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LETTER TO THE EDITOR

MULTIPLE QUANTUM COHERENCE IN DIPOLAR RELAXATION MEASUREMENTS

S. EMID, A. BAX, J. KONIJNENDIJK and J. SMIDT
Laboratorium voor Technische Natuurkunde, Technische Hogeschool Delf, Lorentzweg 1, P.O.B. 5046, 2600 GA Delft, The Netherlands

and

A. PINES
Department of Chemistry and Material and Molecular Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

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It is shown that multiple quantum coherence is contained in the transverse magnetization following the Jeener–Broekaert pulse program ($90^0_x-\tau_1-45^0_y-t-45^0_y-\tau_2$) The measurements have been done on CH_3CN dissolved in Merck V liquid-crystal and on l-alanine, gypsum and adamantane powders at room temperature. The different orders of multiple quantum transitions were distinguished by setting the r.f. frequency off-resonance. With an offset of Δ the transverse magnetization as a function of t were then modulated with frequencies $n\Delta$, revealing n quantum transitions For the solid samples, in order to enhance resolution, the responses have been divided into odd and even quanta

The so-called Jeener–Broekaert pulse program [1], see fig. 1, was originally designed and was for more than a decade in use as the standard pulse method for measuring dipolar relaxations in solids. In such measurements the time t is varied and the component $\langle I_y \rangle$ of the transverse magnetization is observed as a function of t. The purpose of this note is to show that multiple quantum transitions are present in $\langle I_y \rangle$.

The spin systems considered can be described by the hamiltonian:

$$H(t) = H_Z + H^0_D + H_{r.f.}(t) + H_{rel}(t) ;$$

$$H^0_D = H^0_{D\,intra} + H^0_{D\,inter} , \qquad (1)$$

where H_Z is the Zeeman system, H^0_D the secular averaged dipolar interaction, presumably consisting of intra and inter molecular interactions, $H_{r.f.}(t)$ is the interaction with an applied radio frequency field which is pulsed and $H_{rel.}(t)$ is the spin–lattice relaxation term.

Recently triple pulse programs [2] have been used to create, let evolve and detect multiple quantum transitions. In those triple pulse programs the procedure is very much like that given in fig. 1. However, so far all those methods have been applied only to cases where $H^0_{D\,inter} << H^0_{D\,intra}$ or $H^0_{D\,inter} = 0$, like in liquids or liquid crystals. No multiple quantum coherence has previously been reported in solids with strong intermolecular interactions, i.e. for $H^0_{D\,inter} \simeq H^0_{D\,intra}$, and not at all with respect to the Jeener–Broekaert pulse program. One of the reasons way the multiple quantum aspects have not emerged from

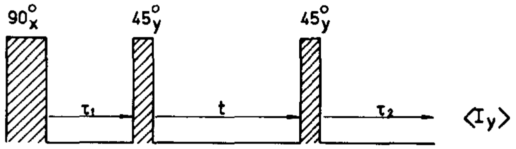

Fig. 1. The Jeener–Broekaert pulse program. $\langle I_y \rangle$ is measured as a function of t for fixed values of τ_1 and τ_2.

dipolar relaxation measurements, at least not in such a manifest way that they could have been recognized, is because such measurements have been done exclusively on resonance. This is done to avoid interference of possible Zeeman signal due to pulse and phase imperfections, and of course relaxation.

To observe multiple quantum transitions, the simplest way in our opinion is to set the r.f. frequency off-resonance. For a resonance offset Δ the presence of n quantum transition will then show up as a modulation with frequency $n\Delta$ of the transverse magnetization after τ_2, as a function of t.

For our purpose we therefore apply the Jeener–Broekaert pulse program, to a spin system initially in equilibrium with the lattice, set the r.f. frequency off-resonance and observe the changes in the transverse magnetization. With the initial density matrix $\rho_0 = 1-\alpha_Z I_z$, the component $\langle I_y \rangle$ is given by.

$$\langle I_y \rangle = \alpha_Z \operatorname{Tr} I_y^-(-\tau_2)\, e^{iHt} I_y^+(\tau_1)\, e^{-iHt}\,, \qquad (2)$$

where

$$H = H_Z + H_D^0 \quad \text{and} \quad I_y^\pm(\tau) = U_\pm(\tau) I_y U_\pm^\dagger(\tau)$$

with

$$U_\pm(\tau) = \exp(\pm i\pi I_y/4)\,\exp(iHt)\,\exp(\mp i\pi I_y/4)$$

$I_y^\pm(\tau)$ has multiple quantum matrix elements. Since eq. (2) has the form of a free induction decay we call it a multiple quantum free induction decay. Its Fourier transform is a multiple quantum spectrum. We demonstrate the results of measurements on the protons in the following two cases (the details of the techniques are not essential for the present purpose).

1) CH_3CN of about 28% by mole dissolved in Merck V liquid-crystal at room temperature. The measurements have been done on our 300 MHz home-built FT spectrometer. The Fourier transform of the transverse signal $\langle I_{tr} \rangle$ is given in fig. 2 as a magnitude spectrum. The energy level diagram of the protons of the rapidly reorienting CH_3 group is also given (insert, see e.g. [3]) showing the possible transitions. single (S), double (D) and triple (T) quantum. Further, ω_0 is the Larmor frequency, ω the r.f. frequency, $2\pi\Delta = \omega_0 - \omega$, d the intramolecular dipolar shift. The lines S_- and D_- are folded back, since $\Delta < d/2\pi$. In fig. 2 the triple quantum transition

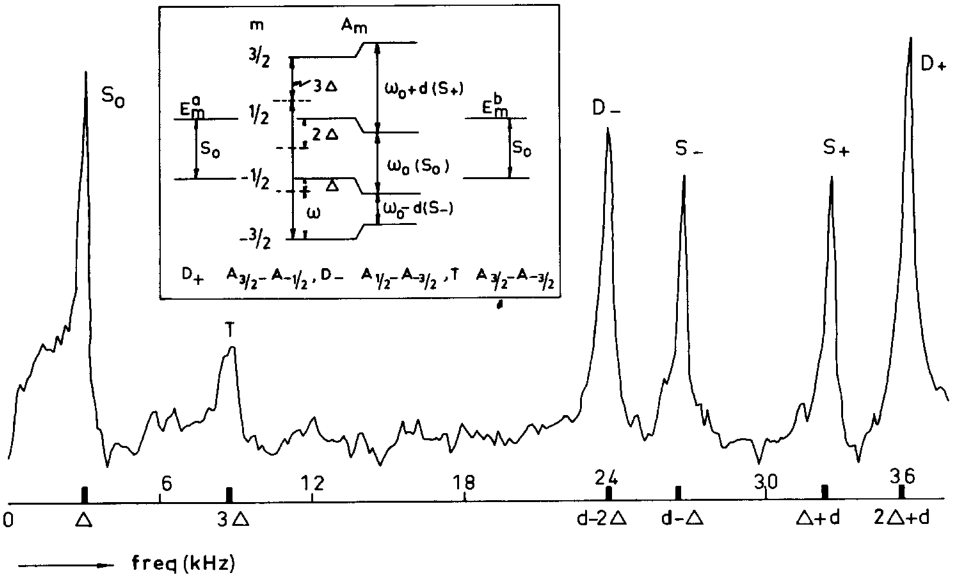

Fig. 2. Multiple quantum magnitude spectrum of 28 mole% of CH_3CN dissolved in Merck V liquid-crystal at room temperature, obtained with the Jeener–Broekaert pulse-program. The intra molecular shift $d/2\pi \simeq 3 \times 10^3$ Hz, $\tau_1 = 700\ \mu s$ and $\Delta = 300$ Hz. S_-, S_0 and S_+ denote the single quantum lines, D_- and D_+ denote the double quantum lines and T denotes the triple quantum line. The resonance frequency is 300 MHz.

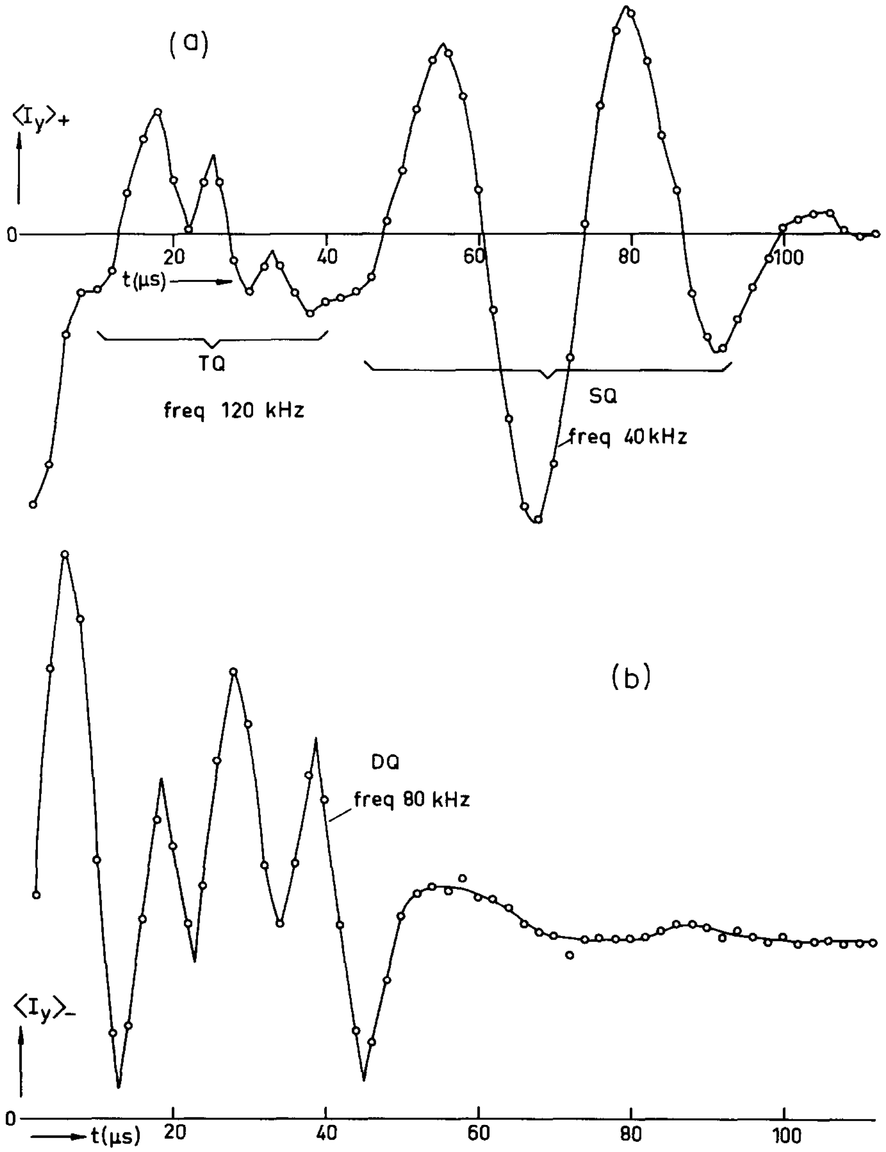

Fig. 3 Multiple quantum free induction decay of $ND_3^+CHCH_3COO^-$ (l-alanine) powder at room temperature, obtained with a combination of two Jeener–Broekaert pulse programs. $\langle I_y \rangle_+$ and $\langle I_y \rangle_-$ contain odd and even quantum transitions, respectively, $\Delta = 40$ kHz, $\tau_1 = \tau_2 = 40$ μs and the resonance frequency is 60 MHz. (a) The presence of single and triple quantum transitions in $\langle I_y \rangle_+$ shows up as modulations with frequencies of 40 kHz and 120 kHz, respectively (b) The presence of double quantum transitions shows up as a modulation with frequency of 80 kHz

is weak. However, this is not a limitation of the method. Selective excitation and detection of multiple quantum transitions by order is possible [2,4].

2) CH_3 group in solid l-alanine (powder) in which the NH_3 group has been deuterated. This is a case where $H^0_{\text{Dinter}} \simeq H^0_{\text{Dintra}}$. The measurements have been done on a Bruker CXP pulse spectrometer, at 60 MHz and room temperature. In fig. 3 $\langle I_y \rangle$ is given as a function of t. The offset frequency $\Delta = 40$ kHz, $\tau_1 = \tau_2 = 40$ μs. In solids the lines are broad. To enhance resolution we have combined the program of fig. 1

with a second Jeener–Broekaert program in which the second pulse is a 45^0_{-y} pulse. From the transformation properties of the irreducible tensor components H_D^m of the dipolar interaction [5] one can prove

$$\mathrm{e}^{\mathrm{i}\beta I_y} H_D^0\, \mathrm{e}^{-\mathrm{i}\beta I_y} = \tfrac{1}{2}(3\cos^2\beta - 1)\, H_D^0 + \tfrac{1}{4}\sqrt{6}\,\sin^2\beta (H_D^2 + H_D^{-2}) + \tfrac{1}{4}\sqrt{6}\,\sin 2\beta (H_D^1 - H_D^{-1})\,. \tag{3}$$

It follows from eqs. (2) and (3) that the sum $\langle I_y \rangle_+$ of the responses of the two programs contains only odd quanta, whereas the difference of the responses, $\langle I_y \rangle_-$, contains only even quanta.

It is clear from fig. 3(a) that triple quantum (TQ) and single quantum (SQ) transitions are present in $\langle I_y \rangle_+$. The presence of double quantum (DQ) transitions in $\langle I_y \rangle_-$ is obvious. fig. 3(b). We have also done measurements on undeuterated l-alanine, gypsum and adamantane powders. The results for the undeuterated l-alanine are qualitatively the same as for the partly deuterated l-alanine. In gypsum we have observed the expected single and double quantum transitions. We have observed zero, single, double and triple quantum transitions in adamantane. These and other results will be dealt with in a more extended paper on multiple quantum spectroscopy in solids [6]. In another note [7] we deal with the short time behaviour of dipolar relaxations, solving a long standing problem.

In conclusion, we have used a familiar pulse program to show that multiple quantum spectroscopy is possible not only in liquids and liquid crystals, but also in ordinary solids. Finally we mention that line-narrowing techniques can be applied during the evolution time t and thus obtain a high-resolution multiple quantum spectrum, as confirmed by preliminary measurements. We hope to report on this in the near future.

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