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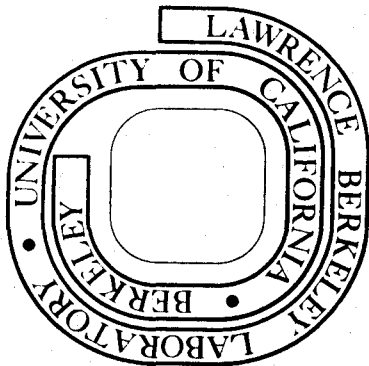
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Fourier Transform Double-Quantum NMR in Solids*S. Vega,[†] T. W. Shattuck and A. Pines[‡]

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ABSTRACT

An approach to high resolution nmr of deuterium in solids is described. The $m = 1 \rightarrow -1$ 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 splittings and broadening. If the deuterium nuclei are dilute and the protons are spin decoupled, the double-quantum spectrum is a high resolution one and yields information on the deuterium chemical shifts $\Delta\omega$. The relationship $Q(\tau) \sim \cos 2\Delta\omega\tau$ is checked and the technique is applied to a single crystal of oxalic acid dihydrate enriched to $\sim 10\%$ in deuterium. The carboxyl and the water deuterium shifts are indeed resolved and the anisotropy of the carboxyl shielding tensor is estimated to be $\Delta\sigma = 32 \pm 4$ ppm. A simple illustrative theoretical analysis is presented.

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Fourier Transform Double-Quantum NMR in Solids

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 resonance¹ and the coherence properties of multiple-quantum transitions.²

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 $m = 1 \rightarrow 0$ and $m = 0 \rightarrow -1$, which are shifted by the quadrupolar interaction, ω_Q . To first order, the $m = 1 \rightarrow -1$ splitting is not shifted, however. We induce the transition $m = 1 \rightarrow -1$ with a radio frequency 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 as²

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

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 shift 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 $(\text{COOD})_2 \cdot 2\text{D}_2\text{O}$ where the carboxyl deuteriums have a quadrupole splitting of ~ 31 KHz and a line width of ~ 73 ppm.

The following pulse sequence was applied:

$$(P_1 - \tau - P_2 - t) \quad (2)$$

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^{2c} and by Ernst et al.^{2d} 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.

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 $\sim 10\%$ 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 spin decoupling the protons by intense irradiation at resonance. The double-quantum decay and Fourier transform from free induction decay intensities at small t appear in Figure 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) the chemical shielding tensor is axially symmetric and ii) the principal axes are aligned with those of the electric field gradient tensor, yield an anisotropy of the chemical shift of:

$$\Delta\sigma = 32 \pm 4 \text{ ppm} \quad (3)$$

and an isotropic value of $\sigma_1 = -15$ ppm relative to D_2O . This $\Delta\sigma$ is larger than that measured by Yeung⁵ ($\Delta\sigma = 25$ 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 and coupled to an axially symmetric electric field gradient. Radio frequency 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):

$$H = -\omega_0 I_z + \frac{1}{3} \omega_Q (3I_z^2 - I(I+1)) - 2\omega_1 I_x \cos \omega t \quad (4)$$

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:

$$H_R = -\Delta\omega I_z + \frac{1}{3} \omega_Q (3I_z^2 - I(I+1)) - \omega_1 I_x \quad (5)$$

During the first pulse P_1 , we assume:

$$\Delta\omega \ll \omega_1 \ll \omega_Q \quad (6)$$

yielding for the effective (secular) Hamiltonian during the pulse in a tilted quadrupolar frame for spin-1:⁷

$$H_{P_1} = -\frac{\omega_1^2}{2\omega_Q} (I_x^2 - I_y^2) + \frac{1}{3} \omega_Q (3I_z^2 - I(I+1)) \quad (7)$$

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

$$\rho(0) = e^{\frac{i}{2}\theta (I_x^2 - I_y^2)} \rho_0 e^{-\frac{i}{2}\theta (I_x^2 - I_y^2)} \quad (8)$$

where $\theta = \frac{\omega_1^2}{\omega_Q} t_{P_1}$, $\rho_0 = \beta I_z$, and t_{P_1} is the length of P_1 . Evaluating (8), we find:

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

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

$$\rho(0) = \beta (I_x I_y + I_y I_x) \quad (10)$$

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

$$\rho(\tau) = e^{-i(-\Delta\omega I_z + H_Q)\tau} \rho(0) e^{i(-\Delta\omega I_z + H_Q)\tau} \quad (11)$$

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

$$\rho(\tau) = \beta \{ (I_x I_y + I_y I_x) \cos 2\Delta\omega\tau + (I_x^2 - I_y^2) \sin 2\Delta\omega\tau \} \quad (12)$$

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

$$\omega_1 \gg \omega_Q, \Delta\omega \quad (13)$$

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 $Q(t)$:

$$\langle I_y \rangle \propto \beta \cos 2\Delta\omega\tau \quad (14)$$

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

To summarize, we have demonstrated successfully the resolution of deuterium chemical shifts in solids. Our approach offers for the first time an attractive alternative to solid state proton nmr, since large molecules can be labeled at specific sites. 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 Figure 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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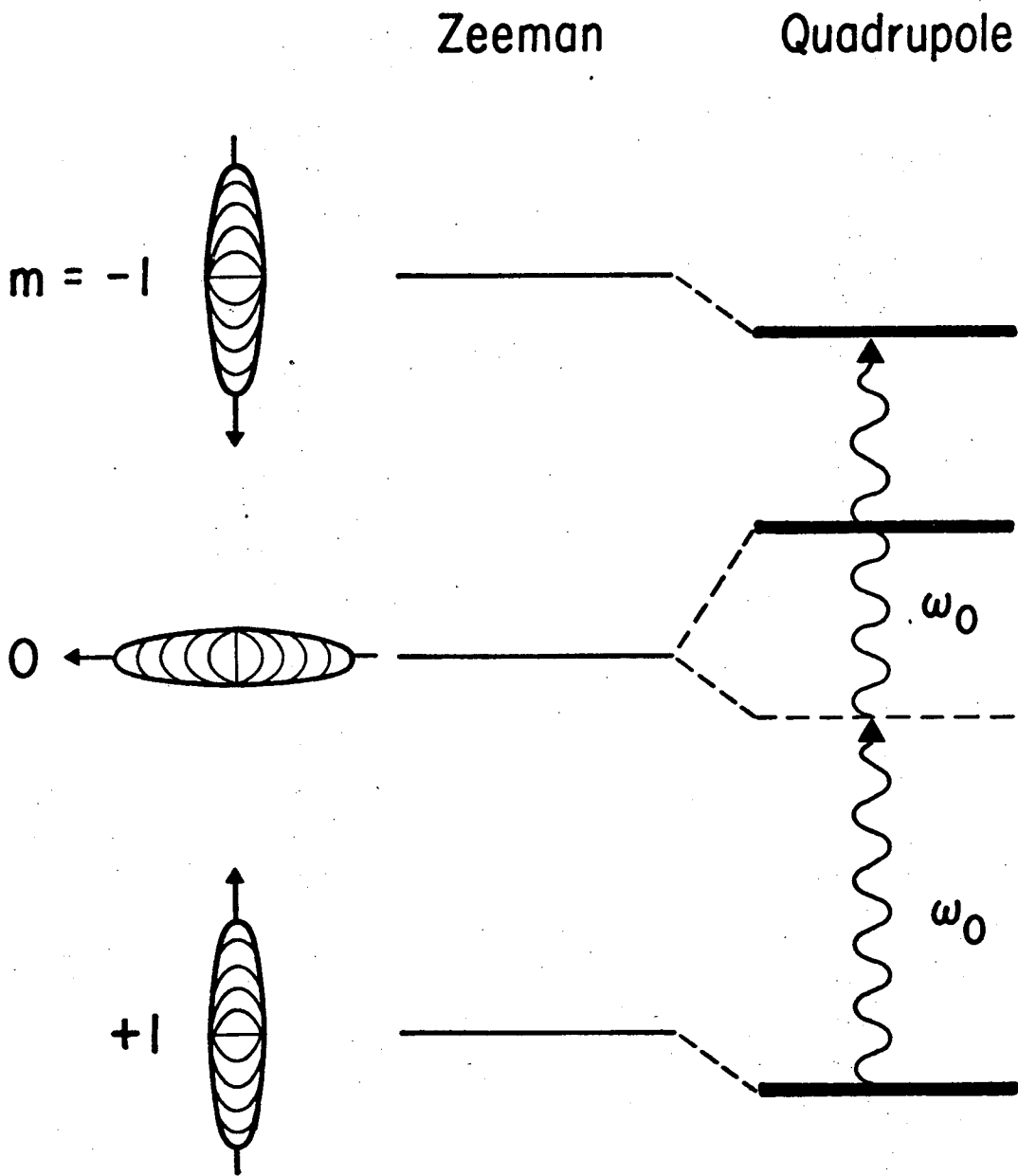
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Figure Captions

1. Deuterium spin-1 energy levels are shifted by $-\frac{1}{3}\omega_Q$ and $+\frac{2}{3}\omega_Q$ due to interaction of the electric quadrupole with an axially symmetric electric field gradient. The transition $m = 1 \rightarrow -1$ is induced by a double-quantum transition at the unshifted frequency ω_0 , with a radio frequency field of intensity ω_1 and duration t_{P_1} where $\omega_1 \ll \omega_Q$ and $\frac{\omega_1^2}{\omega_Q} t_{P_1} = \frac{\pi}{2}$.
2. Double-quantum decay of carboxyl deuterons in crystal of perdeuterated oxalic acid dihydrate. A $\frac{\pi}{2}$ double-quantum pulse was applied as in Figure 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.
3. Proton decoupled double-quantum decay of deuterium (a) in crystal of $\sim 10\%$ deuterated oxalic acid dihydrate. The normal nmr spectrum at this orientation shows reasonably sharp (~ 10 ppm) carboxyl deuterium satellites and extremely broad (~ 120 ppm) water satellites. The Fourier transform double-quantum spectrum shows resolved chemically shifted carboxyl (right) and water (left) lines. The deuterium Larmor frequency was 28.4 MHz.

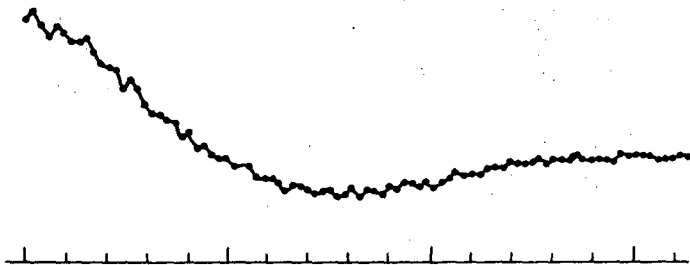
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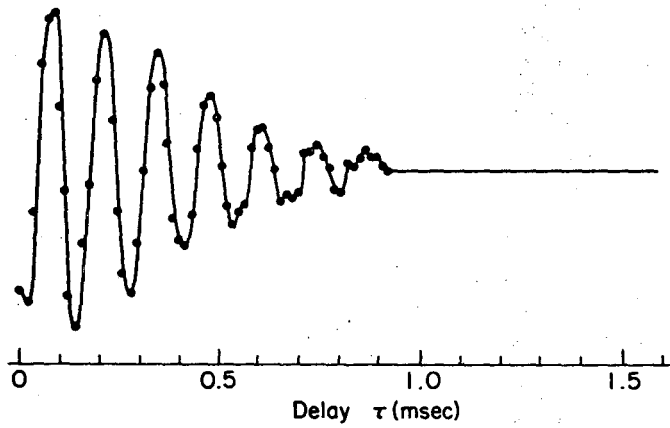
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Figure 1

a. At Resonance

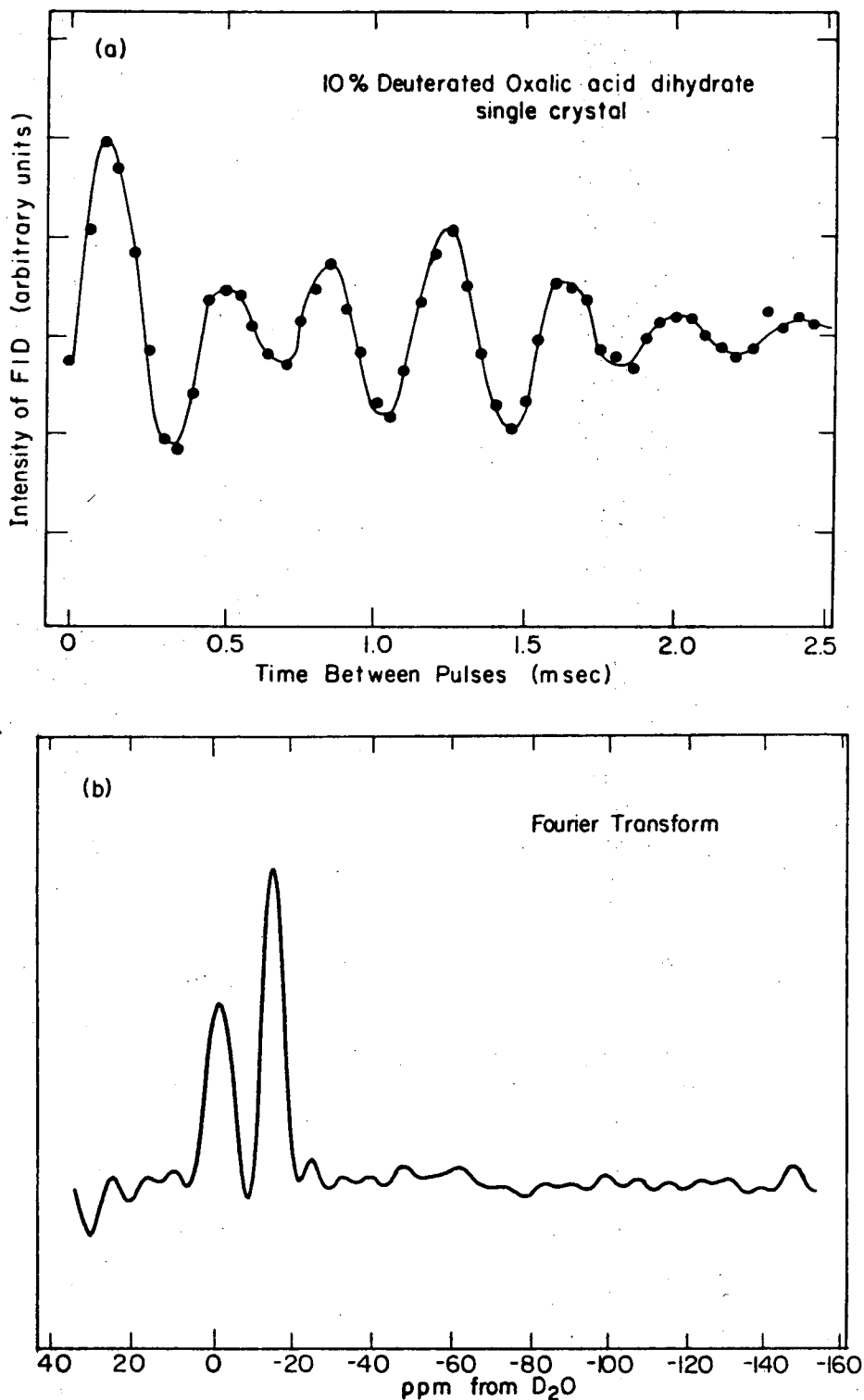


b. 2 kHz Off Resonance



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Figure 2



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Figure 3

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