

# DOUBLE QUANTUM NMR IN SOLIDS

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In this paper double quantum NMR of deuterium in solids is described. By Fourier transformation of the time evolution, detected by a suitable train of pulses, a high resolution spectrum devoid of quadrupole splittings and broadening is obtained. The experiment is performed to a single crystal of oxalic acid dihydrate enriched to  $\sim 10\%$  in deuterium and the chemical shift anisotropy of the carboxyl deuteron is estimated to be  $\Delta\sigma = 32 \pm 3$  ppm.

## I. INTRODUCTION

Solid state NMR is rapidly being developed into a powerful means of probing electronic structure, molecular conformation and molecular dynamics. We performed the measurements of the chemical shift of deuterium in a solid by means of a new method<sup>1)</sup> developed recently.

Instead of observing the proton magnetic resonance we choose to observe deuterium nuclei (spin-1) which have been substituted into the molecule of interest. This isotopic dilution serves to decrease the strong dipole-dipole interactions which might obscure chemical shift information.<sup>2)</sup> On the other hand, the ability to extract information from deuterium resonance is severely hampered by extreme broadening caused by the interaction of the nuclear quadrupole moment with electric field gradient. We used Fourier transform double quantum (FTDQ) spectroscopy developed for dealing with this problem. Figure 1 demonstrates that the deuterium spin-1 levels are shifted by quadrupolar interaction in such a way that extremely broad spectra are normally found. However, by a double quantum transition we can induce transitions between  $m = \pm 1$ . The coherent state thus produced oscillates at frequencies independent of quadrupolar splitting. The decay of this coherence does not contain the quadrupole broadening, and yields on Fourier transformation a high resolution spectrum.

In the second section the theoretical treatment of double quantum NMR is described. Some experimental results are presented in the fourth section.

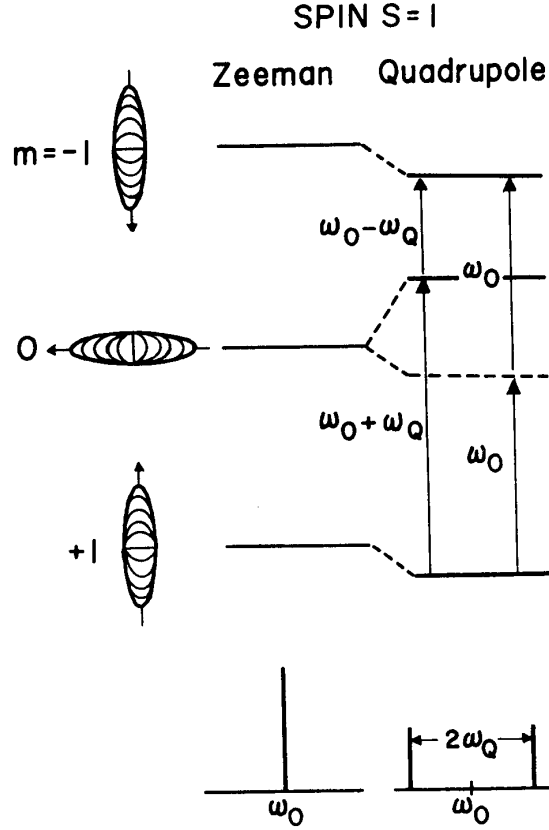


Figure 1. Energy levels for quadrupolar spin-1 in high magnetic field.

## II. THEORY

We now consider a deuterium spin ( $S$ -spin) in a magnetic field  $H_0$ , coupled to an axially symmetric electric field gradient. The radiofrequency irradiation of intensity  $2\omega_1$  is applied at frequency  $\omega$ , close to the central frequency  $\omega_0$ . We assume a quadrupole coupling of  $\omega_Q$  and assume further that  $\omega_0 \gg \omega_Q \gg \Delta\omega$ , where  $\Delta\omega = \omega_0 - \omega$ . In the rotating frame the Hamiltonian for system is given by:

$$H = -\Delta\omega S_z - \omega_1 S_x + \frac{1}{3}\omega_Q(3S_z^2 - S(S+1)) \quad (1)$$

where the first term is the Zeeman coupling, the second term is the interaction with the rf-field and the third term is the quadrupole coupling. Casting this in

Table I. Fictitious spin-1/2 operators for three level system.

$S_{x,1} = \frac{1}{2}S_x$	$S_{y,1} = \frac{1}{2}S_y$	$S_{z,1} = \frac{1}{2}S_z$
$S_{x,2} = \frac{1}{2}(S_y S_z + S_z S_y)$	$S_{y,2} = \frac{1}{2}(S_z S_x + S_x S_z)$	$S_{z,2} = \frac{1}{2}(S_x S_y + S_y S_x)$
$S_{x,3} = \frac{1}{2}(S_z^2 - S_y^2)$	$S_{y,3} = \frac{1}{2}(S_x^2 - S_z^2)$	$S_{z,3} = \frac{1}{2}(S_y^2 - S_x^2)$

term of the fictitious spin  $-\frac{1}{2}$  operators<sup>3)</sup> from Table I, this can be written as :

$$H = -2\Delta\omega S_{z,1} - 2\omega_1 S_{x,1} + \frac{2}{3}\omega_Q(S_{x,3} - S_{y,3}) \quad (2)$$

Let us now transform the Hamiltonian by the unitary transformation operator:

$$U_{r,2}(\theta) = \exp(-i\theta S_{x,2}) \quad (3)$$

where U denotes a tilted frame<sup>4)</sup> and

$$\theta = \tan^{-1}\left(\frac{2\omega_1}{\omega_Q}\right), \quad \omega_e = (4\omega_1^2 + \omega_Q^2)^{1/2} \quad (4)$$

The transformed Hamiltonian is :

$$\begin{aligned} H_T &= U_{r,2}^* H U_{r,2} \\ &= -2\Delta\omega \left( S_{z,1} \cos \frac{\theta}{2} + S_{y,2} \sin \frac{\theta}{2} \right) + \omega_e S_{x,3} - \frac{1}{3}\omega_Q(S_{y,3} - S_{z,3}) \end{aligned} \quad (5)$$

With the conditions  $\Delta\omega \ll \omega_1 \ll \omega_Q$  we neglect the term  $2\Delta\omega \sin \frac{\theta}{2} S_{y,2}$  yielding

$$H_T \approx -2\Delta\omega S_{z,1} - \frac{1}{2}(\omega_e - \omega_Q) S_{z,3} + \left( \frac{2}{3}\omega_Q + \frac{1}{2}(\omega_e - \omega_Q) \right) (S_{x,3} - S_{y,3}) \quad (6)$$

The third term in Equation (6) commutes with the first two

$$\begin{aligned} [S_{p,i}, S_{q,3} - S_{r,3}] &= 0 & p, q, r = x, y, z \\ & & i = 1, 2, 3 \end{aligned}$$

and will therefore play no role in any system where we start in the thermal equilibrium. Thus we can discard it. Since  $\omega_1 \ll \omega_Q$ , we can expand the coefficient of the second term and obtain the double quantum Hamiltonian :

$$H_{DQ} \approx -2\Delta\omega S_{z,1} - \frac{\omega_1^2}{\omega_Q} S_{z,3} \quad (7)$$

Equation (7) contains two terms in exact analogy to the spin  $-\frac{1}{2}$  case. The first term corresponds to a resonance offset of  $2\Delta\omega$  along the  $z, 1$  axis. The second term correspond to an rf-field of intensity  $\omega_1^2/\omega_Q$  along the  $z, 3$  axis. This is exactly analogous to the spin  $-\frac{1}{2}$  case where we have a resonance offset  $\Delta\omega$  along the  $z$ -axis and an rf-field  $\omega_1$  along the  $x$ -axis.

We can now discuss the evolution of the spin density matrix under the Hamiltonian of Equation (7), namely during a double quantum rf-pulse. We assume the density matrix is initially given in equilibrium by :

$$\rho_0 = 2\beta\omega_0 S_{z,1} \quad (8)$$

where  $\beta$  is the laboratory inverse temperature. Taking  $H_{DQ}$  from Equation (7) and assuming

$$\frac{\omega_1^2}{\omega_Q} \gg 2\Delta\omega \quad (9)$$

we can neglect  $2\Delta\omega$  during the pulse and obtain to a good approximation :

$$\rho(t) \approx 2\beta\omega_0 \left( S_{z,1} \cos \frac{\omega_1^2}{\omega_Q} t - S_{z,2} \sin \frac{\omega_1^2}{\omega_Q} t \right) \quad (10)$$

Thus we see that we are rotating the effective density matrix around the z, 3 axis at an angular frequency of  $\omega_1^2/\omega_Q$ . This we might term "double quantum rotary free induction decay" and it has already been treated and observed by Hatanaka et al.<sup>5)</sup> We define a  $\frac{\pi}{2}$  double quantum pulse :

$$\frac{\omega_1^2}{\omega_Q} t = \frac{\pi}{2} \quad (11)$$

in which case we obtain the density matrix after preparation as

$$\rho = -2\beta\omega_0 S_{z,2} \quad (12)$$

This indicates that the pulse has created a coherence superposition of the  $|x\rangle$  and  $|y\rangle$  levels, without affecting the other transitions. In case of this

$$\begin{aligned} |x\rangle &= \frac{-1}{2}(|+1\rangle - |-1\rangle) \\ |y\rangle &= \frac{i}{2}(|+1\rangle + |-1\rangle) \\ |z\rangle &= |0\rangle \end{aligned} \quad (13)$$

where  $|+1\rangle$ ,  $|-1\rangle$  and  $|0\rangle$  are the eigenfunctions of  $S_z$  for  $S=1$ . The time dependence of this coherent superposition is governed by the Hamiltonian (equation (2)) :

$$H = -2\Delta\omega S_{z,1} + \frac{2}{3}\omega_Q(S_{r,3} - S_{y,3}) \quad (14)$$

yielding

$$\rho(t) = -S_{z,2} \cos 2\Delta\omega t + S_{z,3} \sin 2\Delta\omega t \quad (15)$$

So as expected the precession frequency for this double quantum transition is twice the offset frequency.

This coherence cannot be observed directly since it remains entirely in the z-space, i. e.,

$$\text{Tr}(S_{r,j} S_{z,k}) = \text{Tr}(S_{y,j} S_{z,k}) = 0 \quad j, k = 1, 2, 3 \quad (16)$$

We must apply a second pulse to transfer this coherence to one of the observable transitions. We hope that if at a particular time  $\tau$  we apply a strong pulse we will elicit a magnetization which will be proportional to the double quantum coherence

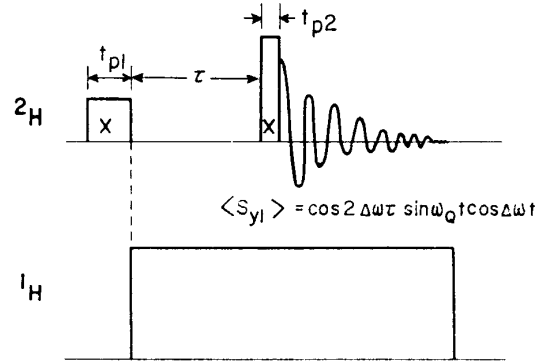


Figure 2. Double quantum pulse sequence with simultaneous proton decoupling.  $t_{p1}$  and  $t_{p2}$  are the coherence pulse length and the probing pulse length respectively.

at time  $\tau$ . This is the case as depicted schematically by Figure 2. If the first pulse is selected to be a double quantum  $\frac{\pi}{2}$  pulse, then the density matrix for  $\rho_i = S_{i,1}$  is given after this pulse by

$$\rho(t_{p1}) = -S_{i,2} \quad (17)$$

The evolution of  $\rho(\tau)$  during the time  $\tau$  between the pulses is given by

$$\rho(t_{p1} + \tau) = -S_{i,2} \cos 2\Delta\omega\tau + S_{i,3} \sin 2\Delta\omega\tau \quad (18)$$

and the strong second detection pulse results in

$$\rho(t_{p1} + \tau + t_{p2}) = S_{y,2} \cos 2\Delta\omega\tau + \frac{1}{2} (S_{r,3} - (S_{y,3} - S_{i,3})) \sin 2\Delta\omega\tau \quad (19)$$

where we took  $\omega_1 t_{p2} = \frac{\pi}{2}$  with  $\omega_1 \gg \omega_Q$ .

This results in a signal intensity.<sup>3)</sup>

$$\begin{aligned} A_x &= \gamma \langle S_x \rangle = A_0 \cos 2\Delta\omega\tau \sin \omega_Q t \sin \Delta\omega t \\ A_y &= \gamma \langle S_y \rangle = A_0 \cos 2\Delta\omega\tau \sin \omega_Q t \cos \Delta\omega t \end{aligned} \quad (20)$$

where  $\gamma$  is gyromagnetic ratio:

$$A_0 = \frac{2}{3kT} \gamma \omega_0 N \quad (21)$$

and  $N$  is the number of spins in sample.

### III. EXPERIMENTAL

The samples chosen were single crystals of oxalic acid dihydrate. Commercial oxalic acid dihydrate was dissolved in either 100 %  $D_2O$  or 10 %  $D_2O$  in  $H_2O$  and filtered then allowed to stand at room temperature to evaporate yielding large single crystal. The experimental method have been described in the reports by Pines et al.<sup>1)</sup>

#### IV. RESULTS AND DISCUSSION

The double quantum free induction decays (DQFID) of deuterium in a crystal of 100 % deuterated oxalic acid dihydrate are shown in Figure 3 (a), (b) for offset frequencies  $0 \pm 50$  Hz and  $2000 \pm 50$  Hz, respectively. The Fourier transforms are shown in Figure 3 (c). In (a) a double quantum pulse was applied near resonance and we see a FID lasting almost 1 millisecond. The deuterium field strength for the coherence pulse was  $\omega_{1s} = 26.8$  kHz giving  $\omega_1/\omega_Q \approx 1.9$  and  $t_z = 13.2$   $\mu$ sec, where  $t_z$  is the theoretical  $90^\circ$  pulse for the double quantum transition. The pulse widths used were  $t_{p1} \approx 36$   $\mu$ sec ( $270^\circ$  pulse) and  $t_{p2} \approx 5$   $\mu$ sec ( $\omega_{1s} = 50$  kHz). The shift between (a) and (b) should be  $2\Delta\omega \approx 4$  kHz. Experimentally, Fourier transforming the two decays from (a) and (b) we get spectra in (c) which are shifted by  $\sim 4$  kHz showing the  $2\Delta\omega$  effect. In addition, the lines are  $\sim 37$  ppm wide, which is considerably narrower than the width of the quadrupolar satellites in the original single quantum spectrum, so that we are eliminating inhomogeneous distributions of quadrupole coupling.

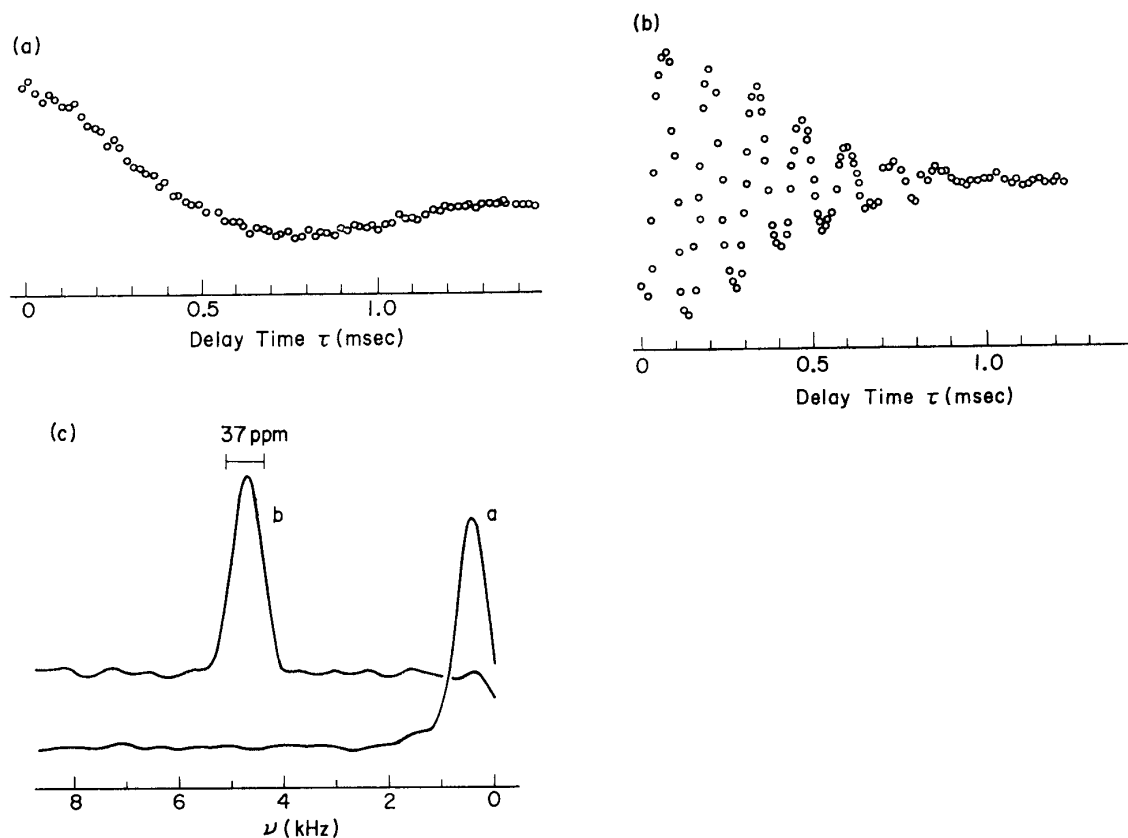


Figure 3. Double quantum free induction decay of deuterium in a crystal of perdeuterated oxalic acid dihydrate. (a) near resonance and (b)  $\Delta\omega \approx 2$  kHz off resonance. Figure (c) contains the Fourier transform of those decays showing the double quantum offset is  $2\Delta\omega \approx 4$  kHz.

To resolve a deuterium chemical shift the preceding double quantum experiment was repeated using the same crystal of 10 % deuterated oxalic acid dihydrate. The double quantum spectrum was obtained for two different orientation. The same two pulse sequence was used as before (Figure 2) but with the following parameter :

$$\nu_Q = \frac{\omega_Q}{2\pi} \approx 40 \text{ kHz}, \quad \frac{\omega_1}{\omega_Q} = 0.79$$

$$\nu_z = \frac{\omega_z}{2\pi} = 18 \text{ kHz} \quad (\omega_z = \frac{1}{2} (\sqrt{\omega_Q^2 + (2\omega_1)^2} - \omega_Q))$$

$$\omega_z \tau = \frac{\pi}{2}$$

In order to obtain high resolution spectra it was necessary to apply proton decoupling during the delay between the pulses,  $\tau$ , as well as after the probing pulse,  $P_2$ . The strength of the decoupling was  $\frac{\omega_{H1}}{2\pi} \approx 30 - 35 \text{ kHz}$ . The decoupled DQFID's for the carboxyl deuterium are shown for the two orientations in Figure 4. The Fourier

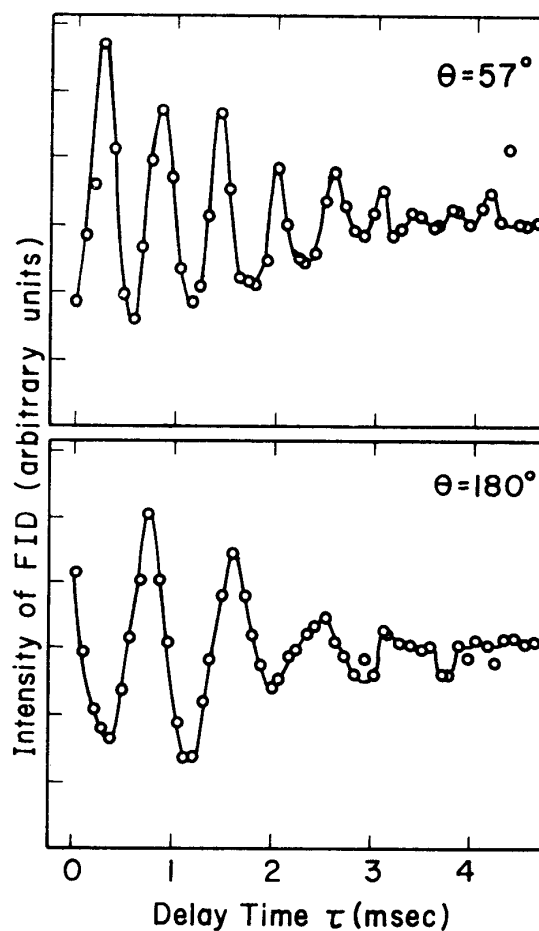


Figure 4. Double quantum FID of deuterium in 10 % deuterated crystal of oxalic acid dihydrate for the two orientations.  $\theta$  is the angle of the crystal axis relative to the external field.

transform double quantum spectra obtained from the DQFID's in Figure 4 are shown in Figure 5. The spectra are shown here plotted in ppm from an internal water reference.

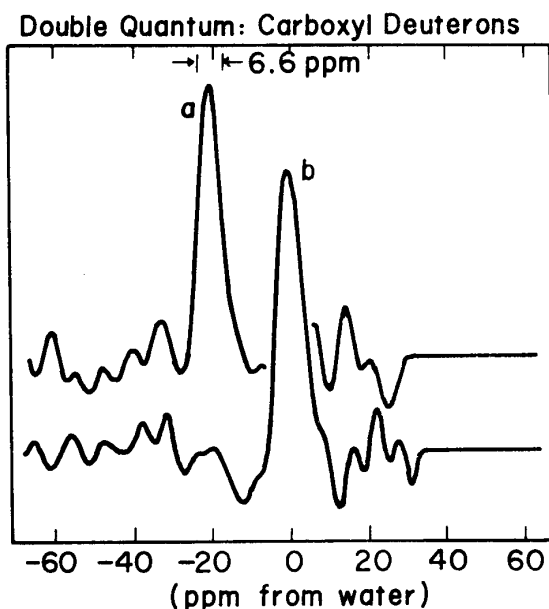


Figure 5. Fourier transform double quantum spectra obtained from the DQFID's in Figure 4. Spectrum a is from the  $57^\circ$  orientation and spectrum b is from the  $180^\circ$  orientation.

We can also measure the chemical shift anisotropy of the deuterium and the measurement is shown in Figure 6. Here the double quantum peak of the carboxylic deuterium was monitored as the crystal was rotated and compared with the chemical shift measured from a single quantum experiment. The latter is done in a good crystal by observing the quadrupolar satellites with high resolution while proton decoupling. We can see that this result shows the large chemical shift

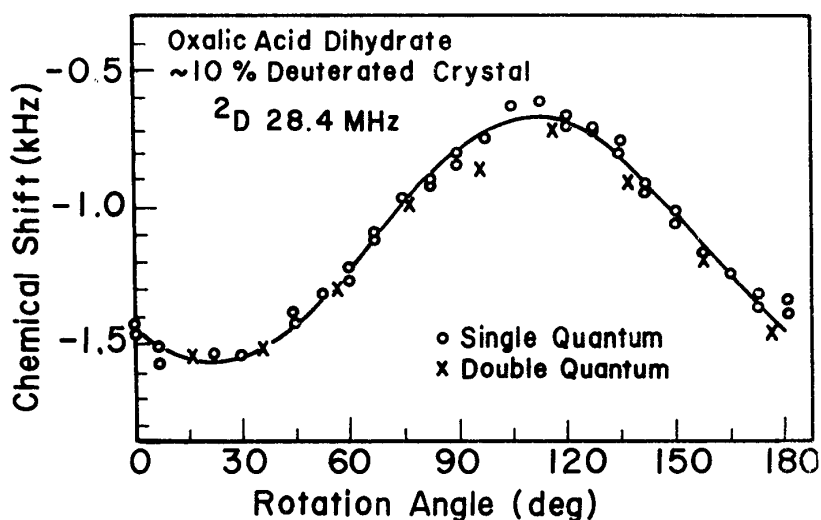


Figure 6. Chemical shift of carboxyl deuterium as the crystal is rotated.



anisotropy.

Fourier transform DQ-NMR of deuterium was reported in this paper. An exciting extension of this work would be the observation of oxygen 17 and nitrogen 14 chemical shifts. Nitrogen 14 is spin-1 and the extension of this theory is immediate. Its quadrupole moment is 10 times bigger than deuterium's however, necessitating a different detection technique, perhaps that of Hatanaka et al. Oxygen 17, spin- $\frac{5}{2}$ , has a quadrupole coupling also of the same order as nitrogen, but the electric field gradients may be somewhat smaller than deuterium's for some classes of compounds.

## V. ACKNOWLEDGMENT

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