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August 1988

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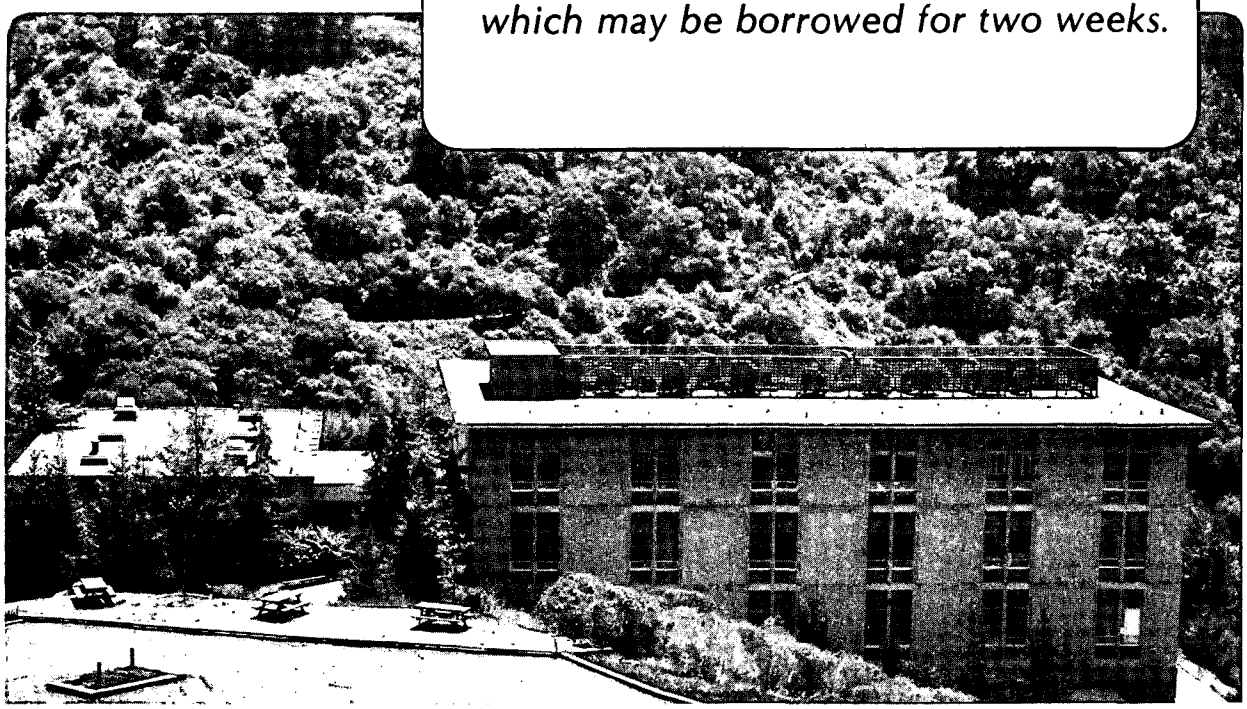

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HIGH RESOLUTION SOLID-STATE NMR: AVERAGING OF SECOND-ORDER EFFECTS BY MEANS OF A DOUBLE-ROTOR(*)

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Running Title: Double-Rotation in Solid-State NMR

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ABSTRACT

By means of rotations around two axes inclined at zeroes (magic angles) of the $\ell = 2$ and $\ell = 4$ Legendre polynomials, first-order and second-order NMR broadening can be averaged away. Experiments with a double-rotor on the central ($1/2 \leftrightarrow -1/2$) transition of sodium-23 in polycrystalline sodium oxalate illustrate the elimination of broadening due to second-order quadrupolar effects, leading to a thirtyfold increase in resolution compared to magic-angle spinning.

Spectral broadening due to anisotropic second-order frequency shifts has been one of the serious obstacles to high resolution NMR of quadrupolar nuclei in the solid state. One now understands that neither rotation of the sample around any one axis, as in (say) magic-angle spinning (MAS)[1], nor radiofrequency manipulations of the spins[2] can eliminate such effects of second-order spatial anisotropy. It is therefore commonly surmised that the only solutions to this problem are either to perform MAS experiments in higher magnetic fields (since second-order effects are inversely proportional to the field strength)[3], or to remove the magnetic field and recover a scalar Hamiltonian as in zero-field NMR.[4]

There is, however, an alternative approach[5,6], one version of which we demonstrate experimentally in this communication, namely to rotate the sample around more than one axis. To appreciate why this is so and how it can be done, consider the arrangement in Figure 1, where the rotor containing the sample is itself suspended inside a second rotor. Recall that the spatial anisotropy of secular nuclear interactions is conveniently described by a sum of spherical harmonics of increasing rank ℓ. In high field, the leading terms in the orientation-dependent NMR frequencies

$$\omega = \omega_0 + \sum_{\ell} \sum_{m=-\ell}^{+\ell} A_{\ell m} Y_{\ell m}(\Omega) \quad , \tag{1}$$

are of rank $\ell = 2$ and 4, where $Y_{\ell m}(\Omega)$ are spherical harmonics (for non-secular terms an expansion in full Wigner matrices $D^{(\ell)}$ is necessary), Ω denotes the two angles (θ,ϕ) specifying the orientation of the magnetic field in a coordinate system fixed with the sample and the coefficients $A_{\ell m}$ depend on the principal values and axes of the spin interaction tensors. First-order effects such as chemical shift anisotropy and secular dipole-dipole couplings are contained in

the $\ell = 2$ term, while second-order effects (which arise from correction terms to the average Hamiltonian[2]) are expressed by both $\ell = 2$ and $\ell = 4$ terms. The frequency ω_0 describes the sum of the isotropic chemical shift and the isotropic part of the high-order couplings.

If the sample undergoes reorientation so that Ω is made time dependent, then the average frequency from (1) is given by

$$\langle\omega\rangle = \omega_0 + \sum_{\ell} \sum_{m=-\ell}^{+\ell} A_{\ell m} \langle Y_{\ell m}(\Omega)\rangle \quad , \tag{2}$$

where $\langle\ \rangle$ denotes average values over the realized values of Ω. The terms $\langle Y_{\ell m}(\Omega)\rangle$ are zero for motion around an axis if the magnetic field assumes at least $\ell + 1$ equally spaced directions on a cone with half-apex angle $\theta_m^{(\ell)}$ viewed in the sample coordinate system, where $\theta_m^{(\ell)}$ is a zero (<u>ℓ'th-rank magic angle</u>) of the ℓ'th-rank Legendre polynomial:

$$P_\ell(\cos\theta_m^{(\ell)}) = 0 \quad . \tag{3}$$

In the usual case of first-order broadening ($\ell = 2$), this corresponds to threefold (or higher) hops[7] or, in the continuous MAS limit, to rotation at the "normal" magic angle $\theta_m \equiv \theta_m^{(2)} = 54.74^\circ$, leaving an $\ell = 4$ powder pattern with sidebands[8]. Similarly, to remove $\ell = 4$ terms and to leave an $\ell = 2$ powder pattern, the appropriate angle for the axis of rotation is $\theta_m^{(4)} = 30.56^\circ$ or 70.12°.

Removal of both $\ell = 2$ and $\ell = 4$ terms calls for a pattern of sample orientations (by no means unique) in which each of the three directions of the $\ell = 2$ cone (half-apex angle $\theta_m^{(2)}$) is split into five equally spaced directions of the $\ell = 4$ cone (half-apex angle $\theta_m^{(4)}$). The continuous limit of this polyhedral symmetry[9] is a double-rotation which can be implemented by the arrangement of Figure 1. Under a double-rotation with angles θ_1 and θ_2 (avoiding certain integer ratios of the two rotation frequencies) the average frequency in (2) is

given by

$$\langle\omega\rangle = \omega_0 + \sum_{\ell} A_\ell P_\ell(\cos\theta_1) P_\ell(\cos\theta_2) \quad , \tag{4}$$

and the $\ell = 2$ and $\ell = 4$ terms can therefore be removed by choosing $\theta_1 = \theta_m^{(2)}$ and $\theta_2 = \theta_m^{(4)}$ or $\theta_1 = \theta_m^{(4)}$ and $\theta_2 = \theta_m^{(2)}$.

The apparatus used in our experiments consists of a DELRIN-MACOR rotor of diameter 5mm, filled with a powder sample and spinning with gas-lubricated journal bearings inside a VESPEL rotor of 20mm diameter, maintained by independent gas-lubricated bearings and air jet. The angles used are $\theta_1 = 54.7^\circ$ and $\theta_2 = 30.6^\circ$ and the mass distribution is designed to minimize inertial forces on the inner rotor by dynamic balance[9,10]. Figure 2 shows experimental results for the central ($1/2 \leftrightarrow -1/2$) transition of sodium-23 in polycrystalline sodium oxalate ($e^2qQ/h \sim 2.5$ MHz, $\eta \sim 0.7$) at 105 MHz. The top spectrum, from a static sample, exhibits a linewidth of about 12000 Hz due primarily to dipolar couplings and second-order quadrupolar broadening. This linewidth is reduced to about one third of its static value under magic-angle spinning in the middle trace, and the lineshape is characterized by the average $\ell = 4$ term of the second-order quadrupolar coupling[8]. Sidebands are apparent at the MAS frequency of ~4000 Hz. Under double-rotation frequencies of ~2000 Hz for the inner rotor and ~400 Hz for the outer one, the spectrum collapses to a centerband of linewidth ~140 Hz together with double-rotation sidebands (<u>second-order quadrupolar echoes</u> appear in synchronism with cycles of the big rotor)[11]. To denote this particular experimental arrangement, the terms <u>double-rotation (DOR)</u> and <u>second-order spinning (SOS)</u> have been used; we henceforth adopt the former.

It has been pointed out that the effect of double-rotation can also be regarded as an example of rapid rotation around a hinged axis inclined at an angle $\theta(t)$ with respect to the magnetic field such that

$$\langle P_\ell(\cos\theta)\rangle = \int P_\ell(\cos\theta)W(\theta)d\theta = \int_0^T P_\ell(\cos\theta(t))dt = 0 \qquad (5)$$

for a set of ℓ, an approach dubbed dynamic angle spinning (DAS)[5,6]. $W(\theta)$ is a probability distribution for θ. Equation (5) is obviously solved for all ℓ by an isotropic distribution $W(\theta) = (1/2)\sin\theta$. Double-rotation corresponds to $\cos\theta(t) = \cos\theta_m^{(2)}\cos\theta_m^{(4)} + \sin\theta_m^{(2)}\sin\theta_m^{(4)}\cos(\omega_R t + \gamma)$. Experimental results have indeed been achieved[12] using two orientations of the rotor axis, for example $\theta(0) = 37.4^\circ$ and $\theta(T) = 79.2^\circ$[5,6,13], where the coherence is stored (in two-dimensional NMR tradition) during flips of the axis[14].

While DAS and, in particular, DOR have obvious applications to quadrupolar nuclei such as boron-11, sodium-23, oxygen-17 and aluminum-27, they should also be useful in eliminating broadening due to other second-order effects such as those due to dipole-dipole couplings[15] and magnetic susceptibility[16] in both quadrupolar and spin-1/2 systems. Extension of our arguments to other sets of ranks $\{\ell\}$, and therefore to higher-order broadening, is straightforward. Other rotor designs have also been examined[17]. Finally, it may occasionally prove advantageous to work in lower magnetic fields thereby enhancing, by means of isotropic second-order (and perhaps higher-order) shifts, the frequency dispersion normally provided by chemical shifts alone. Particularly intriguing is the promise of such general sample-reorientation trajectories in the context of Tycko's recent scalar reconstruction techniques[18].

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FIGURE CAPTIONS

Figure 1: Schematic diagram of the BETA (Berkeley-Tallinn) double-rotor. The angles are θ_1 between B_0 and R_1, θ_2 between R_1 and R_2, and $\theta(t)$ between B_0 and R_2.

Figure 2: NMR experiments on the central ($1/2 \leftrightarrow -1/2$) transition of sodium-23 in polycrystalline sodium oxalate at 105 MHz. The isotropic shift is at 0 Hz in the figure. Top: static sample, linewidth dominated by dipole-dipole and second-order quadrupolar couplings. Middle: magic-angle spinning (MAS) at ~4000 Hz, displaying a characteristic $\ell = 4$ lineshape due to averaged second-order quadrupolar coupling. Lower: spectrum under double-rotation (DOR) frequencies of ~2000 Hz and ~400 Hz, illustrating the averaging of second-order line-broadening effects.

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rotating small rotor over the orientations of its axis on the cone.

12. A. Llor and J. Virlet, to be published. G.C. Chingas, K.T. Mueller, B.Q. Sun, T. Terao and A. Pines, to be published. There is a continuum of solutions (θ_1, θ_2, k) to the equations: $P_2(\cos\theta_1) = -|k|P_2(\cos\theta_2)$, $P_4(\cos\theta_1) = -|k|P_4(\cos\theta_2)$.

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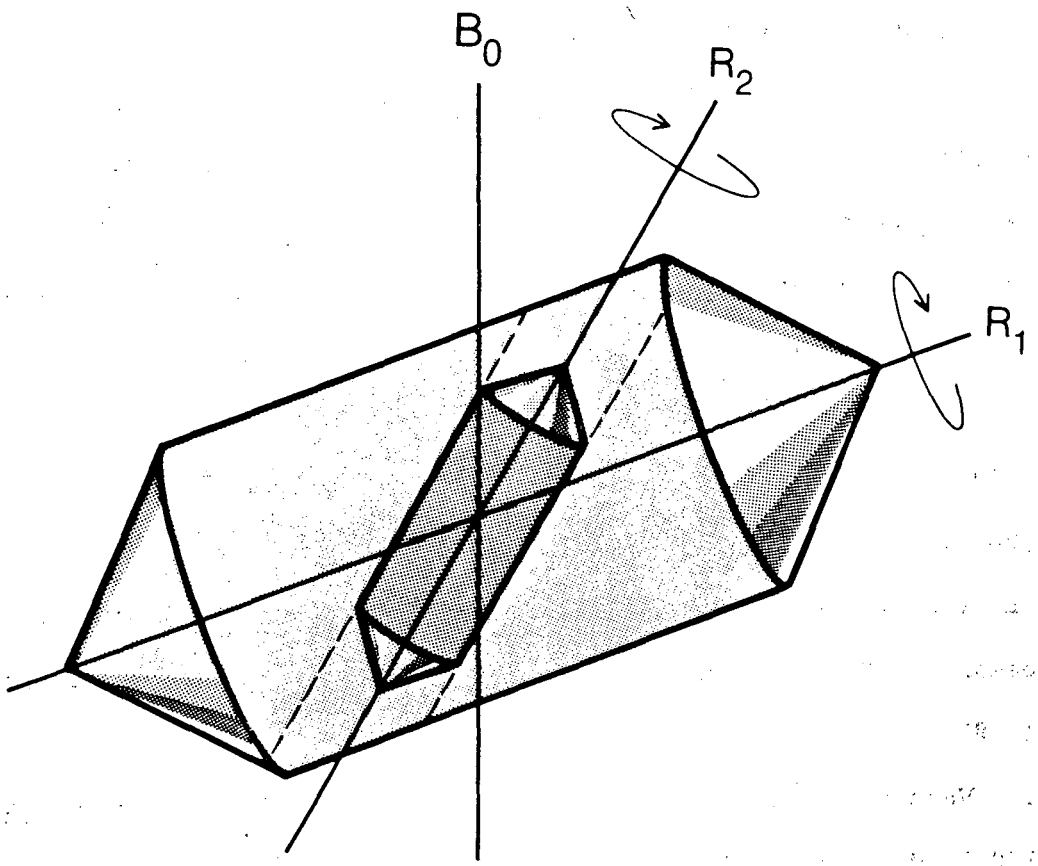

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Figure 1

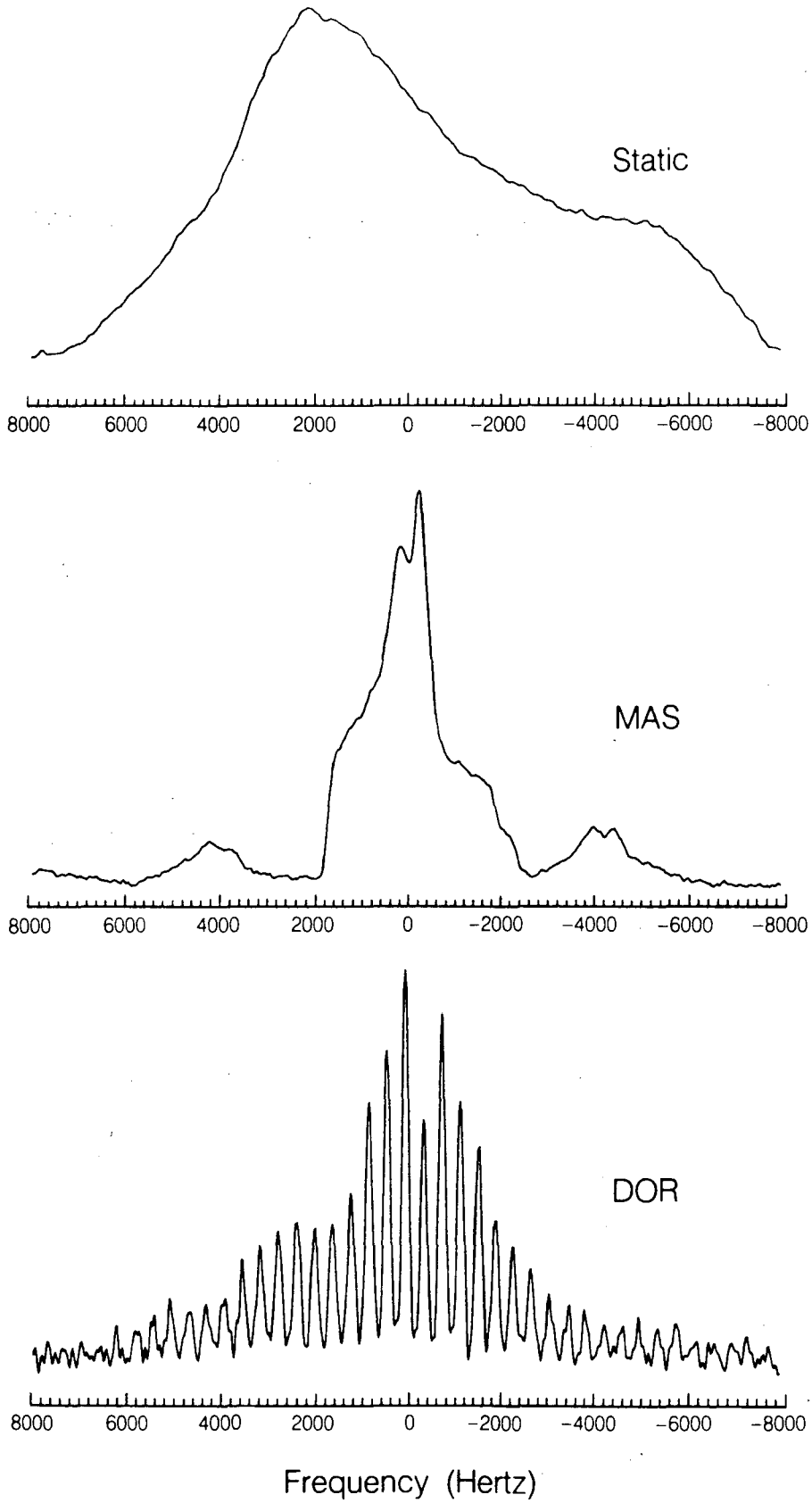

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Figure 2

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