Fig. 2(B), a $\pi/2 - \tau - \pi$ pulse sequence is used to generate an NQR spin echo. During the evolution period t_1 the spin system is subjected to a Zeeman perturbation, while during the detection period the Zeeman field is switched off. Since during the t_1 period the effects of the site inequivalences in dephasing the magnetization created by the first $\pi/2$ pulse are refocused by the second π pulse, the resultant 2D spectra in this case reflect only the Zeeman, and not the NQR shift features, along the ω_1 axis. The projection of the 2D spectra on the ω_2 axis gives the conventional 1D spectrum. By a proper analysis of the relevant cross sections, parallel to the ω_1 axis, the η values for the individual sites can be obtained.

EXPERIMENTAL

We used the "home-built" FT NMR spectrometer described previously,[14] except it is now equipped with a Nicolet 1280 data system (Madison, WI). A single-coil parallel resonant circuit[15] was employed as the sample probe. $\pi/2$ pulse widths were typically in the range of ~ 10 μs. The Zeeman field was produced by a Helmholtz coil arrangement, and the computer-controlled switching of the Zeeman field was effected by routing the output from a dc power supply to the Helmholtz coil through an FET switch. The (static) Zeeman field was calibrated with a Gauss meter [model 615, F. W. Bell, FL].

RESULTS AND DISCUSSION

We show in Fig. 3(A) the ^{35}Cl PNQR signals obtained from a polycrystalline specimen of 2, 4, 6-trichloro-1, 3, 5-triazine ($C_3N_3Cl_3$, "cyanuric chloride") at room temperature. Two ^{35}Cl PNQR lines, with an intensity ratio of 1 : 2, have already been reported for this system,[3] and as expected two well resolved resonances are observed. However, as shown in Fig. 3(B), the application of even a relatively small (~ 1.3 mT) Zeeman field ($H_0 \parallel H_1$) causes considerable overlap between the two Zeeman powder patterns, making extraction of e^2qQ and η information from the powder spectrum difficult. In sharp contrast, the 2D ZNQR spectrum of cyanuric chloride exhibits well resolved Zeeman structure on both NQR shifted resonances. We show in Figs. 4(A) and 4(B) the 2D spectra (absolute value mode) obtained using the one pulse sequence shown in Fig. 2(A), with $H_0 = 0$ and $H_0 \simeq 1.4$ mT ($H_0 \parallel H_1$), respectively. The 2D data matrix was generated with 128 points in the t_1 domain and 1024 points in the t_2 domain. "Zero filling" in the t_1 domain was effected to improve spectral display. t_1 increments of 6 and 3 μs, with 400 and 1200 scans per t_1 value, respectively, were employed for obtaining the 2D spectra shown.

We show in Figs. 5(A) and 5(B) cross sections (parallel to the ω_1 axis) through the 2D spectrum of Fig. 4(B), for each of the two sites. The powder patterns represented by the cross sections are in satisfactory agreement with the line shapes expected. Preliminary work based on the spin-echo sequence is underway in our laboratory, and initial results indicate that much better resolution is obtained along the ω_2 axis using the spin-echo method (data not shown).

Overall, the results presented in this publication indicate that two-dimensional Zeeman perturbed nuclear quadrupole resonance spectra may be readily obtained and interpreted. The schemes presented above will have their maximum utility in chemical systems where the pure NQR resonance lines are very closely spaced, precluding the use of high static Zeeman fields to obtain e^2qQ and η information.

ACKNOWLEDGMENTS

We thank Nathan Janes, Rebecca L. Smith, and Tane Ray for useful discussions and help with the experiments, and Carl Reiner for developing the rapid Zeeman field switching circuitry.

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