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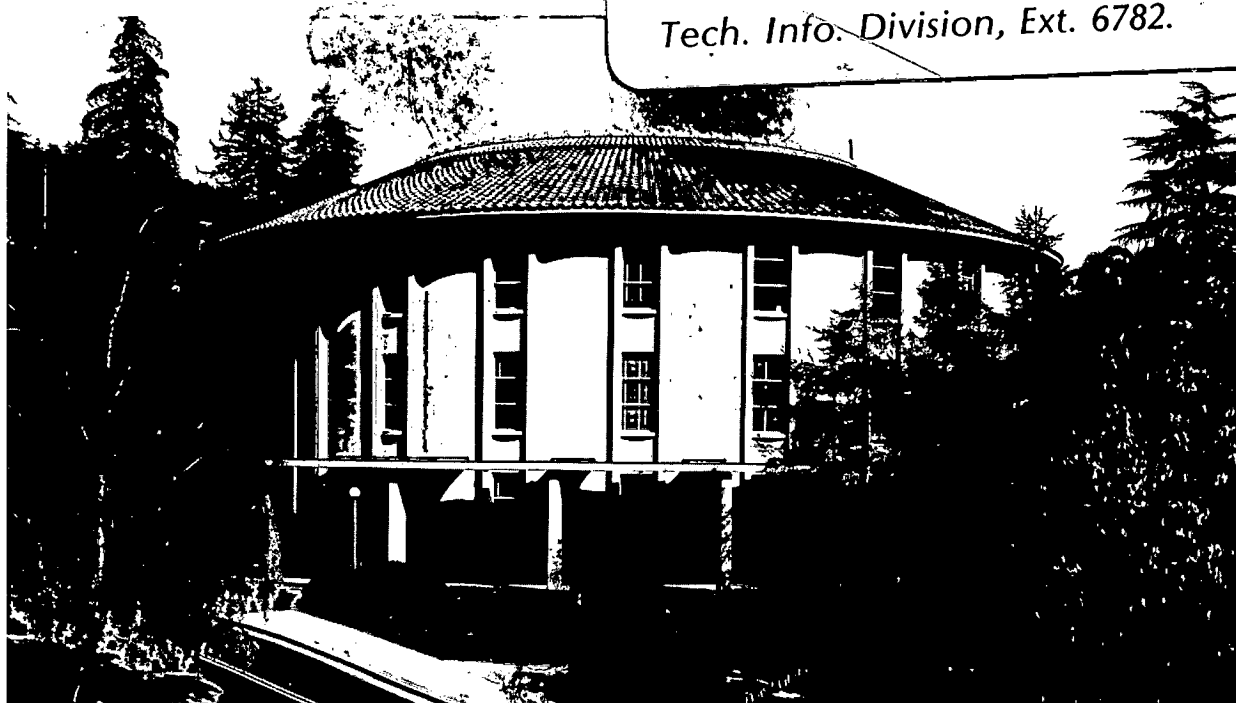
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A ^{14}N NMR STUDY OF TETRAALKYLAMMONIUM
COMPOUNDS IN THE SOLID STATE

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Abstract

The ^{14}N NMR powder patterns of various quaternary ammonium salts have been measured over the temperature region 155°K to 273°K . Some of the spectra are dominated by motion, while others appear to arise from a rigid lattice and from which values of the quadrupole coupling constant (e^2qQ) and the asymmetry parameter (η) are determined. The quadrupole coupling constants fall in the range commonly observed for deuterium, while the asymmetry parameters take on virtually all possible values from 0 to 1. For some compounds the parameters appear to derive completely from lattice (crystalline field) effects, while for others there is probably a combination of lattice and intramolecular effects.

Introduction

The use of ^{14}N NMR as a probe of order in model membrane systems has increased in recent years (1-7). ^{14}N is a spin one nucleus and as such exhibits a quadrupolar interaction which provides dynamic and structural information, but which can also broaden the NMR spectrum greatly. For this reason, previous studies have in all cases been restricted to symmetrically substituted nitrogen compounds (e.g. phosphatidylcholine, hexadecyltrimethylammonium bromide, etc.). In order for such studies to have meaning, values of the quadrupole coupling constant (e^2qQ) and the asymmetry parameter (η) are required. These can be estimated from the isotropic phase spin lattice relaxation time (T_1) if the correlation time for molecular reorientation is known (1), or from the residual quadrupolar splitting in a partially ordered phase if the pertinent order parameters are known (4,5,6).

The quadrupole coupling parameters (hereafter referred to as electric field gradient [efg] parameters) are more accurately determined by observing the static couplings in the solid state via NQR, or quadrupole perturbed NMR. The former technique suffers from a lack of sensitivity when small quadrupole couplings exist, which can be alleviated by the use of field cycling techniques (8), while the latter is both sensitive and experimentally simple.

The first order perturbation of a spin one NMR line by the quadrupole coupling causes the line to be split into two components (9). The orientation dependence of this splitting in a single crystal suffices to determine all efg parameters, and also the relationship between the efg tensor and the crystalline reference frame. The efg

parameters may also be determined from the lineshape of a powder in which all orientations are represented, although the orientational relationship between the efg and the crystalline reference frame is lost.

We have undertaken a study of the efg parameters in tetraalkylammonium compounds via their ^{14}N NMR powder lineshapes. For many of these compounds a single crystal study is not feasible due to the difficulty of obtaining sufficiently large single crystals.

The NMR lineshape of a spin one nucleus exhibiting a non-zero quadrupolar interaction will show three characteristic doubly degenerate inflection points. These occur at:

$$\nu_0 \pm 0.375(1-\eta) e^2 q Q / h,$$

$$\nu_0 \pm 0.375(1+\eta) e^2 q Q / h,$$

$$\nu_0 \pm 0.750 e^2 q Q / h,$$

where $\nu_0 = \gamma H_0$. These points define the efg components V_{xx} , V_{yy} , and V_{zz} . Any two inflection points suffice to determine $e^2 q Q$ and η , but observation of all three adds a considerable degree of certainty to the determination.

Analysis of the powder lineshapes observed is, in some cases, complicated by the presence of motion. When the frequency of the motion is rapid in comparison with the principle value of the static efg, the observed couplings are the result of an averaged efg whose symmetry is replaced by that of the motion. This results in a powder spectrum having the appearance of one which is produced by a rigid efg, but which is narrowed by incomplete motional averaging. The NMR literature abounds with examples of this (10).

As the motional frequency slows to that of the static quadrupolar

couplings, the spin-spin relaxation time (T_2) decreases; leading to lower S/N, the washing out of spectral features, the appearance of large amplitude spikes in the lineshape (the result of an anisotropic T_2), or a combination of the above. These effects have been observed in previous deuterium NMR studies, and their origin discussed in detail (11-16).

The presence of motion can almost always be detected by recording the spectrum at various temperatures. Since the motions we are considering are thermally activated, motionally averaged spectra will have distinct variations in lineshape as a function of temperature. The temperature dependent measurements we present here are intended to either confirm or rule out motional contributions.

Experimental Procedures

The compounds used in this study were obtained from a variety of sources, including Eastman Kodak, Sigma, and Calbiochem. Tetraethylammonium triiodide was prepared from an equimolar mixture of tetraethylammonium iodide and iodine in methanol. Subsequent elemental analysis of this compound showed it to be of high purity.

All compounds, with the exception of phosphorylcholine chloride, were recrystallized at least once from an appropriate solvent. After recrystallization, all were dried in vacuo (3×10^{-5} atm) over P_2O_5 at $85^\circ C$ for at least 12 hours prior to being sealed in glass tubes under a dry argon atmosphere.

Dimyristoyl phosphatidylcholine samples were prepared in a variety of ways prior to drying. The compound was either taken

directly from the manufacturer's (Calbiochem) bottle, precipitated from a chloroform solution with diethyl ether (17), or prepared by slow evaporation of a chloroform-methanol solution (17). The samples were all analyzed by TLC after drying and found to be of high purity. A powder x-ray diffraction pattern of the sample precipitated from chloroform showed the Bragg spacings to be similar to those which had been reported previously (17).

Spectra were recorded on a homebuilt spectrometer operating at a ^{14}N resonance frequency of 19.507 MHz (18) by fourier transformation of the second half of a two pulse quadrupolar echo (19); 90° pulses of amplitude 60-75 kHz were used with interpulse delays of 60-150 usec. The echoes were both excited and recorded in the presence of proton decoupling (45-50 kHz r.f. field amplitude). The quadrature phase detector was adjusted such that the echo was predominately captured in one channel, but the other channel was not discarded as this tends to lead to misinterpretation of the observed lineshapes by imposing a false symmetry upon them. The echoes were sampled at rates between 0.5 and 5 usec per point in order to obtain a proper representation of the time domain echo signal. The sample temperature, measured with a thermocouple placed close to the sample, was regulated to within one degree Celsius. It is estimated that the thermocouple and sample temperatures differed by at most two degrees Celsius.

In approximately one half of the cases reported, the signal was enhanced by a single contact with either a spin locked, or an adiabatically demagnetized proton reservoir (20,21). We point out here that, for many of the compounds, the ^{14}N T_1 's exceed one minute,

and it would therefore not have been possible to amass such a large amount of data without some type of polarization transfer technique.

The lineshapes were analyzed by successively fitting the experimental data to a rigid lattice powder lineshape convolved with a broadening function (generally the same as the linebroadening applied prior to fourier transformation) and multiplied by a function which accounted for the response rolloff due to the finite duration of the excitation and echo pulses (22). The cross polarized spectra showed further distortions which were minimized by the proper choice of experimental parameters (21). The errors quoted in table 1 give the range of quadrupole coupling parameters which appear to adequately fit the data. Aside from S/N considerations, the accuracy of the data is limited by two factors: (1) the amount of distortion introduced by the cross polarization, and (2) T_2 broadening mechanisms not accounted for by the proton-nitrogen heteronuclear dipolar interaction.

Overview of Experimental Results

The data in table 1 reveal that the range of quadrupole coupling constants for these compounds is approximately 10-200 kHz. This implies a fairly symmetric electronic environment, as would be expected for a tetra substituted nitrogen. The asymmetry parameters cover the entire range from 0 to 1.0. This result is rather surprising since it would be expected that a tetraalkylammonium ion would have at least a three-fold intramolecular symmetry axis. The non-zero asymmetry parameters could be explained by a specific type of

anisotropic jumping motion (23,24,12), and some of the efg parameters we have measured, in particular those of the amphiphiles, are strongly suggestive of a 180° flip-flop motion. If this is to be the case, the activation energy for this motion must be small enough for it to be rapid on the NMR time scale at 175° K. Slow motion would lead to previously noted effects (i.e. temperature dependent lineshape distortions) which we do not observe for these compounds. Some of our spectra are indeed affected by motion (as noted in table 1) leading to characteristic lineshapes which are strongly temperature dependent (see figure 1).

A small, nearly linear, temperature dependence of the efg parameters is observed for most of the compounds studied (see table 1). This phenomenon likely originates in thermally activated field gradient averaging mechanisms involving small amplitude torsional motions (25) or variation of the crystalline field due to expansion or contraction of the unit cell with temperature (26). The belief that these small variations are not the result of large amplitude motions of the efg is supported by the observation of T_2 's which are not strongly temperature dependent for these compounds.

Under the assumption we are observing rigid molecules, we must consider two factors responsible for the observed quadrupole coupling parameters. (1) The deviation from tetrahedral symmetry of the nitrogen electronic distribution due to intramolecular effects, and (2) the contribution of the lattice or extramolecular crystalline field to the field gradient at nitrogen. Based upon simple arguments, the former effect would be expected to dominate over the latter; although antishielding effects could increase the extramolecular

contribution greatly (27).

Discussion of Specific Compounds

Of the compounds listed, complete structural information is available for the following: tetramethylammonium [TMA] chloride, bromide and iodide (28), tetraethylammonium [TEA] iodide (29), tetraethylammonium [TEA] triiodide (30), tetrapropylammonium [TPrA] bromide (31), choline chloride (32), and choline iodide (33). In addition, partial structural information is available for choline bromide (34) and hexadecyltrimethylammonium bromide [HTAB] (35). A discussion in some detail is warranted for these compounds.

(a) Tetraalkylammonium Salts and Choline Halides

Based upon the available structural data, the intramolecular nitrogen symmetry for the TMA compounds is tetrahedral; while that of TEA iodide and TPrA bromide show very slight deviations from tetrahedral symmetry which leave the nitrogen in a highly symmetric environment. Thus, at least for these compounds, intramolecular effects do not suffice to explain the observed quadrupolar couplings.

Proton NMR studies have shown that the TMA halides undergo isotropic reorientation at room temperature, and that this motion persists down to a temperature between 250°K and 200°K depending upon the halide (36,37). If intramolecular effects do exist, they would be greatly reduced or averaged to zero by this motion. The data in table 1 show that TMA iodide exhibits a small linear temperature dependence of $43 \text{ Hz}/^{\circ}\text{K}$ for its quadrupole coupling constant over the temperature range investigated. This is not the type of behavior we expect to see

over a temperature regime in which a field gradient averaging mechanism is quenched. More revealing are the data for TMA chloride, which are plotted in figure 2. Here we see that the efg parameters are constant down to the λ point at 184.9°K (38). In this regime the efg is axially symmetric and of small magnitude while the lattice is tetragonal. Below the λ point both the coupling constant and the asymmetry parameter increase rapidly, indicating that the electronic symmetry at nitrogen is decreasing with further lowering of the temperature. Although the symmetry of the lattice below the λ point has not been determined, it is not unreasonable to assume that it is lower than tetragonal. Whether it is orthorhombic or monoclinic cannot be determined from our data since the efg tensor will always possess three twofold symmetry axes, while orthorhombic is the lowest symmetry lattice to possess these properties. We would also like to point out that one field gradient component is static within experimental error throughout the temperature range studied (see figure 2b). An analysis similar to the above can also be applied to ammonium bromide, where no quadrupole coupling is observed in the cubic β phase, while a small axial quadrupole coupling is observed in the tetragonal γ phase (39,40).

TPrA bromide and TEA iodide show axially symmetric efgs (see figure 3) at all temperatures investigated. It is not likely that longer chain tetraalkylammonium compounds such as these undergo isotropic reorientation in the temperature range studied (41,42), but the high degree of intramolecular symmetry present in these two compounds leads us to believe that here too the efgs can be ascribed to the tetragonal lattices both compounds possess.

TEA triiodide and choline chloride show definite deviation of the intramolecular environment from that of tetrahedral symmetry; these compounds also possess orthorhombic lattices. Whether the efg parameters are dominated by intramolecular or crystalline field effects is unknown, but it is likely that the crystalline field has some effect. In TEA triiodide, an interesting discontinuity of the efg parameters occurs between 248°K and 213°K. Perhaps a differential scanning calorimetry, or x-ray study would confirm the existence of a phase transition in this temperature region. In choline chloride we have the added complication of motion at room temperature. At the lowest temperature investigated the spectrum appeared to arise from rigid molecules.

For choline iodide, the x-ray structural data are insufficient to describe accurately the intramolecular nitrogen environment. The situation here is very similar to that of choline chloride; the efg parameters are such that they could be determined entirely by crystalline field effects (the lattice here is monoclinic), but there may also be some intramolecular contribution. Here again there are complications arising from the presence of motion which apparently is rapid at room temperature, but slows as the temperature is lowered (see figure 1). It seems likely that this motion is connected with that which can be inferred from the x-ray structure determination (33), in which the molecule flips about an axis passing through the nitrogen and oxygen atoms.

The quadrupole coupling of choline bromide differs substantially from that of the other two halides. It is unfortunate that no detailed structure is available for this compound; the dimensions of its

orthorhombic cell differ considerably from those of choline chloride (both compounds have four molecules per unit cell) and this may have some effect upon the crystalline field. In contrast to the other two halides, choline bromide shows no motional effects upon the ^{14}N NMR spectrum over the temperature range investigated.

(b) Amphiphiles

The long chain amphiphilic molecules studied (HTAB, decyltrimethylammonium bromide [DTAB], didodecyldimethylammonium bromide [DDAB]) exhibit very large asymmetry parameters (see figure 4), with DDAB having the largest quadrupole coupling constant of those we have studied. As we have previously noted, the observed asymmetry parameters may be the result of a flip-flop motion of low activation energy. We also report that DDAB can be dispersed in water (0.5gm/ml) to form a lyotropic lamellar mesophase in which we observe a residual quadrupolar splitting of 8.85 kHz at 20°C. This splitting is of the same order as that observed for dimyristoyl phosphatidylcholine [DML] dispersions at room temperature (4,6). It should be emphasized that, in the presence of a non-zero rigid lattice asymmetry parameter, the orientational order of the system is not uniquely described by the residual quadrupolar splitting and at least one other independent measurement is required (44).

The efg parameters in HTAB could be due entirely to the crystalline field (the lattice is monolitic), but this material is known to give rise to quadrupolar relaxation in isotropic phases the analysis of which (1) leads to a quadrupolar coupling not inconsistent with our measurements in the solid. Thus we know that there must be

some contribution to the efg from intramolecular effects. It is interesting to note that in the related compound hexadecyltrimethylammonium dichloriodide the crystal structure (43) reveals, within experimental error, no deviation from tetrahedral symmetry at the nitrogen.

The experiments on DML and phosphorylcholine chloride [PCC] yielded disappointing results. Each compound gave what could more or less be described as a gaussian curve (see figure 5) upon fourier transformation of its echo. For DML, the lineshape was independent of the method of sample preparation. For PCC and some preparations of DML, the room temperature signal to noise was nearly sixty times lower than that at 158 K. Since this observation is independent of recycle delay, it can only be explained by the presence of motions which slow to the reciprocal of the rigid lattice quadrupole interaction as the temperature is lowered (i.e. it is a T_2 rather than a T_1 effect). The observed lineshapes can also be explained by the same motional arguments, but we once again cannot discount the effect of the crystalline field as the powder x-ray diffraction pattern of DML shows fairly diffuse lines indicating a lack of long range order which may imply a distribution of efg's and hence featurless spectra.

Insufficient data are available to warrant detailed discussion of the other compounds listed in table 1. We would, however, like to point out some observations with respect to TEA chloride. This compound was prepared four times (the first three were not recrystallized) and a distinctly different ^{14}N NMR spectrum was observed for each preparation. The first three samples were probably

hydrated to varying degrees for they were not dried as thoroughly as the final sample, which was also recrystallized prior to drying. The first three samples gave rigid lattice lineshapes indicative of an axially asymmetric efg, but the efg parameters differed considerably between samples. The final sample gave a featureless spectrum (very similar to that of DML) from which we can only estimate the range of quadrupolar coupling. This experience emphasizes, once again, the importance of extramolecular effects in this study.

Conclusion

The origin of the observed efg parameters can only be stated with certainty for the TMA halides, TEA iodide and TPrA bromide. For these compounds, a small axial quadrupolar coupling is associated with a tetragonal crystal lattice. The other compounds which we have discussed exhibit efgs which originate from some combination of intra and extramolecular effects. It is not unreasonable that the intramolecular structure may dictate the extramolecular structure (and vice versa), so these two effects may not be strictly separable.

Finally, it should be pointed out that the crystalline field effect arguments presented here have been used in the past to rationalize efg parameters in ammonium hydrogen oxalate (45), ammonium dihydrogen phosphate (46), and ammonium aluminum alum (47). For these three compounds the averaging of the intramolecular efg would no doubt be complete due to ammonium ion reorientation and the agreement between the observed efg symmetry and the crystalline field symmetry is good.

Acknowledgments

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Table 1. Quadrupole coupling constant (e^2qQ/h) and the asymmetry parameter (η) for various tetraalkylammonium compounds.

Figure 1. Proton decoupled quadrupolar echo spectra of choline iodide as a function of temperature. The echo sequence in all spectra used 3.7 usec 90° pulses and 80 usec interpulse delays. The recycle time was 2 seconds in all spectra; T_1 was found to be much less than 2 seconds at all temperatures. (a) 5400 acquisitions at -70°C (b) 3000 acquisitions at -59°C (c) 2608 acquisitions at -40°C (d) 3000 acquisitions at 18°C .

Figure 2a. The efg parameters e^2qQ/h and η as a function of temperature for tetramethylammonium [TMA] chloride. The solid line through the upper points follows the equation: $\eta = 0.93[(T_c - T)/T_c]^{0.24}$ below the phase transition, while that through the lower follows: $e^2qQ/h = 17.3 + 47.66[(T_c - T)/T_c]^{0.41}$. T_c is the temperature at the λ point; 184.9°K .

Figure 2b. From top to bottom: The electric field gradient components V_{zz} , V_{xx} and V_{yy} as a function of temperature; the algebraic signs are arbitrary. The solid line through the upper points follows the equation: $V_{zz} = 12.99 + 36.23[(T_c - T)/T_c]^{0.41}$ below the phase transition, while that through the lower points follows: $V_{yy} = -6.49 - 36.60[(T_c - T)/T_c]^{0.41}$. V_{xx} is invariant within experimental error at -6.49 kHz .

Figure 3. Proton decoupled quadrupolar echo spectrum of tetraethylammonium [TEA] iodide at -90°C . The signal is the result of 200 acquisitions using an ADRF cross polarization technique. The mixing time was 10 msec, a 80 usec delay followed the mixing period and this was followed by a 3.5

usec 90° pulse. The dotted line represents a rigid lattice powder spectrum with $e^2qQ/h = 42.3$ kHz and $\eta = 0.0$; this has been convolved with 300 Hz of lorentzian linebroadening and multiplied by a function to account for the finite duration of the echo pulse.

Figure 4. Proton decoupled quadrupolar echo spectrum of decyltrimethylammonium bromide [DTAB] at -50° C. The echo sequence consisted of 3.7 usec 90° pulses and a 60 usec interpulse delay; this signal is the result of 12,000 acquisitions. The dotted line represents a rigid lattice powder spectrum with $e^2qQ/h = 106$ kHz and $\eta = 0.98$; this has been convolved with 800 Hz of lorentzian linebroadening and multiplied by a function which accounts for the finite duration of the excitation and echo pulses.

Figure 5. Proton decoupled quadrupolar echo spectrum of dimyristoyl phosphatidylcholine [DML] at -80° C. The echo sequence consisted of 3.7 usec 90° pulses separated by a 60 usec interpulse delay; this signal is the result of 87,960 acquisitions.

TABLE 1

 ^{14}N Quadrupole Coupling Constants (e^2qQ/h)
and Asymmetry Parameters (η)

Compound	e^2qQ/h (kHz)	η	Temp. ($^{\circ}\text{K}$)
Tetraalkylammonium Salts			
TMA Br	26.6 ± 0.2^a	0.00 ± 0.02	290
TMA I	31.5 ± 0.2^a	0.00 ± 0.02	293
"	34.0 ± 0.2	0.00 ± 0.02	223
"	35.7 ± 0.4	0.00 ± 0.02	193
TMA Cl	17.3 ± 0.2^a	0.00 ± 0.02	293
"	17.4 ± 0.2	0.00 ± 0.02	187
"	17.2 ± 0.2	0.00 ± 0.02	185
"	24.9 ± 0.2	0.31 ± 0.03	183
"	26.4 ± 0.8	0.36 ± 0.04	181
"	31.8 ± 1.0	0.47 ± 0.02	175
"	37.3 ± 1.0	0.55 ± 0.03	163
"	40.0 ± 2.0	0.60 ± 0.04	155
TEA Cl	approx. 65.	----	273-188
TEA Br	68.0 ± 1.0	0.40 ± 0.05	292
"	69.0 ± 1.0	0.37 ± 0.03	238
"	78.2 ± 0.5	0.40 ± 0.03	193
TEA I	40.5 ± 0.2	0.00 ± 0.01	292
"	41.3 ± 0.2	0.00 ± 0.01	238
"	42.3 ± 0.2	0.00 ± 0.01	173
TEA I ₃	49.0 ± 1.0	0.66 ± 0.02	292
"	52.0 ± 2.0	0.61 ± 0.02	248
"	63.0 ± 1.0	0.45 ± 0.02	213
"	65.0 ± 1.0	0.42 ± 0.02	198
"	68.0 ± 1.0	0.44 ± 0.03	178
TPrA Br	47.0 ± 0.5	0.00 ± 0.02	293
"	49.2 ± 0.3	0.00 ± 0.03	238
"	51.0 ± 0.3	0.00 ± 0.03	198
TPrA I	99.0 ± 1.0	0.54 ± 0.02	198
"	102.0 ± 2.0	0.55 ± 0.02	183
TBA Br	26.4 ± 0.2	0.44 ± 0.02	293
"	24.4 ± 0.2	0.55 ± 0.01	213
"	22.5 ± 0.3	0.65 ± 0.01	175
"	21.8 ± 0.3	0.68 ± 0.01	164
TBA I	11.8 ± 0.2	0.70 ± 0.02	293
"	11.4 ± 0.2	0.60 ± 0.02	273
"	11.4 ± 0.2	0.50 ± 0.02	239
"	12.1 ± 0.2	0.36 ± 0.02	188
TPnA Br	40.0 ± 1.0	0.79 ± 0.03	292
"	39.0 ± 1.0	0.85 ± 0.03	233
"	37.0 ± 0.4	0.92 ± 0.03	193
"	36.1 ± 0.6	0.95 ± 0.04	177

TMA= tetramethylammonium

TEA= tetraethylammonium

TPrA= tetrapropylammonium

TBA= tetrabutylammonium

TPnA= tetrapentylammonium

TABLE 1 (continued)

 ^{14}N Quadrupole Coupling Constants (e^2qQ/h)
and Asymmetry Parameters (η)

Compound	e^2qQ/h (kHz)	η	Temp. ($^{\circ}\text{K}$)
Choline Halides			
Choline Cl	$40.0^b \pm 0.5$	0.38 ± 0.02	291
"	$48.0^b \pm 1.0$	0.34 ± 0.06	213
"	51.0 ± 2.0	0.24 ± 0.02	175
Choline Br	156.0 ± 1.0	0.31 ± 0.02	290
"	172.0 ± 1.0	0.48 ± 0.02	223
"	179.0 ± 2.0	0.52 ± 0.02	193
Choline I	46.7 ± 0.4	0.08 ± 0.02	290
"	$48.3^b \pm 0.4$	0.22 ± 0.02	233
"	$48.5^b \pm 0.4$	0.27 ± 0.02	214
"	$48.5^c \pm 0.6$	0.29 ± 0.02	203
PCC	approx. 120. ^d	----	190-158
Amphiphiles			
DTAB	116.0 ± 1.0	0.85 ± 0.02	293
"	106.0 ± 1.0	0.98 ± 0.02	223
"	101.0 ± 1.0	1.00 ± 0.02	193
"	104.0 ± 2.0	1.00 ± 0.02	175
HTAB	98.0 ± 1.0	0.90 ± 0.02	293
"	95.0 ± 1.0	1.00 ± 0.02	223
DDAB	190.0 ± 3.0	0.73 ± 0.03	293
"	177.0 ± 4.0	0.64 ± 0.04	178
DML	approx. 90. ^d	----	190-158

DTAB= decyltrimethylammonium bromide

HTAB= hexadecyltrimethylammonium bromide

DDAB= didodecyltrimethylammonium bromide

PCC= phosphorylcholine chloride

DML= dimyristoyl phosphatidylcholine

a) these values have been reported previously in ref. 6.

b) the spectral lineshapes here appear to have some motional contribution.

c) the spectral lineshapes here appear to be dominated by motion.

d) the spectra here are completely washed out and featureless, this is discussed in the text.

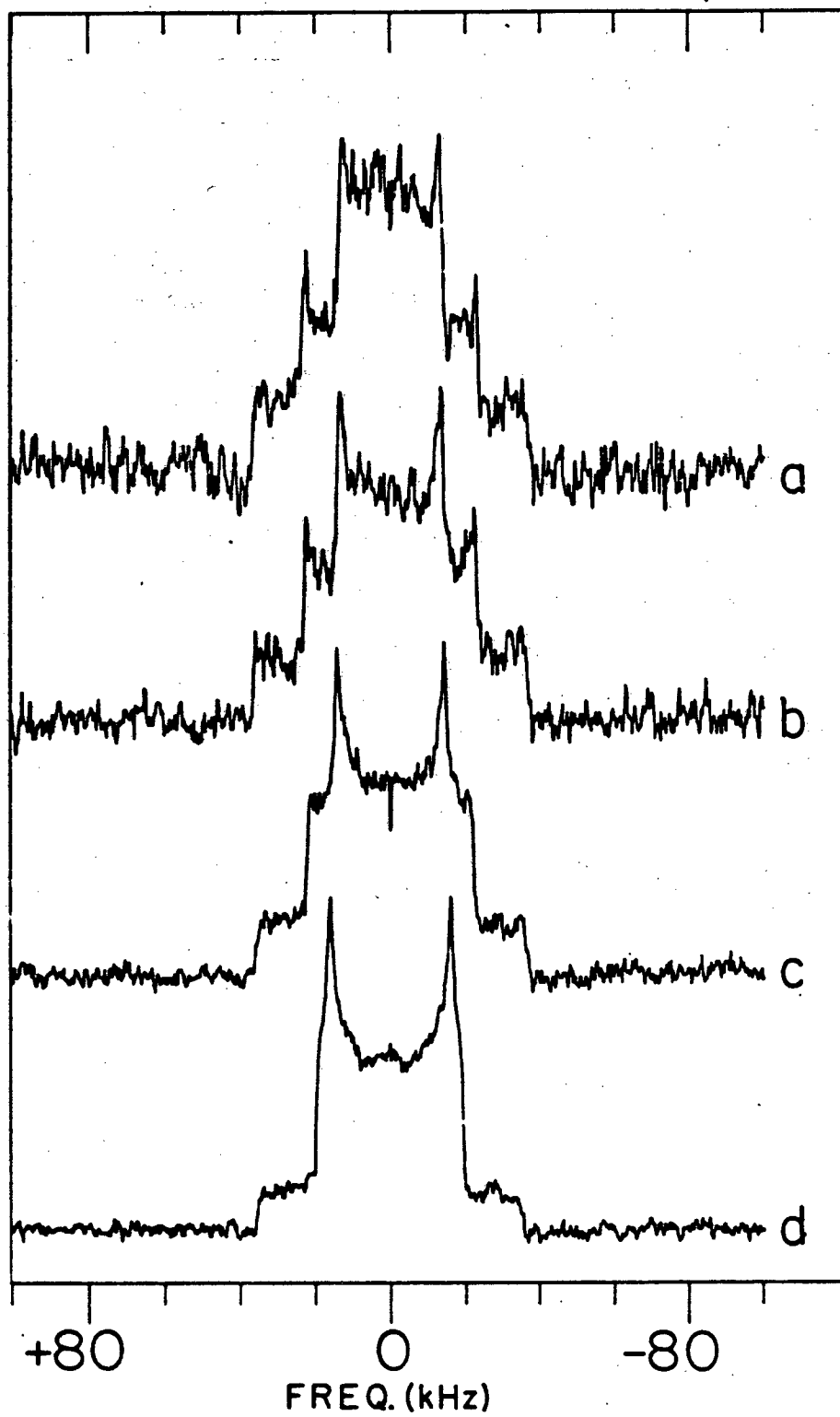


Figure 1

XBL 831-7628

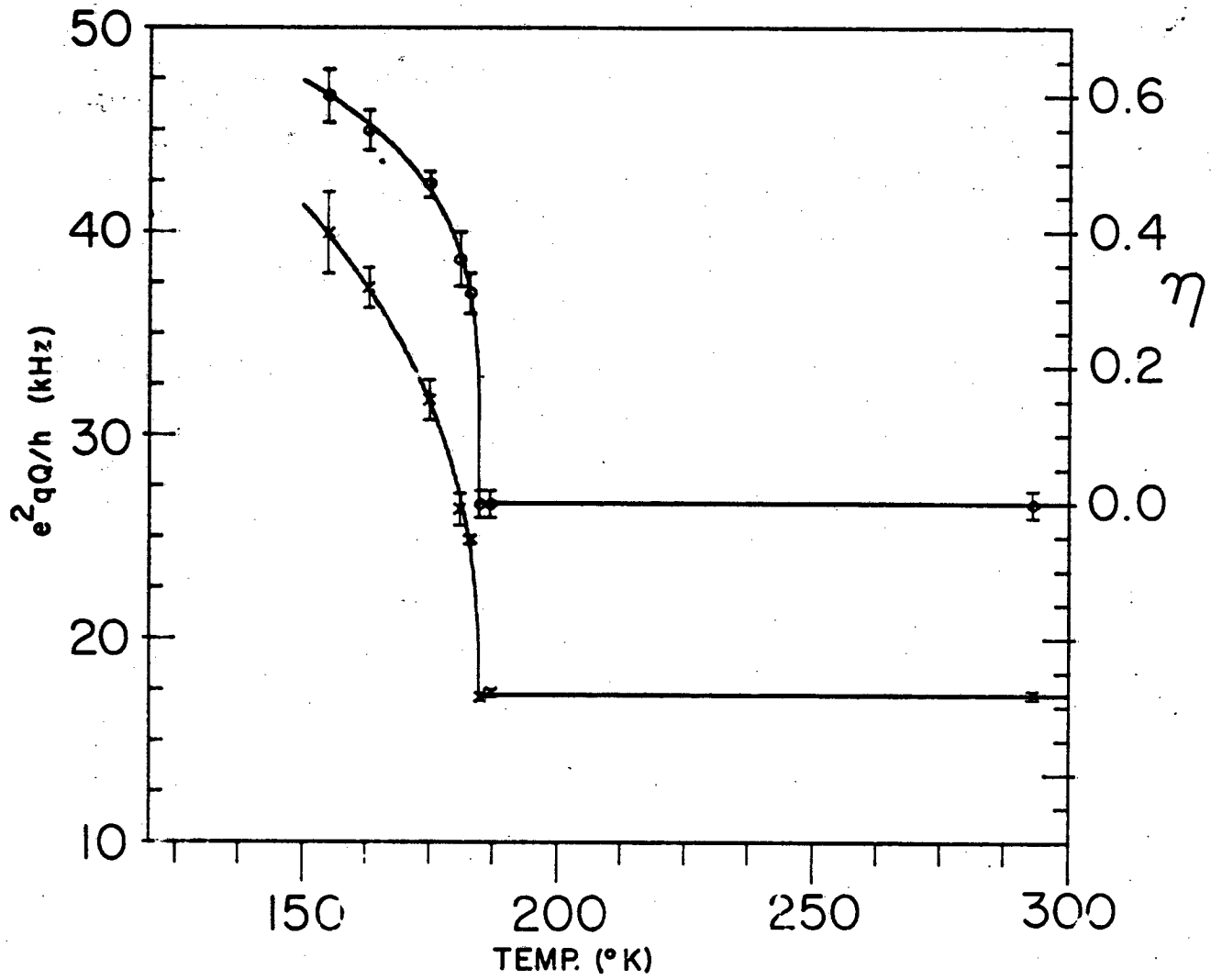


Figure 2a

XBL 831-7632

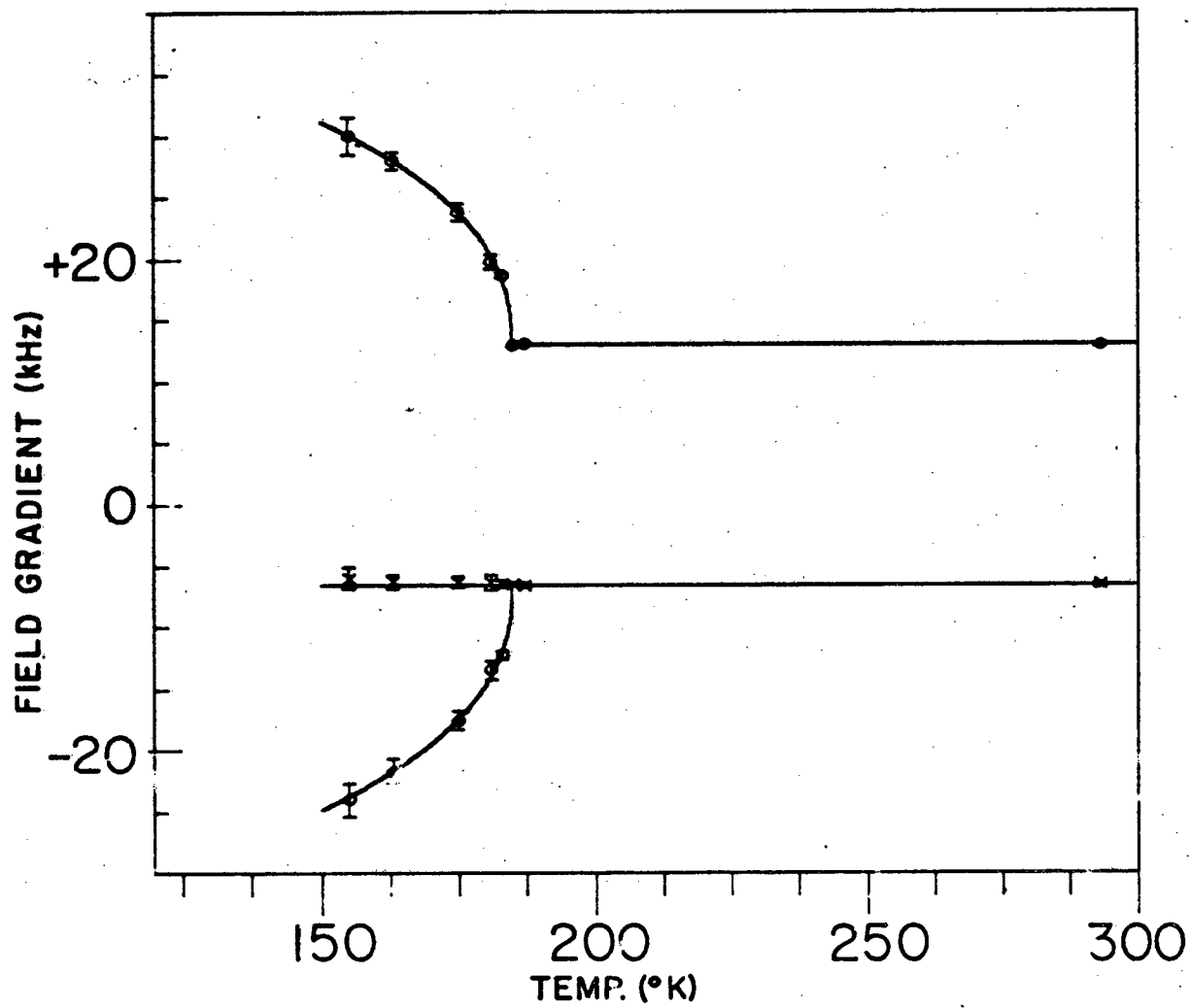
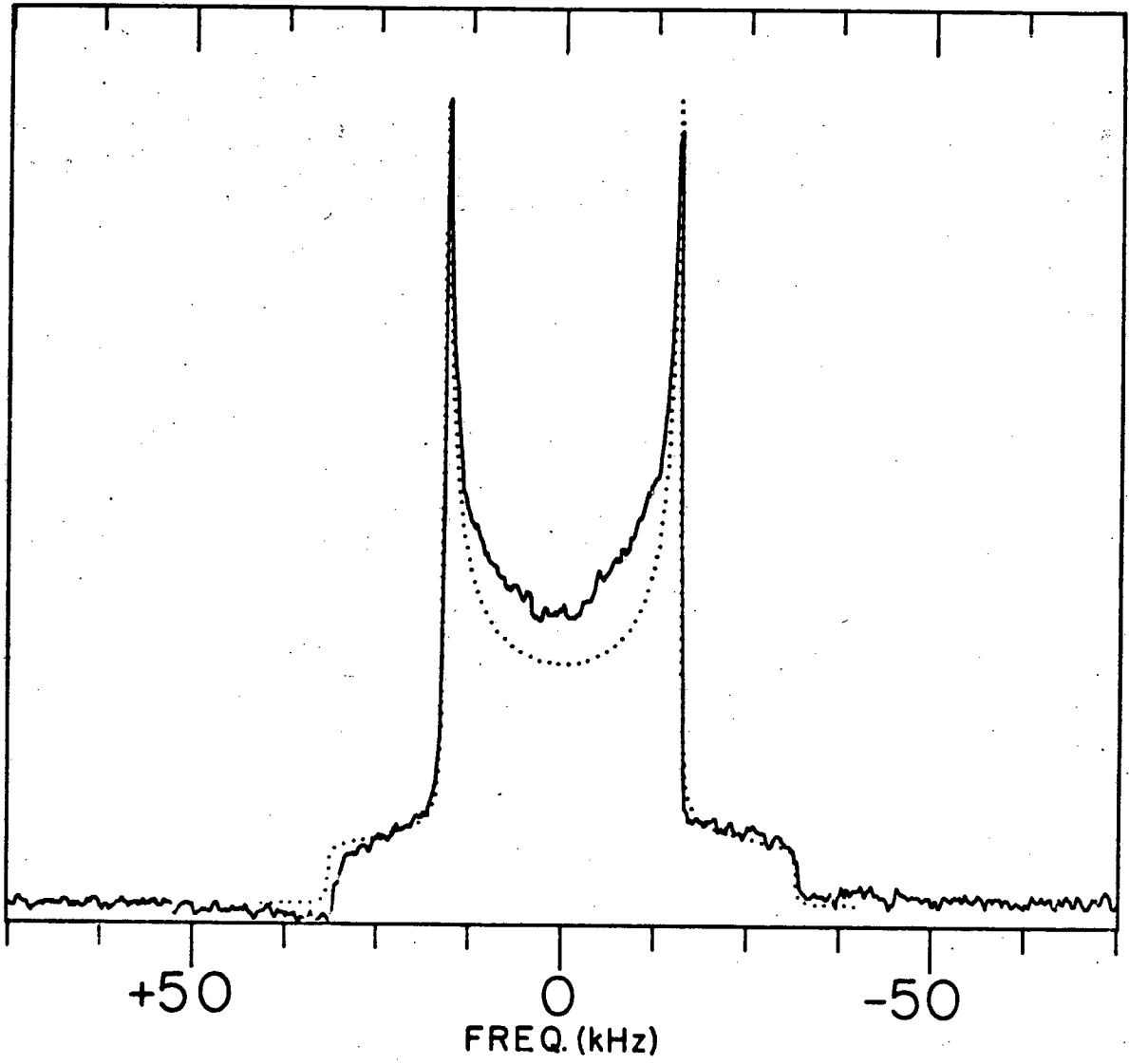


Figure 2b

ADL 931-7633



XBL 831-7631

Figure 3

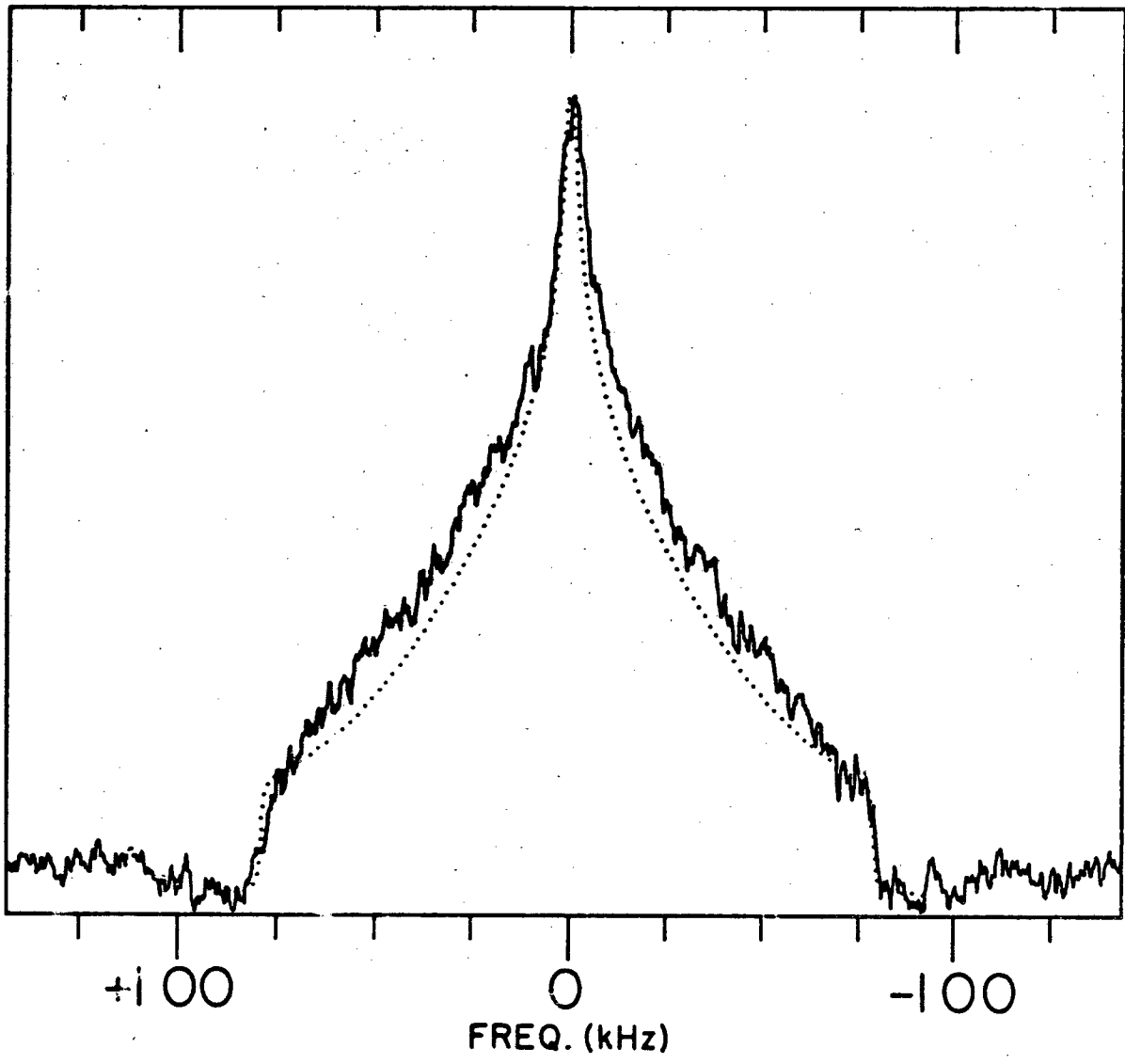


Figure 4

XBL 831-7630

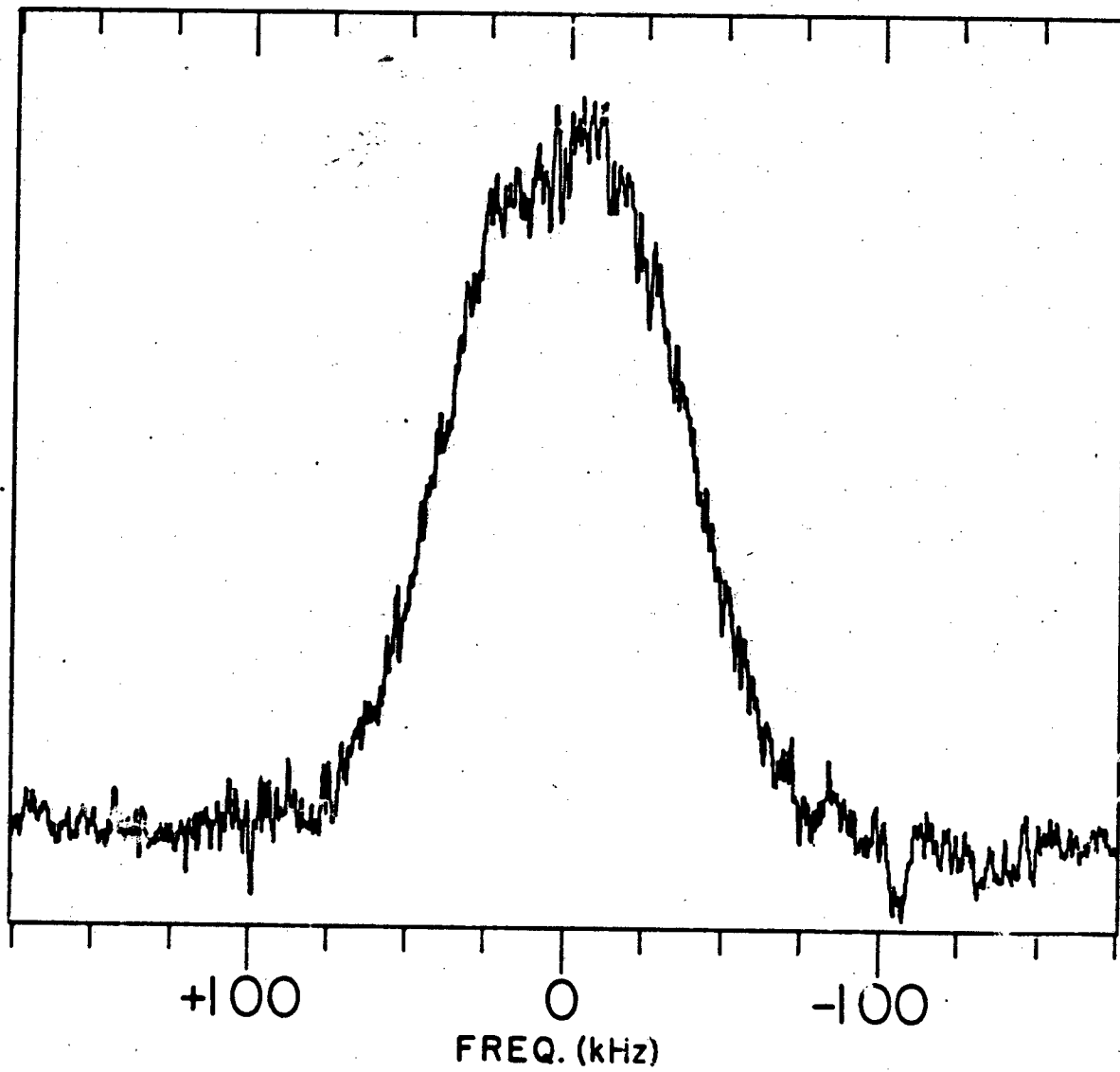


Fig. 5

XBL 831-7629

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