Fourier-Transform Double-Quantum NMR in Solids*

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An approach to high-resolution NMR of deuterium in solids is described. The $m = 1$ $\to -1$ transition is excited by a double-quantum process and the decay of coherence $Q(\tau)$ is monitored. Fourier transformation yields a deuterium spectrum devoid of quadrupole broadening, and if the deuterium nuclei are dilute, the double-quantum spectrum is a high-resolution one. The technique is applied to a single crystal of oxalic acid dihydrate enriched to $\sim 10\%$ in deuterium, and the carboxyl and the water deuterium shifts are indeed resolved.

We describe in this Letter what we believe to be the first measurement of the chemical shift of deuterium in a solid. This includes the resolution of chemical shifts for different deuterium nuclei in a crystal and a measure of the anisotropy of the chemical shifts as the crystal is rotated. To perform the measurements we have exploited a novel technique involving the combination of dilute spin double resonance[1] and the coherence properties of multiple-quantum transitions.[2] Our approach offers for the first time an attractive alternative to solid-state proton NMR, since large molecules can be labeled at specific sites.

The problem with high-resolution solid-state NMR for any but spin-$\frac{1}{2}$ nuclei is the spectral splitting and broadening induced by the interaction of the nuclear quadrupole moments with electric field gradients. For deuterium (spin 1) the quadrupolar splittings are typically of the order of ~ 200 kHz, whereas the chemical shifts are expected to span a range of ~ 500 Hz. Figure 1 demonstrates the basis of our solution to this problem. The normal allowed transitions for the spin 1 are $m = 1 \to 0$ and $m = 0 \to -1$, which are shifted by the quadrupolar interaction, ω_Q. To first order, the $m = 1 \to -1$ splitting is not shifted, however. We induce the transition $m = 1 \to -1$ with a radiofrequency field of intensity ω_1 at the unshifted frequency ω_0,[3] placing the levels ± 1 in coherent superposition. This coherence, which we label tentatively $Q(\tau)$, now evolves as[2]

$$Q(\tau) \sim a(\tau) \cos 2\Delta\omega\tau, \qquad (1)$$

where $\Delta\omega$ is the resonance offset or chemical shift and $a(\tau)$ is the decay due to relaxation. Clearly, $Q(\tau)$ does not contain ω_Q and thus we have effectively removed the quadrupole broadening. If the deuterium nuclei are dilute and the protons are simultaneously spin decoupled, *then*

(1) yields on Fourier transformation a high-resolution spectrum containing chemical information. We term this a high-resolution Fourier-transform double-quantum spectrum.

To see the effect of eliminating ω_Q and the resonance offset or chemical shift behavior we have performed a series of preliminary experiments. The first is on an oriented crystal of perdeuterated oxalic acid dihydrate,[4] $(COOD)_2 \cdot 2D_2O$, where the carboxyl deuteriums have a quadrupole splitting of ~ 31 kHz and a linewidth of ~ 73 ppm. The following pulse sequence was applied:

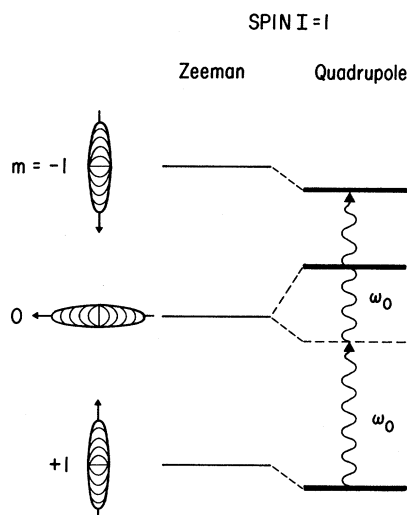$$P_1\text{-}\tau\text{-}P_2\text{-}t, \qquad (2)$$

FIG. 1. Deuterium spin-1 energy levels are shifted by $-\frac{1}{3}\omega_Q$ and $+\frac{2}{3}\omega_Q$ by interaction of the electric quadrupole with an axially symmetric electric field gradient. The transition $m = 1 \to -1$ is induced by a double-quantum transition at the unshifted frequency ω_0, with a radiofrequency field of intensity ω_1 and duration t_{P_1}, where $\omega_1 \ll \omega_Q$ and $(\omega_1{}^2/\omega_Q)t_{P_1} = \frac{1}{2}\pi$.

where P_1 is a pulse to induce the double-quantum transition and τ is the time during which the double-quantum decay occurs. P_2 is a probing pulse, necessary since $Q(\tau)$ normally induces no observable signal, i.e., $\langle I_+(\tau)\rangle = 0$. The signal following P_2 determines for each ω_Q the double-quantum decay as a function of τ. This is an example of two-dimensional Fourier-transform spectroscopy introduced by Jeener[2a] and by Aue, Bartholdi, and Ernst[2b] integrated over one axis.

Figure 2 shows the results of experiments at two different irradiation frequencies separated by ~2 kHz. The Fourier transform of the double-quantum decays indeed result in two lines separated by $2\Delta\omega \sim 4$ kHz. Their linewidths are ~18 ppm indicating an improvement in resolution over the normal spectrum by a factor of 4. The $2\Delta\omega$ behavior has also been observed in the double-quantum echo experiments of Hatanaka, Terao, and Hashi.[2c]

To demonstrate the application of our technique to the resolution of chemical shifts for inequivalent deuterium nuclei, a second experiment was performed on a single crystal of oxalic acid dihydrate enriched to ~10% in deuterium, oriented so that the carboxyl and the water deuterium resonances were both observable, the latter with a large linewidth of ~120 ppm. Pulse sequence (2)

was again applied to the deuterium spins, while the protons were spin decoupled by intense irradiation at resonance. The double-quantum decay and Fourier transform from free-induction decay intensities at small t appear in Fig. 3, showing separate chemical shifts from the carboxyl and water deuterium spins. Note also the dramatic improvement in the resolution of the line from the water resonance.

The final illustrative experiment involves the anisotropy of the chemical shielding tensor. The double-quantum peak for the carboxyl deuterium was observed as the crystal was rotated about an axis perpendicular to the magnetic field. An analysis of the data under the two assumptions (i) that the chemical shielding tensor is axially symmetric and (ii) that the principal axes are aligned with those of the electric field gradient
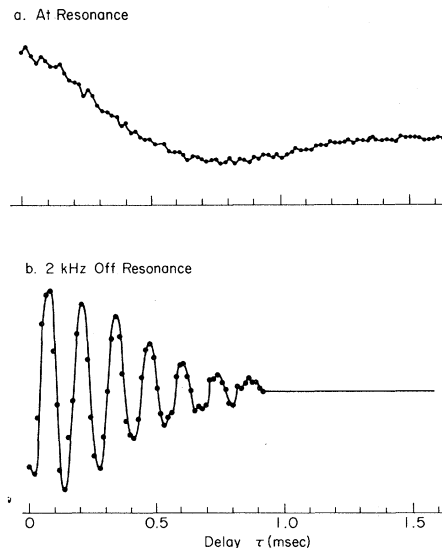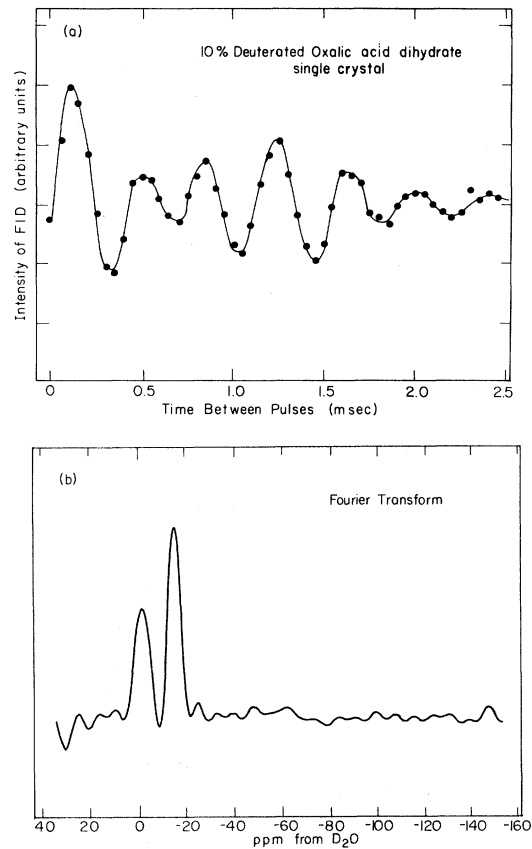

FIG. 2. Double-quantum decay of carboxyl deuterons in a crystal of perdeuterated oxalic acid dihydrate. A $\frac{1}{2}\pi$ double-quantum pulse was applied as in Fig. 1, and the decay monitored by observing the signal following a second pulse at time τ later. The shift of frequency (magnetic field) by $\Delta\omega \sim 2$ kHz shows up as $2\Delta\omega \sim 4$ kHz. The deuterium Larmor frequency was 16.3 MHz.

FIG. 3. Proton-decoupled double-quantum decay of deuterium (a) in a crystal of ~10% deuterated oxalic acid dihydrate. The normal NMR spectrum at this orientation shows reasonably sharp (~120 ppm) water satellites. The Fourier transform double-quantum spectrum (b) shows resolved, chemically shifted, carboxyl (right) and water (left) lines. The deuterium Larmor frequency was 28.4 MHz.

tensor yields an anisotropy of the chemical shift of

$$\Delta\sigma = 32 \pm 4 \text{ ppm} \tag{3}$$

and an isotropic value of $\sigma_i = -15$ ppm relative to D_2O. This $\Delta\sigma$ is larger than that measured by Yeung[5] ($\Delta\sigma = 25$ ppm) for the carboxyl protons by multiple-pulse techniques.[6]

We describe now a simple theoretical analysis based on idealized conditions for the pulses and interactions. A full analysis as well as detailed experimental results will be presented in a full paper. Consider a deuterium spin in a magnetic field H_0, coupled to an axially symmetric electric field gradient. Radiofrequency irradiation of intensity $2\omega_1$ is applied at frequency ω, close to the central frequency ω_0. We assume a quadrupole coupling of ω_Q and assume further that $\omega_0 \gg \omega_Q \gg \Delta\omega$, where $\Delta\omega = \omega_0 - \omega$. The Hamiltonian can be written (in angular frequency units):

$$H = -\omega_0 I_z + \tfrac{1}{3}\omega_Q[3I_z^2 - I(I+1)]$$
$$- 2\omega_1 I_x \cos\omega t, \tag{4}$$

where the three terms are the Zeeman coupling, the quadrupole coupling H_Q, and the interaction with the rf field, respectively.

In the rotating frame at frequency ω this transforms effectively to

$$H_R = -\Delta\omega I_z + \tfrac{1}{3}\omega_Q[3I_z^2 - I(I+1)] - \omega_1 I_x. \tag{5}$$

During the first pulse P_1, we assume

$$\Delta\omega \ll \omega_1 \ll \omega_Q, \tag{6}$$

yielding for the effective (secular) Hamiltonian during the pulse in a tilted quadrupolar frame, for spin 1,[7]

$$H_{P_1} = -(\omega_1^2/2\omega_Q)(I_x^2 - I_y^2)$$
$$+ \tfrac{1}{3}\omega_Q[3I_z^2 - I(I+1)]. \tag{7}$$

The term $(\omega_1^2/2\omega_Q)(I_x^2 - I_y^2)$ is the rigorous quantum mechanical operator for what we term loosely the double-quantum transition. The cross section ω_1^2/ω_Q comes from second-order perturbation theory.[3] If the spin system is originally in equilibrium before P_1, described by the reduced high-temperature density operator ρ_0, then the density operator becomes after this pulse

$$\rho(0) = \exp[i\theta(I_x^2 - I_y^2)/2]$$
$$\times \rho_0 \exp[-i\theta(I_x^2 - I_y^2)/2], \tag{8}$$

where $\theta = (\omega_1^2/\omega_Q)t_{P_1}$, $\rho_0 = \beta I_z$, and t_{P_1} is the

length of P_1. Evaluating (8), we find

$$\rho(0) = \beta\{I_z \cos\theta + (I_x I_y + I_y I_x)\sin\theta\}. \tag{9}$$

Selecting a $\tfrac{1}{2}\pi$ double-quantum pulse, i.e., $\theta = \tfrac{1}{2}\pi$, yields

$$\rho(0) = \beta(I_x I_y + I_y I_x). \tag{10}$$

Note that $\rho(0)$ is a sort of tensor alignment, in the terminology of de Boer,[8] with coherence in the x-y plane. $\rho(0)$ now evolves during τ according to

$$\rho(\tau) = \exp[-i(-\Delta\omega I_z + H_Q)\tau]$$
$$\times \rho(0) \exp[i(-\Delta\omega I_z + H_Q)\tau] \tag{11}$$

which can be easily evaluated for spin 1, since $[H_Q, \rho(0)] = 0$:

$$\rho(\tau) = \beta\{(I_x I_y + I_y I_x)\cos2\Delta\omega\tau$$
$$+ (I_x^2 - I_y^2)\sin2\Delta\omega\tau\}. \tag{12}$$

Note that $\text{Tr}[\rho(\tau)I_+] = 0$, so we do require the second pulse. *During the second pulse P_2, we assume*

$$\omega_1 \gg \omega_Q, \Delta\omega. \tag{13}$$

Taking P_2 to be a normal 90° pulse, i.e., $\omega_1 t_{P_2} + \pi/2$, where t_{P_2} is the length of P_2, we find for the expectation value of I_y following the second pulse what we termed previously the double-quantum coherence $Q(t)$:

$$\langle I_y \rangle \propto \beta \cos2\Delta\omega\tau, \tag{14}$$

which yields (1) when relaxation $a(\tau)$ is added.

To summarize, we have demonstrated successfully the resolution of deuterium chemical shifts in solids. In addition, the resolution is expected to be excellent since only heteronuclear decoupling is involved. We mention parenthetically that the chemical shifts can in many cases be determined by directly observing the quadrupolar satellites in the normal (single-quantum) deuterium NMR spectrum. In these cases, this is clearly the most convenient approach. However, any distribution of quadrupolar interactions due to crystal imperfections or chemical exchange, for example, completely eliminates the resolution, since $\omega_Q \gg \Delta\omega$. In such a case, the advantages of the double-quantum spectra are clear and are dramatically illustrated by the results in Fig. 3; this demonstrates a reduction in the water linewidth from ~120 ppm in the normal NMR spectrum to ~5 ppm in the double-quantum spectrum. Another example is the determination of deuterium chemical shift tensors from powders, which

we shall describe in the future.

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Scattering of Conduction Electrons by Magnetic Excitons in a Singlet Ground State System

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The electrical resistivity of $Tb_cY_{1-c}Sb$ has been measured as a function of temperature and of Tb concentration. The resistivity contribution from scattering of conduction electrons by Tb $4f$ electrons has been calculated in the paramagnetic regime in order to examine the competing effects of the crystal field and the exchange interaction. Excellent agreement with experiment is obtained for the entire range of c with one value for each of the two adjustable parameters, the Fermi momentum, and the electron-ion exchange constant.

Rare-earth metals and compounds normally undergo a magnetic phase transition due to the indirect exchange interaction between the magnetic $4f$ electrons. If the rare-earth ion is of the non-Kramers type, the crystal field may split the $4f$ multiplet in such a way that the lowest level is a singlet. Depending on whether the ratio of exchange to crystal field is larger or smaller than a critical value, the crystal will or will not order at the lowest temperatures.[1] The $Tb_cY_{1-c}Sb$ system is of particular interest since the exchange interaction between the Tb ions varies with c whereas the crystal field is virtually unaffected, thus allowing the behavior to be studied as the ratio passes through its critical value.[2] In this Letter we calculate the effect of the coexist-

ence of magnetic exchange and crystal field on the resistivity in the paramagnetic temperature regime and compare this to our measured resistivity.

We have measured the resistivity of fifteen 2–6-mm-long single crystals of $Tb_cY_{1-c}Sb$ with various values of the Tb concentration in the temperature range from 1.5 to 300 K. The resistivity was determined by a four-terminal dc method and the temperature measured with a thermocouple.

Figure 1 shows the experimental results in the temperature range up to 30 K. The residual resistivity has been subtracted and each resistivity versus temperature curve has an arbitrary origin. Since the absolute resistivity for some of