QUADRUPOLAR ECHO TRAIN RELAXATION OF SPIN S = 3/2 NUCLEI

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ABSTRACT

The time evolution of the spin S = 3/2 density operator under a $\pi/2$ pulse string has been calculated using perturbation theory in an interaction representation in which no external rf fields occur. The quadrupolar echo train relaxation curve is biexponential with amplitude ratio 0.8:0.2. The fast relaxation rate may be sensitive to the pulse cycle time and is a probe to study slowly fluctuating electric field gradients.

INTRODUCTION

In complex macromolecular systems, spin S = 3/2 NMR is an important experimental tool to investigate the intricate behavior of small ions. In previous work it was shown that biexponential relaxation under a spin-lock field yields information about slowly fluctuating processes of the order kHz. However, the latter method is characterized by a number of experimental drawbacks such as serious spin heating and a rather time consuming data acquisition. Accordingly, it is desirable to devise a pulsed version of the latter experiment.

RESULTS

The quadrupolar echo train relaxation of spin S = 3/2 has been analyzed as a function of pulse cycle time and pulse width. The decay curve is represented by (at times t = nT)

$$s(t) = (1/5)(4\exp\{R_3^{(qe)}t\} + \exp\{R_4^{(qe)}t\})$$

with the relaxation rates

$$R_3^{(qe)} = -(eQ/\hbar)^2\{(3/4)J_{20}(T) + J_1(\omega_0) + (1/4)J_2(2\omega_0)\}$$

$$R_4^{(qe)} = -(eQ/\hbar)^2\{J_1(\omega_0)+J_2(2\omega_0)\}$$

and in the δ-function pulses limit the cycle time T dependent spectral density function is given by

$$J_{20}(T) = A\tau_c[1 - (2\tau_c/T)\tanh(T/2\tau_c)]$$

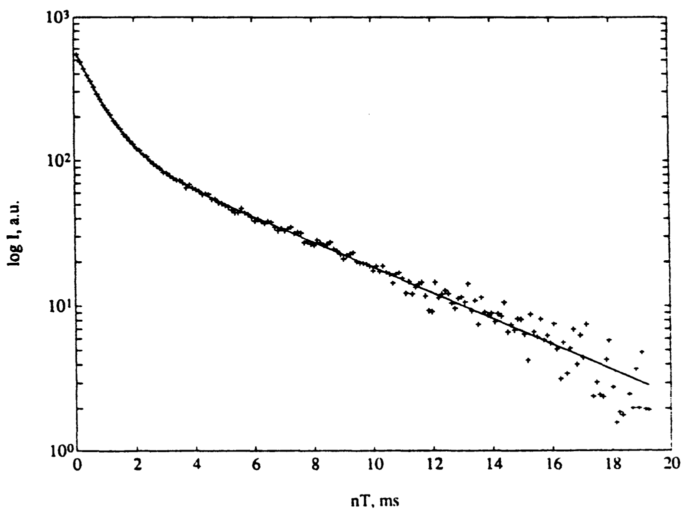

Fig. 1

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The quadrupolar echo train relaxation is similar to relaxation in the presence of a spin-lock field, but with a pulse cycle time dependent spectral density function. Furthermore, is shown that outside the extreme narrowing limit due to relaxation under the $\pi/2$ pulse string triple quantum coherences may be excited. A quadrupolar echo train decay curve of ^{23}Na in an ion exchange resin is displayed in Fig. 1 ($T = 110\ \mu s$, $\tau_p = 10\ \mu s$). The solid line represents a least-squares fit to a sum of two exponentials:

$$-R_3^{(qe)} = 1270\ s^{-1},\ -R_4^{(qe)} = 179\ s^{-1},\ \text{amplitude ratio } 0.79{:}0.21$$

A ^{23}Na multiple quantum spectrum, obtained using a 2D quadrupolar echo train experiment with a coherence transfer pulse after the pulse string, is displayed in Fig. 2. The feature on the r.h.s. represents the triple-quantum signal.

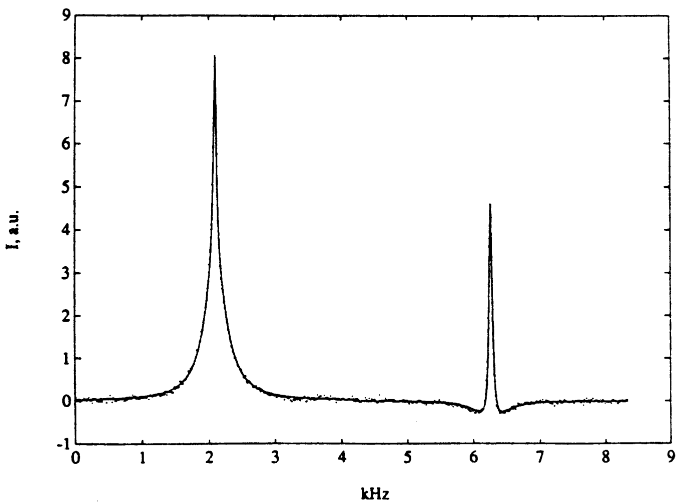

Fig. 2

CONCLUSIONS

The spin S =3/2 quadrupolar echo train experiment is an excellent tool to investigate slowly fluctuating processes in condensed matter. It is characterized by a relatively fast data acquisition and reduced heat dissipation. Accordingly, this experimental method is well suited to study systems with less signal to noise ratio and relatively long relaxation times.

REFERENCES

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