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LETTER TO THE EDITOR

ON THE SHORT TIME BEHAVIOR OF THE DIPOLAR SIGNAL IN RELAXATION MEASUREMENTS BY THE PULSE METHOD

S. EMID, J. KONIJNENDIJK and J. SMIDT
Laboratorium voor Technische Natuurkunde, Technische Hogeschool Delft,
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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Methods have been developed for a direct observation of the dipolar relaxation during the short free induction decay times in solids. Experimental evidence is given that the dipolar energy is a constant of the motion, even during establishment of internal equilibrium. The humps usually observed in dipolar relaxation measurements are explained as due to the decay of multiple quantum coherences.

In this letter we focus on the short time behavior of the dipolar signal in dipolar relaxation measurements and develop methods for its direct observation.

The standard method to measure short dipolar relaxation times in solids is the Jeener–Broekaert pulse method [1] denoted by A in fig. 1. After the free induction decay and establishment of internal equilibrium the relaxation of the dipolar energy is given by $\langle I_y \rangle_A$ as a function of t. Till now one has to take t greater than about 4 or 5 times T_2, the free induction decay time, because usually $\langle I_y \rangle_A$ shows a hump for $t \leqslant 4T_2$, see fig. 2a, where $T_2 \simeq 16\ \mu s$. As shown in a previous letter [2] this hump is due to the decay of the off-diagonal density matrix elements. However, the problem about the behavior of the dipolar energy during establishment of internal equilibrium within the spin system has not been touched upon. One expects that this process will not change the total dipolar energy, since the latter is considered a constant of the motion [3] changed only by relaxation. If one can develop an experimental method which separates the effects of the off-diagonal density matrix elements from the dipolar relaxation, one would then be able to measure the short time behavior of the dipolar relaxation and thus to verify experimentally whether it is indeed constant during establishment of internal equilibrium. In this letter we propose two

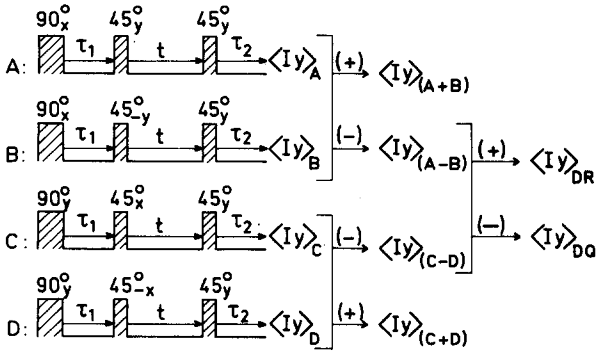

Fig. 1. Pulse programs to measure dipolar relaxation in solids. Usually one of these, mostly A, is used in dipolar relaxation measurements. The several combinations depicted are discussed in the text.

subsequent modifications of the Jeener–Broekaert pulse program, each being adequate to deal with the problem.

The spin system considered can be described by the hamiltonian:

$$H(t) = \omega_0 I_z + H_D^0 + H_{r.f.}(t) + H_{rel.}(t)\,, \qquad (1)$$

where $\omega_0 I_z$ is the Zeeman system, ω_0 being the Larmor precession frequency, H_D^0 is the motional averaged (i.e. static) and secular part of the dipolar interaction, $H_{r.f.}(t)$ is the interaction with a pulsed radio frequency field and $H_{rel.}(t)$ (e.g. fluctuation part of H_D) is the spin–lattice interaction, responsible for relaxation. It is convenient to transform to a frame rotating with angular frequency ω of the r.f. field, with axes (x, y, z). Representing a β pulse along an axis as a rotation over β about that axis and applying the pulse sequence A to the system initially in equilibrium, with the initial density matrix $\rho_0 = 1 - \alpha I_z$, one can derive:

$$\langle I_y\rangle_A = \mathrm{Tr}\, I_y^-(-\tau_2)\, \rho_A(t)\,, \qquad (2)$$

$$\rho_A(t) = \{\alpha(t)\}\, e^{iHt} I_y^+(\tau_1)\, e^{-iHt}\,,$$

with $H = \Delta\omega I_z + H_D^0$, $\Delta\omega = \omega_0 - \omega$ and

$$I_y^\pm(\tau) = U_\pm(\tau)\, I_y U_\pm^\dagger(\tau)\,, \qquad (3)$$

with $U_\pm(\tau) = e^{\pm i\pi I_y/4}\, e^{iH\tau}\, e^{\mp i\pi I_y/4}$.

In eq. (2) α becomes time dependent because of relaxation; the curly brackets indicate that this time-dependence may be different for different matrix elements of $\rho_A(t)$ (Zeeman, dipolar and multiple quantum coherences relax at different rates). Relaxations may also be mutually coupled [4].

For an arbitrary value of $\Delta\omega$, $\langle I_y\rangle_A$ contains dipolar (D) and Zeeman (Z) signals.

One can show that

$$\mathrm{D} \propto \cos \Delta\omega\tau_1 \cos \Delta\omega\tau_2\,, \qquad (4)$$

$$\mathrm{Z} \propto \sin \Delta\omega\tau_1 \sin \Delta\omega\tau_2\,. \qquad (5)$$

Dipolar relaxation measurements are therefore usually done on resonance, i.e. $\Delta\omega = 0$, to avoid the Zeeman signal. For $\langle I_y\rangle_A$ one usually obtains a curve like fig. 2a, with a hump for short times. One can resolve this into odd and even quantum transitions by combining programs A and B [2], fig. 1. In B the second pulse is phase shifted by 180° about the z-axis. One can show that $\rho_B(t) = -\exp(i\pi I_z)\, \rho_A(t) \exp(-i\pi I_z)$, so $\langle m|\rho_B|m+n\rangle = -\exp(\pi n)\langle m|\rho_A|m+n\rangle$, where m and n are Zeeman quantum numbers. From this relation and eq. (2) one can derive that the sum of $\langle I_y\rangle_A$ and $\langle I_y\rangle_B$, denoted by $\langle I_y\rangle_{(A+B)}$, contains only odd quantum coherences ($n = \pm 1, \pm 3, ...$), fig. 2b, and their difference $\langle I_y\rangle_{(A-B)}$ contains the diagonal part of the density matrix and the even quantum coherences ($n = 0, \pm 2, \pm 4, ...$), fig. 2c. It follows from fig. 2 that the hump is mainly due to the odd, actually single, quantum coherences. To show that the remaining wiggle in fig. 2c is due to double quantum coherences we set the r.f. frequency off-resonance with $\Delta\omega/2\pi$ = 40 kHz and observed the expected [2,5] modulation

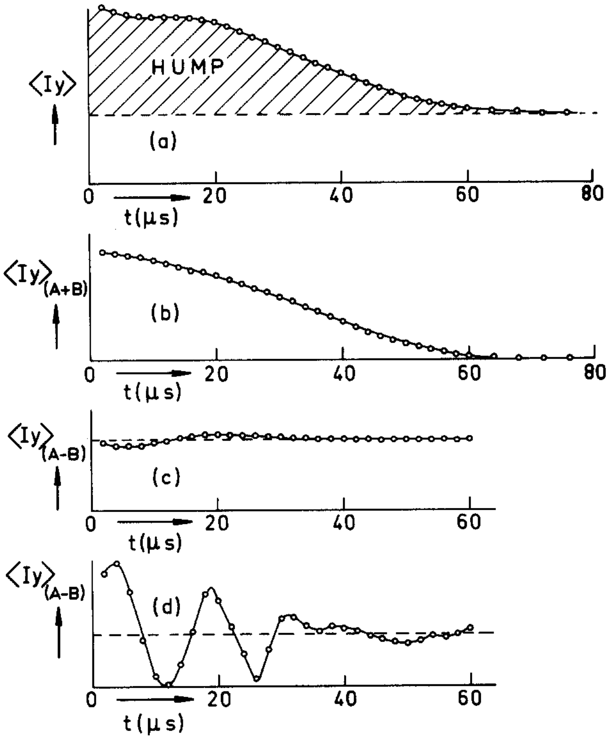

Fig. 2. The observed signals using a combination of two Jeener–Broekaert pulse programs. (a) $\langle I_y\rangle_A$ contains the decay of multiple quantum coherences and the dipolar signal, merged together. (b) $\langle I_y\rangle_{(A+B)}$ contains only odd quantum transitions. (c) $\langle I_y\rangle_{(A-B)}$ contains the dipolar signal and the even quantum transitions. (d) The double quantum transitions in $\langle I_y\rangle_{(A-B)}$ are modulated with about 80 kHz, which is twice the offset frequency. The average is the dipolar signal. The sample is $ND_3^+CHCH_3COO^-$ powder, at room temperature. The resonance frequency is 73 MHz. In (a)–(c): $\tau_1 = \tau_2$ = 16 μs, in (d): τ_1 = 16 μs, τ_2 = 24 μs.

with about 80 kHz, see fig. 2d, where τ_2 has been chosen such that sin $\Delta\omega\tau_2$ is small to reduce the influence of the Zeeman signal, cf. eq. (5). The average is then the dipolar signal. One finds that the dipolar energy remains constant during the establishment of internal equilibrium. We remark that even a single Jeener–Broekart program will do, with $\Delta\omega$ sufficiently off-resonance and such that sin $\Delta\omega\tau_1$ sin $\Delta\omega\tau_2 = 0$, but the resolution is less than in the two-program method.

A further modification is by combining programs A and B with C and D, fig. 1. In C and D the first two pulses are shifted in phase by 90° with respect to A and B. For $\rho_C(t)$ and $\rho_D(t)$ one can derive the relations: $\rho_{C,D}(t) = \exp(i\pi I_z/2)\,\rho_{A,B}(t)\exp(-i\pi I_z/2)$. With this, the relation between ρ_A and ρ_B and eq. (2) one can show that $\langle I_y\rangle_{(C-D)}$ contains only even quantum coherences and the diagonal part of the density matrix. It also follows that the different orders of even quantum coherences in $\langle I_y\rangle_{(C-D)}$ are shifted in phase by $2n \times 90°$ ($n = \pm 1, \pm 2, ...$) with respect to the corresponding orders in $\langle I_y\rangle_{(A-B)}$. The double quantum coherences will get the opposite phase, as observed experimentally. By combining these as indicated in fig. 1 one can separate the dipolar signal $\langle I_y\rangle_{DR}$ from the double quantum coherences $\langle I_y\rangle_{DQ}$, also for $\Delta\omega = 0$, as in fig. 3.

The measurements were on the protons of $ND_3^+CHCH_3COO^-$ and adamantane powders at room temperature, done with a Bruker CXP pulse spectrometer operating at 73 MHz. The dipolar relaxation for the first sample is non-exponential, with a short time-constant of about 500 μs, accounting for 20% of the signal, and a long time-constant of 22 ms. The fast decay is due to thermal equilibration with the deuterons [6] and is therefore rather temperature independent. The long time-constant is the real dipolar spin–lattice relaxation time (T_{1D}). Relaxation is exponential for the second sample with $T_{1D} \simeq 0.6$ s). During the measurements on adamantane we had to adjust for field drift between the acquisitions of $\langle I_y\rangle_{(A-B)}$ and $\langle I_y\rangle_{(C-D)}$. This may explain for the somewhat larger variation in $\langle I_y\rangle_{DR}$ compared to the other sample. With the second method it is also found that the dipolar energy is constant during the time that internal equilibrium is established. It should be remarked that under conditions for maximum transfer of Zeeman to dipolar order and maximum dipolar signal [1], i.e. $\tau_1 = \tau_2 = T_2$, terms linear in τ_1 and τ_2 in eq. (2) dominate; besides the diagonal matrix elements, these terms contain only single and double quantum coherences [2,7], therefore $\langle I_y\rangle_{(A-B)}$ and $\langle I_y\rangle_{(C-D)}$ should contain only diagonal elements and double quantum coherences, as observed. We also note that for a given signal to noise ratio of $\langle I_y\rangle_{DR}$ the measuring times with the modified programs are about the same as with one Jeener–Broekaert program. Since the modified programs separate T_2 effects from the dipolar relaxation, besides in confirming the constancy of the dipolar energy during internal equilibration, they should also be very useful when $T_{1D} \simeq T_2$. This is the case not only for T_{1D} minimum in ordinary solids, but also for dilute solids, where spin diffusion becomes slow, and for example for molecular groups dissolved in liquid crystals, where the dipolar energy remains well defined but spin diffusion is absent.

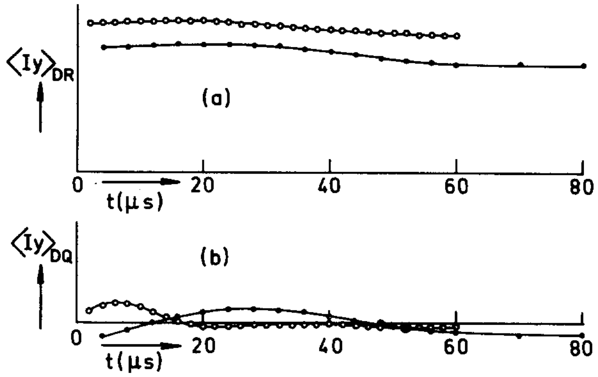

Fig. 3. Separate observations of dipolar relaxation and even quantum transitions on resonance ($\Delta\omega = 0$), using a combination of four Jeener–Broekaert pulse programs. (a) The dipolar signal $\langle I_y\rangle_{DR}$. (b) The double quantum transitions $\langle I_y\rangle_{DQ}$. (○) $ND_3^+CHCH_3COO^-$, $\tau_1 = \tau_2 = 16$ μs; (●) adamantane, $\tau_1 = \tau_2 = 40$ μs. Both samples are powders and the measurements have been done at room temperature and with a resonance frequency of 73 MHz.

To conclude, we have modified the standard pulse method for dipolar relaxation measurements. Using the modifications we have separated the free induction decay of multiple quantum coherences from the dipolar relaxation. We could then directly observe the short time behavior of the dipolar relaxation. We found the dipolar energy to be constant during the time of the free induction decay, when simultaneously internal equilibrium within the spin systems was established. Furthermore, with the four-program method we have shown more clearly than before [2] that the usually observed humps at short times are due to the decay of multiple quantum coherences.

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