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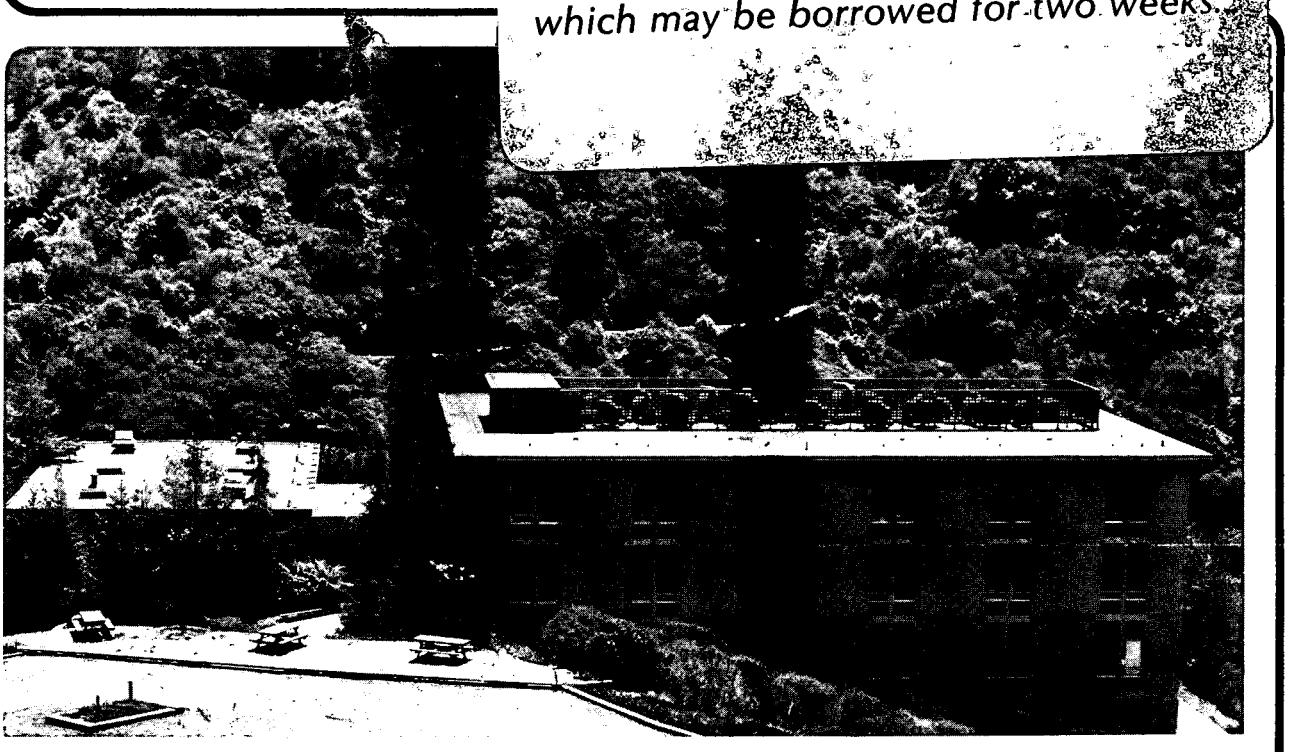

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ZERO FIELD NMR of SMALL AMPLITUDE MOTIONS in a POLYCRYSTALLINE SOLID

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ABSTRACT

The librational motions of the water molecules in polycrystalline barium chlorate monohydrate have been studied using proton and deuterium zero field NMR. In contrast to high field NMR, subtle molecular motions produce readily observable changes in the zero field spectrum. Computer simulations and application of a novel pulsed zero field technique confirm that the splitting observed in the zero field spectrum of the hydrate results from the motionally induced asymmetry of the magnetic dipole-dipole coupling tensor.

INTRODUCTION

NMR has been an excellent tool for the study of motion in condensed matter since one observes a time average over the motion resulting in an average chemical shift, quadrupolar coupling, or dipolar interaction. Because powder patterns[1] are insensitive to the relatively small perturbations of these motions one often resorts to single crystal measurements[2] or oriented liquid crystal measurements.[3] Zero field NMR offers an approach to this problem which is useful for polycrystalline or otherwise disordered materials since it has been demonstrated to provide sharp dipolar[4-6] and quadrupolar information[7-9] from such systems down to very low frequencies. Zero field NMR should be sensitive to small amplitude motions which result in splittings or extra lines in the frequency spectrum. Such motions typically do not result in observable changes in the high field NMR spectrum. In this report we present the first experimental results for the study of libration in a polycrystalline hydrate using proton and deuterium zero field experiments.

The proton zero field spectrum of a static water molecule would consist of lines at zero frequency and at $\pm\nu_d = 3\gamma^2 h/8\pi^2 r^3$, where r is the internuclear distance of the two protons.[4] The characteristic motion of the waters in a typical hydrate are rapid 180° flips about their C_2 axes[10] and librations about three axes.[11,12] To a good approximation the librational modes correspond to rotations about the x, y, and z axes[12] of the molecular coordinate system shown in figure 1 and are commonly referred to as rocking, waving and twisting, respectively. The influence of the motion on the proton zero field spectrum is treated by calculation of its effect on the dipolar Hamiltonian, H_d, which is responsible for the zero field spectrum. The rapid 180° degree flips have no effect since they

merely exchange the two protons. Waving has no effect since it leaves the orientation of the internuclear vector $\vec{r}$ invariant. The dipolar Hamiltonian is therefore motionally averaged by only two of the librational modes. The resulting motionally averaged Hamiltonian, H_d', is given in the molecular frame by

$$H_d' = \langle R_z(\theta_z) \cdot R_x(\theta_x) \cdot H_d \cdot R_x(\theta_x)^{-1} \cdot R_z(\theta_z)^{-1} \rangle$$

$$= \vec{I}_1 \cdot \langle R_z(\theta_z) \cdot R_x(\theta_x) \cdot \underline{D} \cdot R_x(\theta_x)^{-1} \cdot R_z(\theta_z)^{-1} \rangle \cdot \vec{I}_2$$

$$= \vec{I}_1 \cdot \underline{D}' \cdot \vec{I}_2 \qquad (1)$$

where θ_x and θ_z are the librational angles about the x and z axes respectively, and the brackets signify a time average over the motion. To second order in the angles θ_i characterizing the libration, we can write the motionally averaged tensor, $\underline{D}'$, in angular frequency units as[11,13]

$$\underline{D}' = d \begin{bmatrix} 1-3\langle\theta_z^2\rangle & 0 & 0 \\ 0 & -2+3\langle\theta_z^2\rangle+3\langle\theta_x^2\rangle & 0 \\ 0 & 0 & 1-3\langle\theta_x^2\rangle \end{bmatrix} \qquad (2)$$

where $d = \gamma^2 h/2\pi r^3$. Application of the rotations in the reverse order of equation 1 produces the same expression for $\underline{D}'$ to this order of approximation. An unequal intensity in the amplitudes of the two librational modes produces a nonaxially symmetric average dipolar tensor. This is made more clear by defining $\Delta = D'_{22}$ and $\eta = (D'_{11}-D'_{33})/D'_{22}$ and rewriting equation 2 as

$$\underline{D}' = \begin{bmatrix} -\Delta(1-\eta)/2 & 0 & 0 \\ 0 & \Delta & 0 \\ 0 & 0 & -\Delta(1+\eta)/2 \end{bmatrix} \tag{3}$$

Calculation of the sudden experiment zero field spectrum for this case proceeds in a manner analagous to that described previously.[4,5] The normalized high field signal expected for a powder sample is given by

$$S(t_1) = \cos\{\tfrac{\Delta}{4}(3+\eta)t_1\} + \cos\{\tfrac{\Delta}{4}(3-\eta)t_1\} + \cos\{\Delta\eta t_1/4\} \tag{4}$$

where t_1 is the evolution time in zero field. The effect of the motion is to split the lines of the static spectrum by an amount proportional to the asymmetry of the dipolar tensor. These motionally produced splittings or additional lines in the zero field spectrum are in sharp contrast with the shoulders on broad powder patterns which occur in the high field case.

The zero field spectrum of a motionally averaged spin one nucleus follows from a treatment similar to that above. Explicit expressions for the dependence of the quadrupole coupling constants and asymmetry parameter on the librational amplitudes have been calculated.[11,13] Both the quadrupole coupling constant and asymmetry parameter depend on all three librational modes as well as the exchange frequency characterizing the 180^0 flips. In barium chlorate at room temperature, however, the frequency is sufficiently high that one need only consider an average over the two orientations.[10] The 180^0 flips average the static quadrupole tensor, which has its principal axis along the O-D bond, to one with its principal component either along the C_2 axis or perpendicular to the molecular plane of the water molecule.[14] The asymmetry parameter is also affected, its value near unity is a consequence of the motion.[15] One notes however that

librational amplitudes are a function of the reduced mass of the molecule, hence the amplitudes and NQR frequencies will differ slightly in HDO and D_2O.

ZERO FIELD EXPERIMENTS

Proton zero field spectra. All spectra reported here were obtained at room temperature using a homebuilt 180 MHz proton frequency instrument that has been modified for the zero field experiments.[16]

The proton zero field spectrum of isotopic abundance barium chlorate has been published before.[4] Intermolecular dipolar couplings produce linewidths of approximately 7 kHz thus obscuring the splitting due to the motion. The effect of isotopic dilution by deuterium on the linewidth of the proton zero field spectrum is shown for a series of dilution levels in figure 2. An increase in the amount of structure in the spectrum is seen as the level of protonation decreases. The spectrum from a 10% protonated sample, figure 3, shows all three lines predicted by equation 4 for the asymmetric dipolar tensor. By combining equations 2 through 4 one can use the experimental splittings to obtain the difference $\langle\theta_z^2\rangle-\langle\theta_x^2\rangle=0.024$. Using r=1.52 angstroms, a value obtained from neutron diffraction measurements[17], one can calculate $\langle\theta_x^2\rangle=0.044$ and $\langle\theta_z^2\rangle=0.070$ (radians^2).

A second experiment was performed to determine if the observed splittings could be due to residual magnetic fields present during the zero field evolution period. The field cycle is shown in the inset of figure 3b. In this experiment a dc pulse calibrated to rotate the initial magnetization from the z axis to the x-y plane[8] was given immediately after the sudden switch-off of the intermediate field. In addition, an identical dc pulse was given at the conclusion of the t_1 period to store the effect of the zero

field evolution. This sequence being identical with the sudden experiment in every other detail has the effect of simply changing the relative orientation of the stray field with the initial condition of the magnetization. The spectrum obtained with this sequence, figure 3b, is essentially identical with that of the sudden experiment.

Effect of stray fields. Computer simulations of the zero field spectrum of a powder distribution of static pairs of protons in a stray nonzero field were performed as a means of further probing the effects of stray fields. The simulations assumed an internuclear distance of 1.6 angstroms and stray magnetic fields of varying strengths and directions. In the sudden experiment the magnetization at t_1=0 is along the lab z direction. The symmetry of a powder then requires only examination of stray fields with components along the z axis and a perpendicular axis which we define as the x axis. The results of these simulations, some of which are shown in figure 4, bear little or no resemblance to the experimental spectra and indicate that residual fields > 1 gauss are required to produce splittings comparable to those seen in figure 1. Experimental measurements typically place an upper limit of 0.025 gauss on the magnitude of the stray field.

Deuterium spectra. Although the rapid C_2 flips do not manifest themselves in the proton spectrum, they are readily observable via their effect on the deuterium quadrupolar spectrum.[11,14,15] The deuterium zero field NQR spectrum of a 50% deuterated sample of barium chlorate was obtained at room temperature using the indirect detection method which is described in detail elsewhere.[8] Since room temperature deuterium low field T_1's are of the order of milliseconds, an indirect detection method is

necessary. The indirect method is selective for the deuterons in that ideally only they are induced to evolve during the zero field evolution period and hence little or no signal is observed due to the proton pairs. In the spectrum, shown in figure 5, the ν_+, ν_-, and ν_0 lines are all clearly resolved and from their frequencies one calculates e^2qQ/h =122.7 kHz and η=0.960 which is in good agreement with earlier work.[11] If we neglect differences in librational displacements due to reduced mass, we can estimate $\langle\theta_y^2\rangle$ by combining the zero field proton and deuterium data with the quadrupole coupling constants of the static molecule found by Chiba.[11] Using the explicit expressions for the field gradient tensor averaged by libration and the C_2 flipping, one obtains $\langle\theta_y^2\rangle$=0.123(radians^2). We note the librations have a relatively minor effect on the quadrupole spectrum, the value of η near unity is primarily a consequence of the C_2 flips.[15] An advantage of the dipolar measurements is that the static dipole interaction is inherently axially symmetric and any asymmetry is the direct result of motion.

DISCUSSION

The non-axially symmetric dipolar tensor produced by libration is readily observable via the proton zero field spectrum. The excellent agreement between the results of the two versions of the zero field experiment, as well as the results of computer simulations, rule out the possibility of splittings due to residual fields. Our results for the mean square amplitudes of the librational modes are in reasonable agreement with earlier data,[11,18] especially when one considers that the exact librational modes might differ slightly from the inertial rotations assumed.[12] With the high resolution possible in the dipolar zero field experiment one has a sensitive measure of relatively small changes in the dipolar tensor.

The zero field NQR results for HDO demonstrate the high resolution of the experiment and the precision with which it can measure the asymmetry parameter. The parameters relating to the motion are underdetermined with a single NQR experiment since the quadrupolar frequencies are a function of the three librational modes, the rate of the 180^{o} flips, as well as the values of $(e^2qQ/h)_o$ and η_o, the parameters of the static molecule. We note that these are the first room temperature deuterium NQR measurements of a hydrate, since these systems are usually inaccessible to frequency domain techniques because of their relatively short T_1's and low quadrupolar frequencies. In contrast to typical frequency domain NQR methods there is no power broadening[13] and ideally no signal due to protons. This fact generally allows resolution of the ν_o lines, a tremendous aid in the assignment of the spectra.

In summary the zero field experiment has been demonstrated to provide information about the dipolar and electric field gradient tensors in a two spin system and thus provide information about its motional characteristics. In general these should provide complementary information since they possess unique principal axis systems and hence are affected differently by the different motions which occur in a system. The zero field measurements have the significant advantage of being made with a powder sample whereas the earlier measurements required a single crystal.[11] This aspect should allow study of subtle motions in systems inaccessible to single crystal measurements including amorphous and polycrystalline materials as well as biological samples.

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FIGURE CAPTIONS

1. The three librational modes of the water molecules in barium chlorate monohydrate. In this molecular coordinate system the H_2O lies in the plane of the paper with its C_2 axis parallel to the z axis. From top to bottom these modes are referred to as waving, twisting, and rocking. Waving does not produce a reorientation of the internuclear vector, thus only twisting and rocking have an averaging effect on the dipolar tensor.

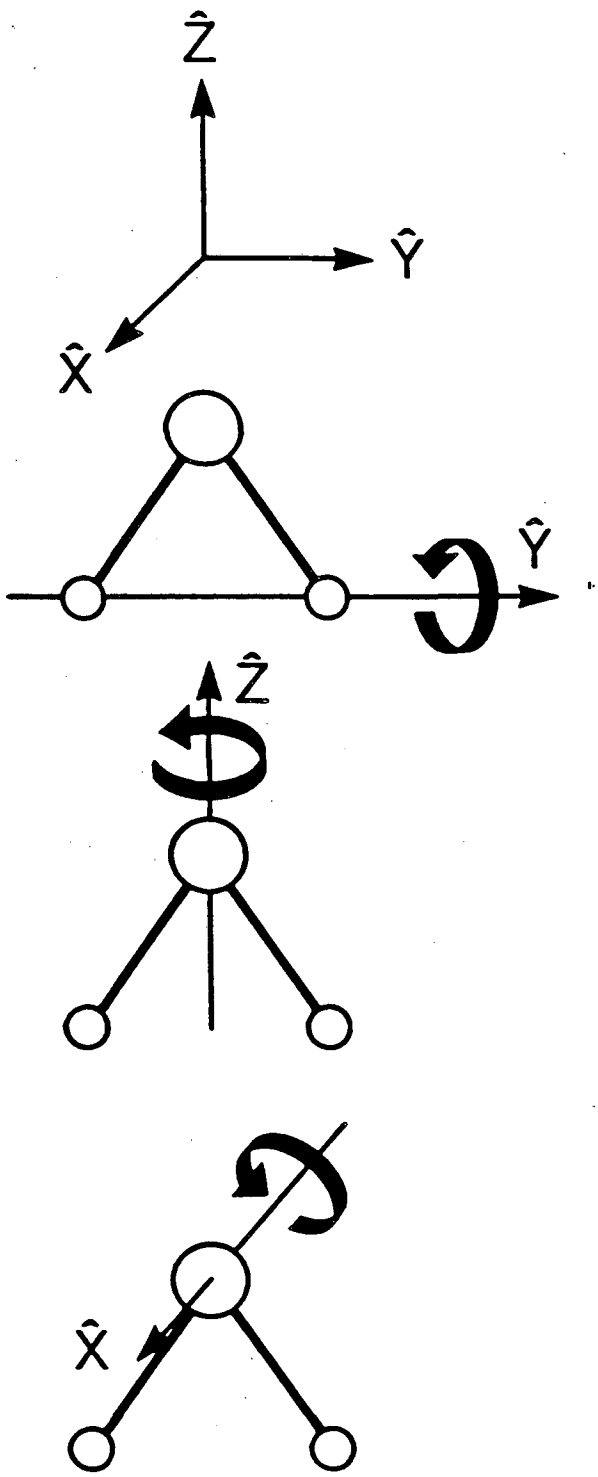
2. Proton sudden zero field spectra of barium chlorate monohydrate as a function of isotopic dilution by deuterium; a) isotopic abundance, b) 60% protons, c) 31% protons, d) 10% protons. Structure due to the asymmetric dipolar tensor of dilute water molecules is observed as the intermolecular contribution to the linewidth is reduced. Unpaired protons in the dilute samples contribute to the line centered at zero frequency.

3. a) Proton zero field spectrum of 90% deuterated $Ba(ClO_3)_2 \cdot H_2O$ obtained with the sudden experiment field cycle. The applied field, B_z, is shown schematically in the inset as a function of time. Zero field evolution is initiated by sudden switch-off of the field. After the t_1 evolution period the field is switched on suddenly and the sample returned to high field where the magnetization M_z is measured as a function of t_1. Here only the positive frequency portion of the spectrum is displayed. All three lines characteristic of the motionally averaged non-axially symmetric dipolar tensor are resolved, appearing at 1.37, 41.8, and 43.4 kHz with linewidths of approximately 2 kHz, considerably narrower than that obtained with the fully protonated material.

b) Zero field spectrum from the sudden field cycle with dc pulses. This cycle, shown in the inset, is identical to the sudden experiment except for the application of 90° dc magnetic field pulses, P_x and P_x', at the initiation and termination of the zero field evolution period. These experiments employed a dc field of 0.010 Tesla oriented orthogonal to B_o. The spectrum obtained is essentially identical with that of the sudden experiment.

4. Simulations of zero field spectra obtained using the sudden field cycle in the presence of variable residual fields for a powder sample of isolated pairs of protons where r=1.6 angstroms. The sudden experiment utilizes a field along the z direction which is suddenly switched off to initiate evolution. Simulations on the right correspond to the residual field aligned along the z axis and those on the right left the x axis of the lab frame. Magnitudes of the residual fields used in the simulations from top to bottom are: a,b) 0.35 gauss; c,d) 1.2 gauss; and e,f) 2.4 gauss. Additional simulations for general orientations of the residual field in the x-z plane are in qualitative agreement with those shown. In all cases quite large residual fields are required to produce splittings in the spectrum.

5. Indirect detection zero field deuterium NQR spectrum of 50% deuterated barium chlorate monohydrate. All three lines expected are resolved from which one calculates e^2qQ/h=122.7 kHz and η= 0.96 in reasonable agreement with single crystal measurements of the perdeuterated material which obtained $e^2qQ/h = 121.5 \pm 0.4$ kHz and $\eta = 0.976 \pm 0.007$.[11] The bump at approximately 40 kHz is due to proton pairs. Its small relative size gives an indication of the deuterium selectivity of the indirect experiment.



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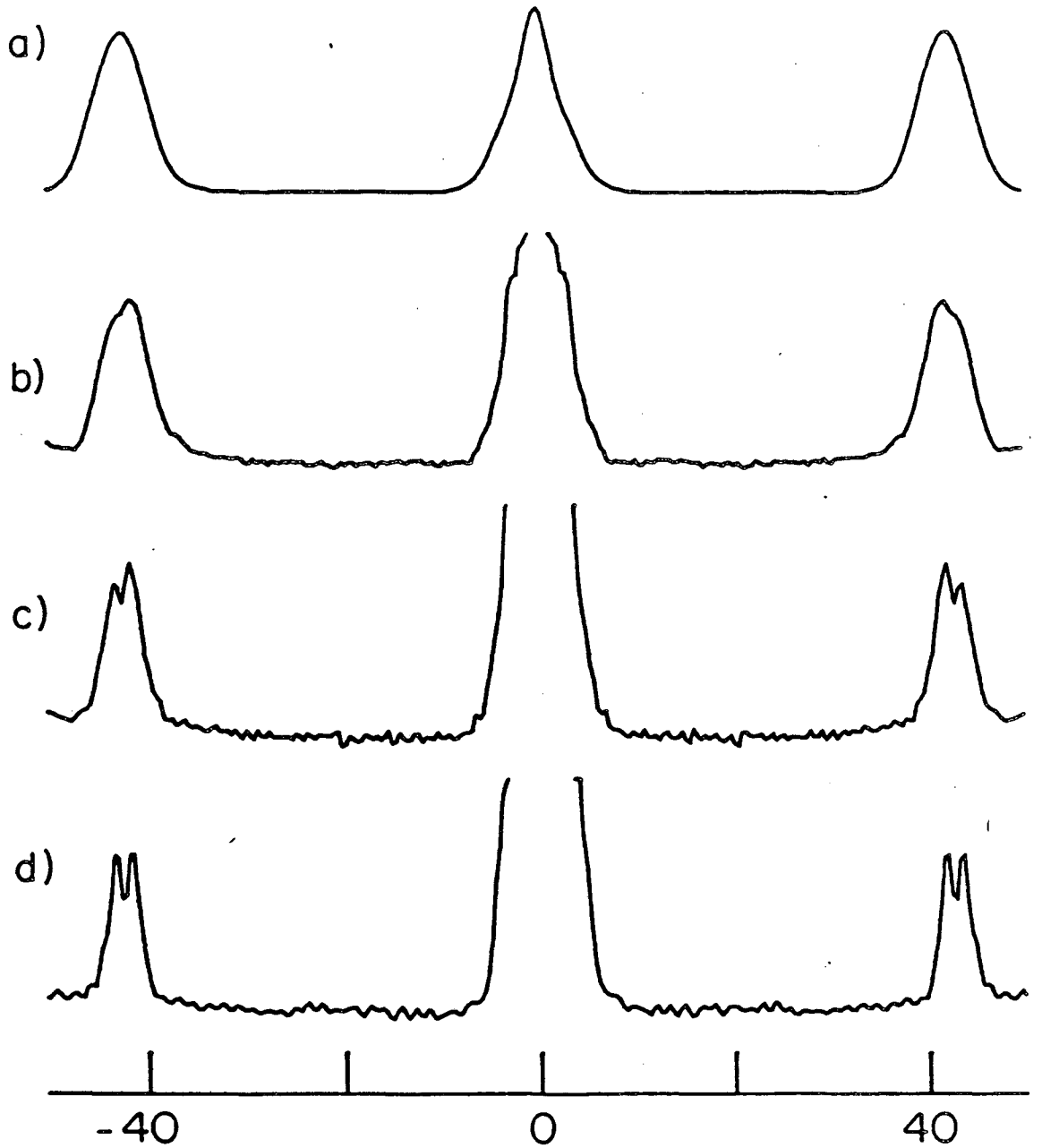

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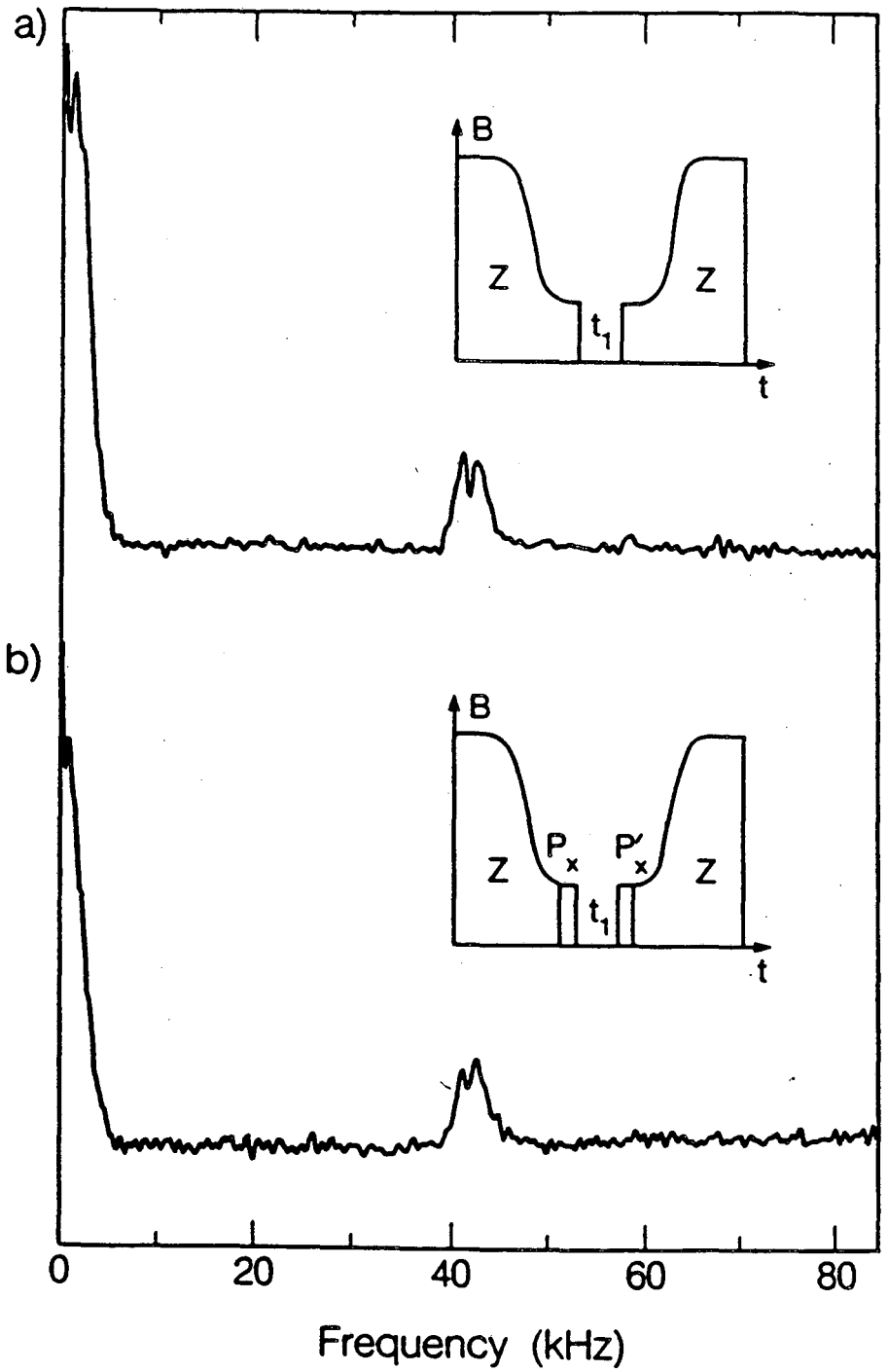

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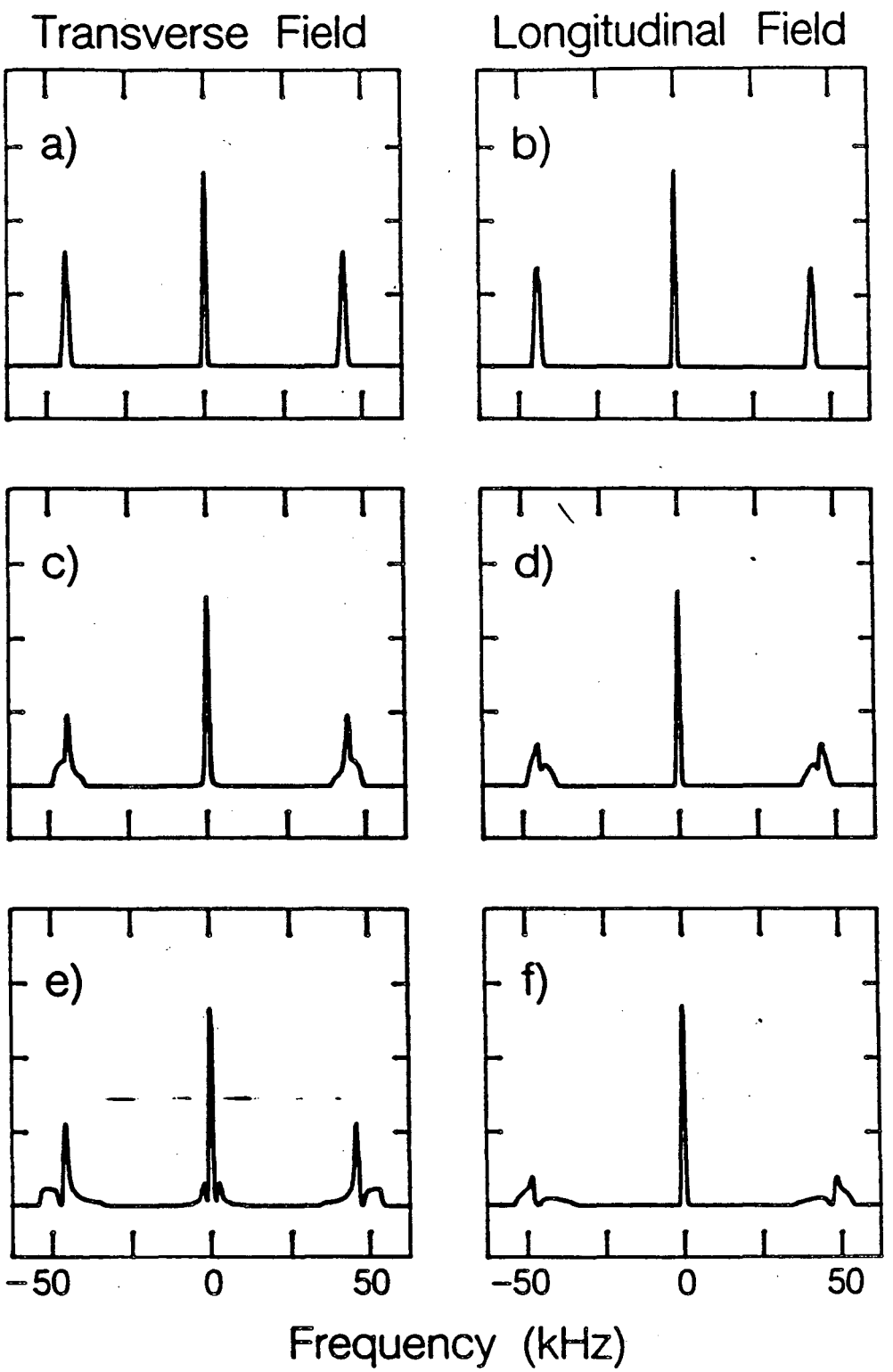
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Longitudinal Field
a)
b)
c)
d)
e)
f)
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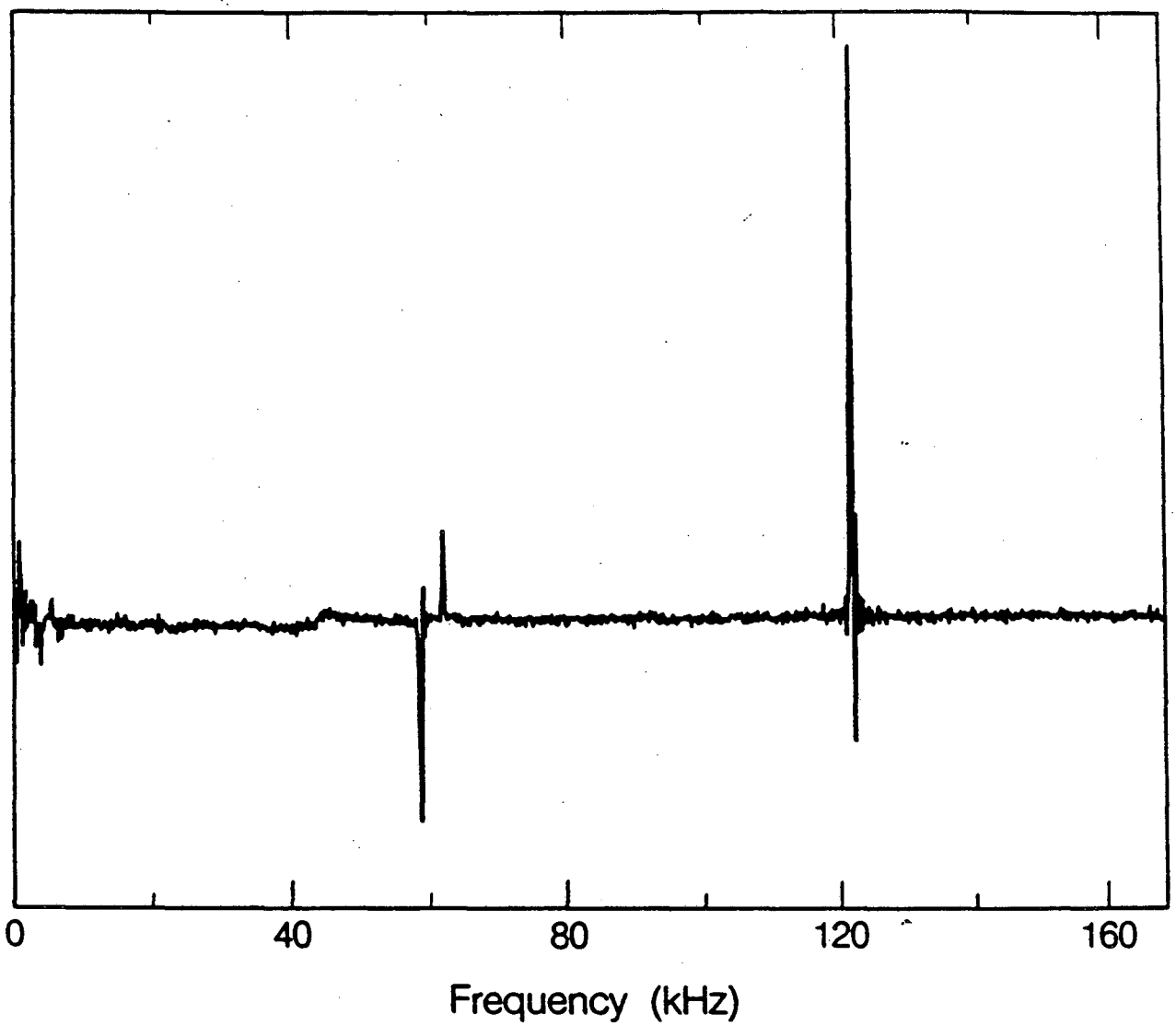
0
50
−50
0
50
Frequency (kHz)

XBL 857-8935



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