NQR STUDY OF SPIN-SPIN INTERACTIONS IN THE FERROELECTRIC PHASE OF SOLID HCl

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Fourier transform NQR spectra of the ^{35}Cl in the low temperature ferroelectric phase of solid HCl reveal fine structure due to intramolecular spin-spin interactions. A detailed calculation of the NQR spectra of $I = 3/2 - I = 1/2$ spin system in the presence of dipolar and electron coupled interactions is given. From the order of the components of the fine structure the sign of the nuclear quadrupole coupling constant was determined to be negative. The motional averaging of the intramolecular dipolar splitting was observed.

1. Introduction

The evolution of pulse technique in NQR spectroscopy, in combination with the method of the Fourier transform of the free induction decay of nuclear magnetization has considerably extended the range of applications of the NQR method. Hitherto, methods of NQR investigation using superregenerative spectrometers did not permit the line shape and fine structure of NQR spectra. Whereas, in particular, the study of spin-spin interaction — the source of fine structure of the NQR spectrum — enables one to glean abundant information concerning the nature of the intra- and intermolecular interactions and the dynamical properties of the crystal lattice.

Two kinds of magnetic spin-spin interaction between the nucleus the NQR spectrum of which we study and other neighbouring nuclei are possible. Firstly, there can be direct

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magnetic dipole-dipole interaction. Secondly, one can be dealing with indirect interaction between two nuclei due to their interaction with the electrons bonding them chemically (so-called "electron-coupled interaction"). In many a case spin-spin interaction has no other effect but a broadening of the NQR line. However, in some molecular crystals, a well apparent fine structure of the NQR spectrum could be observed succesfully [1–3].

In the present work, Fourier transform NQR spectroscopy was applied to study the intramolecular spin-spin interactions in solidified HCl. The NQR signal is accessible to observation in the low-temperature ferroelectric phase only, i. e. below 98.4 K. The structure of the low temperature ferroelectric phase of solid HCl has been shown by X-ray and neutron diffraction studies [4] to be an ordered arrangement of Cl-H...Cl hydrogen bonded zigzag chains forming an orthorhombic lattice (Fig. 1). At about 98 K the ferroelectricity disappears and recent diffraction studies indicate that a disordered orthorhombic
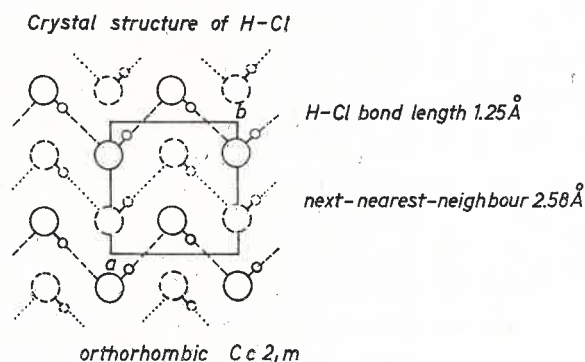

Fig. 1. Crystal structure of the low temperature phase of HCl

structure is formed with rapid fluctuations of the zigzag chains observed. The same diffraction studies show a change of lattice symmetry at 120 K from the orthorhombic to the cubic phase, which is stable to the melting point at 159 K.

The intramolecular distance between the nuclei of chlorine and hydrogen amounts to 1.25 Å, whereas the shortest distance between a chlorine nucleus and the hydrogen of a neighbouring molecule equals 2.58 Å. Since the dipole interaction energy is a function of r^{-3}, the intramolecular interaction is stronger than that between the molecules. Consequently, each bi-atomic molecule can be dealt with as an isolated two-spin system in which the nuclear quadrupole energy levels are perturbed by coupling between the magnetic moments of the nuclei. The energy ratio of intra- and intermolecular dipolar interactions amounts to $(1.25/2.58)^{-3} = 8.79$ for crystalline HCl, but to $(1.1/3.42)^{-3} = 30.05$ [1] in solid nitrogen. Thus, in HCl, the intermolecular contribution is much larger and one can hardly expect its NQR spectrum to exhibit a fine structure so perfectly resolved as in solid nitrogen. Moreover, work has to be carried out at liquid helium temperatures because, as shown experimentally by Marram and Ragle [5], the spin-lattice quadrupole relaxation time becomes very short upwards of 50 K thus leading to NQR line broadening.

2. Calculation of the NQR spectra of $I = 3/2 - I = 1/2$ spin system in the presence of dipolar and electron coupled interactions

The quadrupole interaction Hamiltonian of a nucleus with spin I having the nuclear quadrupole moment eQ and immersed in the electric field gradient eq takes, in the system of principal axes of the gradient tensor, the form:

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}\left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right], \tag{1}$$

where $eq = \dfrac{\partial^2 V}{\partial z^2}$ is the maximal component of the gradient tensor of the electric field

with the potential V, and $\eta = \left(\dfrac{\partial^2 V}{\partial x^2} - \dfrac{\partial^2 V}{\partial y^2}\right)\bigg/\dfrac{\partial^2 V}{\partial z^2}$ is the asymmetry parameter.

The splitting of the quadrupole energy terms of the nucleus is caused by a perturbation in the quadrupole interaction of the resonating ^{35}Cl nucleus due to intramolecular dipole-dipole interaction $\mathcal{H}_d$ and electron-coupled interaction $\mathcal{H}_J$. In the system of principal axes of the electric field gradient tensor, the latter two interactions have the Hamiltonians:

$$\mathcal{H}_d = hd[2I_{1z}I_{2z} - \tfrac{1}{2}(I_{1+}I_{2-} + I_{1-}I_{2+})], \tag{2}$$

$$\mathcal{H}_J = h[J_\parallel I_{1z}I_{2z} + \tfrac{1}{2}J_\perp(I_{1+}I_{2-} + I_{1-}I_{2+})], \tag{3}$$

where $d = \dfrac{\gamma_1\gamma_2\hbar}{2\pi r_{12}^3}$ and r_{12} is the distance between the nuclei in the molecule. $J_\parallel$ and $J_\perp$

are tensor components of indirect spin-spin interactions. The z-axis is the symmetry axis of the HCl molecule.

Since $\mathcal{H}_Q$ is by almost 4 orders of magnitude larger than $\mathcal{H}_d + \mathcal{H}_J$, perturbation calculus is appropriate for determining the effect of spin-spin interaction on the NQR spectrum. The following two cases can be distinguished:

I. The electric field gradient is axially symmetric ($\eta = 0$)

The Hamiltonian (1) for $I = 3/2$ and $\eta = 0$ takes the form:

$$\mathcal{H}_Q = hA[3I_z^2 - I(I+1)], \tag{4}$$

$A = \dfrac{e^2qQ}{12h}$ being the quadrupole coupling constant.

The unperturbed eigen-states are given by the simple products $|m_1\rangle |m_2\rangle = |m_1, m_2\rangle$, where the $|m_1\rangle$ are the eigen-states of the Hamiltonian $\mathcal{H}_Q$ and the indices 1,2 refer to the magnetic quantum numbers of the chlorine and hydrogen nucleus, respectively. When calculating the matrix elements $\langle m_1, m_2|\mathcal{H}_Q + \mathcal{H}_d + \mathcal{H}_J|m_1, m_2\rangle$ we take note of the fact that the perturbation $\mathcal{H}_d + \mathcal{H}_J$ causes a mixing of the states $|\tfrac{1}{2}, -\tfrac{1}{2}\rangle$ and $|-\tfrac{1}{2}, \tfrac{1}{2}\rangle$. In conformity with the rules of perturbation calculus for cases of degenerate states, linear, normalized and orthogonal combinations of the states have to be found so that the first-

-order correction can be calculated applying the rules for non-degenerate states, i. e. $\Delta E_i = \langle \psi_i | \mathscr{H}_d + \mathscr{H}_J | \psi_i \rangle$. The linear combinations ψ_3 and ψ_4 of Table I fulfil the above requirements. Table I contains the results obtained in the first order of perturbation calculus.

TABLE I

Eigenvalues of the quadrupole Hamiltonian $\mathscr{H}_Q$ of ^{35}Cl nucleus in HCl molecule and splitting of the nuclear quadrupole energy levels as calculated by the first-order perturbation theory in the presence of dipolar and indirect spin-spin interactions. All energies are given in frequency units E/h. The quadrupole coupling constant A is assumed to be negative, and $d = \hbar \gamma_1 \gamma_2 / 2\pi r_{12}^3$

$\mathscr{H}_Q$	Eigenfunctions	Energies
$3A$	$\Psi_1 = \lvert \frac{1}{2}, \frac{1}{2} \rangle$	$3A + \frac{1}{2}d + \frac{1}{4}J_{\shortparallel}$
$3A$	$\Psi_2 = \lvert -\frac{1}{2}, -\frac{1}{2} \rangle$	
$3A$	$\Psi_3 = \dfrac{1}{\sqrt{2}}[\lvert \frac{1}{2}, -\frac{1}{2} \rangle - \lvert -\frac{1}{2}, \frac{1}{2} \rangle]$	$3A + \frac{1}{2}d - \frac{1}{4}J_{\shortparallel} - J_{\perp}$
$3A$	$\Psi_4 = \dfrac{1}{\sqrt{2}}[\lvert \frac{1}{2}, -\frac{1}{2} \rangle + \lvert -\frac{1}{2}, \frac{1}{2} \rangle]$	$3A - \frac{3}{2}d - \frac{1}{4}J_{\shortparallel} + J_{\perp}$
$-3A$	$\Psi_5 = \lvert \frac{3}{2}, \frac{1}{2} \rangle$	$-3A + \frac{3}{2}d + \frac{3}{4}J_{\shortparallel}$
$-3A$	$\Psi_6 = \lvert -\frac{3}{2}, -\frac{1}{2} \rangle$	
$-3A$	$\Psi_7 = \lvert \frac{3}{2}, -\frac{1}{2} \rangle$	$-3A - \frac{3}{2}d - \frac{3}{4}J_{\shortparallel}$
$-3A$	$\Psi_8 = \lvert -\frac{3}{2}, \frac{1}{2} \rangle$	

The relative intensity of the resonance transitions is given as:

$$I_{ij} \sim |\langle \psi_i | I_{1+} + I_{1-} | \psi_j \rangle|^2, \tag{5}$$

Table II contains the frequencies of the permitted resonance transitions and their relative intensities for the case of negative quadrupole coupling constant, $A < 0$. The set of energy levels and the theoretical NQR spectrum of the ^{35}Cl nucleus in the HCl molecule, for $\eta = 0$ and $A < 0$, are shown in Fig. 2. In this case, the NQR spectrum consists of an

TABLE II

^{35}Cl NQR transition frequencies and relative intensities. Intramolecular magnetic dipole-dipole and indirect spin-spin interactions are treated as perturbations to first order in the parameters $d = \hbar \gamma_1 \gamma_2 / 2\pi r_{12}^3$, $J_{\shortparallel}$ and $J_{\perp}$. The quadrupole coupling constant $A = e^2 qQ/12h$ is negative

Transition frequency	Relative intensity
$6\lvert A \rvert - d - \frac{1}{2}J_{\shortparallel}$	2
$6\lvert A \rvert + \frac{1}{2}J_{\shortparallel} + J_{\perp}$	1
$6\lvert A \rvert + 2d + \frac{1}{2}J_{\shortparallel} - J_{\perp}$	1

asymmetric triplet with the intensity ratios 2:1:1 towards increasing frequencies. The NQR spectrum for the case $A > 0$ can be derived from the data of Table I by performing the transformation $A \rightarrow -A$. Since a transition frequency between two levels is always a positive magnitude, the change in sign of A will cause a reversal of the dipolar components
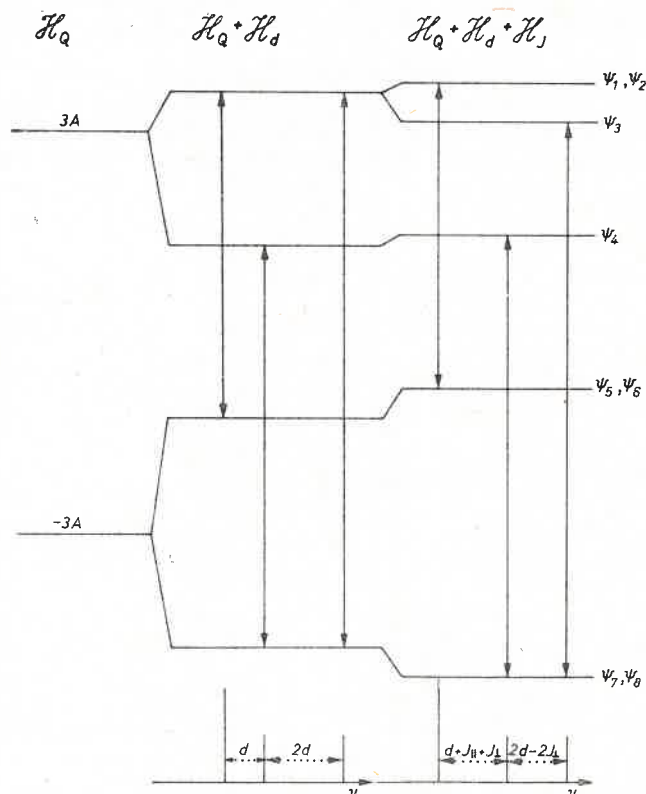

Fig. 2. Theoretical first-order energy level diagram (not to scale) and NQR stick-spectrum of ^{35}Cl nucleus in HCl molecule. The spectra are shown for a negative quadrupole coupling constant A. Changing the sign of A reverses the lines about the unperturbed frequency $v_Q = 6|A|$. The spectrum is an asymmetric triplet with relative intensity 2:1:1. Indirect spin-spin coupling J changes the separation between the component of the spectrum. $(d > J, J_{||} > J_{\perp} > 0), (\eta = 0)$

of the spectrum about the unperturbed frequency $v_Q = 6|A|$. Hence, the sign of A determines the type of asymmetry of the triplet. Indirect spin-spin interaction affects the relative distance between the components of the triplet.

II. The electric field gradient is not axially symmetric $(\eta \neq 0)$

If $\eta \neq 0$, the term of (1) containing the asymmetry parameter η causes a mixing of quantum states differing by $\Delta m = \pm 2$. The functions $|m_1, m_2\rangle$, which are simple products of the states $|m_1\rangle$ and $|m_2\rangle$, are not eigen-states of $\mathcal{H}_Q$. As shown by Dean [6], one has to form linear combinations:

$$\Phi_i = c_{i1}|m_1, m_2\rangle \pm c_{i2}|m_1 \pm 2, m_2\rangle, \qquad (6)$$

choosing the coefficients c_i so that the Φ_i shall be orthonormal eigen-functions of $\mathscr{H}_Q$. It is convenient to write the c_i in the form $\cos\dfrac{\alpha}{2}$ or $\sin\dfrac{\alpha}{2}$, with $\tan\alpha=\dfrac{\eta}{\sqrt{3}}$. Here, too, the principal axis of the field gradient tensor has to be assumed along the H–Cl direction. Otherwise, the Hamiltonian $\mathscr{H}_d$ would not retain its form (2).

<div align="right">TABLE III</div>

Eigenvalues of the quadrupole Hamiltonian $\mathscr{H}_Q$ of ^{35}Cl nucleus in HCl molecule and splitting of the nuclear quadrupole energy levels as calculated by the first-order perturbation theory in the presence of dipolar and indirect spin-spin interactions ($\eta\neq0$). $A'=A\left(1+\dfrac{\eta^2}{3}\right)^{1/2}$

$\mathscr{H}_Q$	Eigenfunctions	Energies
$3A'$	$\Phi_1=\cos\dfrac{\alpha}{2}\,\vert\tfrac{1}{2},\tfrac{1}{2}\rangle-\sin\dfrac{\alpha}{2}\,\vert-\tfrac{3}{2},\tfrac{1}{2}\rangle$	$-\tfrac{1}{4}(J_{\parallel}+2d)\left(4\sin^2\dfrac{\alpha}{2}-1\right)$
$3A'$	$\Phi_2=\cos\dfrac{\alpha}{2}\,\vert-\tfrac{1}{2},-\tfrac{1}{2}\rangle-\sin\dfrac{\alpha}{2}\,\vert\tfrac{3}{2},-\tfrac{1}{2}\rangle$	
$3A'$	$\Phi_3=\dfrac{1}{\sqrt2}(\Phi_7-\Phi_2)$	$\tfrac{1}{4}(J_{\parallel}+2d)\left(4\sin^2\dfrac{\alpha}{2}-1\right)-(J_{\perp}-d)\cos^2\dfrac{\alpha}{2}$
$3A'$	$\Phi_4=\dfrac{1}{\sqrt2}(\Phi_7+\Phi_2)$	$\tfrac{1}{4}(J_{\parallel}+2d)\left(4\sin^2\dfrac{\alpha}{2}-1\right)+(J_{\perp}-d)\cos^2\dfrac{\alpha}{2}$
$-3A'$	$\Phi_5=\sin\dfrac{\alpha}{2}\,\vert-\tfrac{1}{2},\tfrac{1}{2}\rangle+\cos\dfrac{\alpha}{2}\,\vert\tfrac{3}{2},\tfrac{1}{2}\rangle$	$\tfrac{1}{4}(J_{\parallel}+2d)\left(4\cos^2\dfrac{\alpha}{2}-1\right)$
$-3A'$	$\Phi_6=\sin\dfrac{\alpha}{2}\,\vert\tfrac{1}{2},-\tfrac{1}{2}\rangle+\cos\dfrac{\alpha}{2}\,\vert-\tfrac{3}{2},-\tfrac{1}{2}\rangle$	
$-3A'$	$\Phi_7=\sin\dfrac{\alpha}{2}\,\vert\tfrac{1}{2},\tfrac{1}{2}\rangle+\cos\dfrac{\alpha}{2}\,\vert-\tfrac{3}{2},\tfrac{1}{2}\rangle$	$-\tfrac{1}{4}(J_{\parallel}+2d)\left(4\cos^2\dfrac{\alpha}{2}-1\right)$
$-3A'$	$\Phi_8=\sin\dfrac{\alpha}{2}\,\vert-\tfrac{1}{2},-\tfrac{1}{2}\rangle+\cos\dfrac{\alpha}{2}\,\vert\tfrac{3}{2},-\tfrac{1}{2}\rangle$	

Table III shows how the non-axial symmetry of the electric field gradient affects the energy levels of the ^{35}Cl nucleus in the HCl molecule (in the first approximation of perturbation calculus). The levels undergo a relative shift; however, the effect, being proportional to $\cos^2\dfrac{\alpha}{2}$ or $\sin^2\dfrac{\alpha}{2}$, is very small. Applying the trigonometrical identity

$$\cos^2\frac{\alpha}{2}=\tfrac{1}{2}\left[1+\frac{1}{(1+\tan^2\alpha)^{1/2}}\right],\tag{7}$$

for small η, one has the following approximate expression:

$$\cos^2 \frac{\alpha}{2} = \tfrac{1}{2}\left[1 + \frac{1}{(1+\frac{1}{3}\eta^2)^{1/2}}\right] \approx \tfrac{1}{2}\left[1 + \frac{1}{1+\frac{1}{6}\eta^2}\right] \approx \tfrac{1}{2}\left[1 + 1 - \tfrac{1}{6}\eta^2\right] = 1 - \tfrac{1}{12}\eta^2, \qquad (8)$$

and likewise $\sin^2 \dfrac{\alpha}{2} = \dfrac{1}{12}\eta^2$. Thus, the relative shift amounts to no more than a fraction of a hundredth compared to the case $\eta = 0$. For $J = 0$ (the purely dipolar case), η removes the degeneracy of one of the levels, but splitting amounts to but $3d \sin^2 \dfrac{\alpha}{2}$.

3. Experimental procedure

The NQR spectrometer was a phase-coherent pulse system employing a series-tuned single coil with a quarter-wavelength cable between the sample probe and the receiver. The output from the pulse spectrometer was monitored by an oscilloscope and sampled, digitized and averaged by a Fabritek 1070 digital signal averager, equipped with a high-
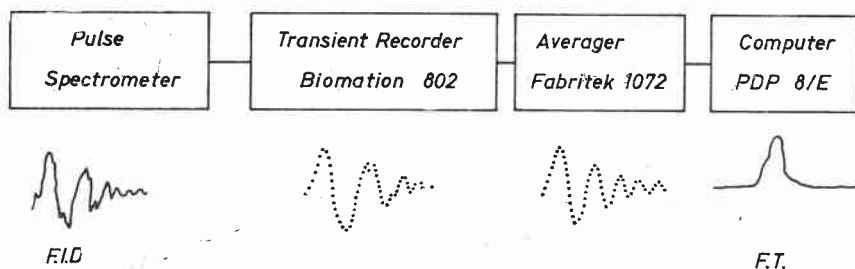

Fig. 3. Experimental set-up

speed digitizer (SD-78) and sweep control unit (TR-802) (Fig. 3). The Fabritek 1070 was interfaced with a PDP 8/e computer and the Fourier transform was calculated by use of the Cooley-Tukey algorithm.

The high-purity HCl sample was annealed for at least 12 hours at a temperature approximately 1 K below melting (158.9 K), 24 hours at a temperature 1 K below 120 K, and 24 hours at a temperature 1 K below the ferroelectric phase transition. The sample temperature was measured to an accuracy of about 0.05 K using a platinum resistance thermometer. Automatic temperature control was provided by the helium cryostat.

4. Results and discussion

Fig. 4 shows the NQR power spectrum of ^{35}Cl nuclei in HCl obtained from the Fourier transform of the free induction decay signal at liquid helium temperature. The spectrum observed is very broad (30 kHz) and exhibits an anomalous two-component structure [7]. The separation ($\approx$ 15 kHz) between the components is too large for interpretation in terms

of direct or indirect spin-spin interaction and points to the presence of two inequivalent positions of the HCl molecules in the crystal. The origin and detailed properties of the lower-frequency component (e. g. its shorter quadrupole relaxation time T_1 compared with that of the higher-frequency one) are at present under investigation separately.
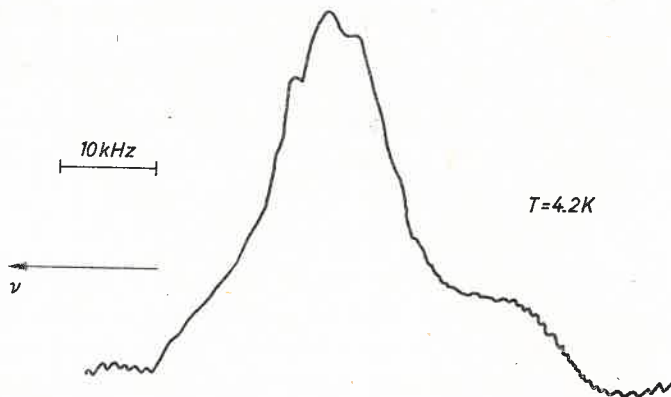

Fig. 4. ^{35}Cl NQR power spectrum (the modulus) of solid hydrogen chloride at 4.2 K. $\nu_Q = 26.697$ MHz. The spectrum was obtained in about 12 hours by Fourier transform of the average of 84 free inductions decays. Repetition time -500 sec, a "90° pulse" width -7 μsec

The higher-frequency component has a triplet structure with peak-to-peak separation about 2.3 and 4.6 kHz, respectively. The separation of the 3 overlapping lines in the power spectrum is much better than in the absorption spectrum which is the real part of the Fourier transformation of the spectrum (Fig. 5a). Lenk and Lucken [8] have shown that the Fourier transformation of a spectrum composed of several overlapping lines in the power spectrum yields a much better separation than for the absorption spectrum, the effect being the more considerable the larger is the part of Lorentz line-shape.

A computer-simulated absorption spectrum is shown in Fig. 5b. Very good agreement with experiment is obtained when assuming the observed triplet structure of the spectrum to be due to intramolecular direct dipole-dipole interaction only. In this case, the NQR spectrum is found to consist of 3 lines with intensity ratios of 2:1:1 and a splitting ratio of 1:2. The asymmetry of the triplet is of a nature pointing to a negative value of the quadrupole coupling constant A for HCl. This confirms earlier theoretical predictions [9].

The dipole interaction constant $d = 1.9$ kHz, determined from the NQR spectrum, is much smaller than the value $d_0 = 2.25$ kHz calculated for HCl molecule. The reduction can be attributed to averaging of the dipole interactions due to molecular librational motion. A similar effect has been observed for the NQR spectrum of solid nitrogen [1]. According to O'Reilly [10], the theoretical librational averaging factor i. e. the ratio of the NQR frequency at absolute zero $\nu_Q(0)$ and that calculated for the rigid crystal lattice $\nu_Q(R)$ is equal to 26.7 MHz/30.1 MHz = 0.88. To within experimental error, this value coincides with the averaging factor d/d_0 determined independently from the dipole structure of the NQR spectrum.
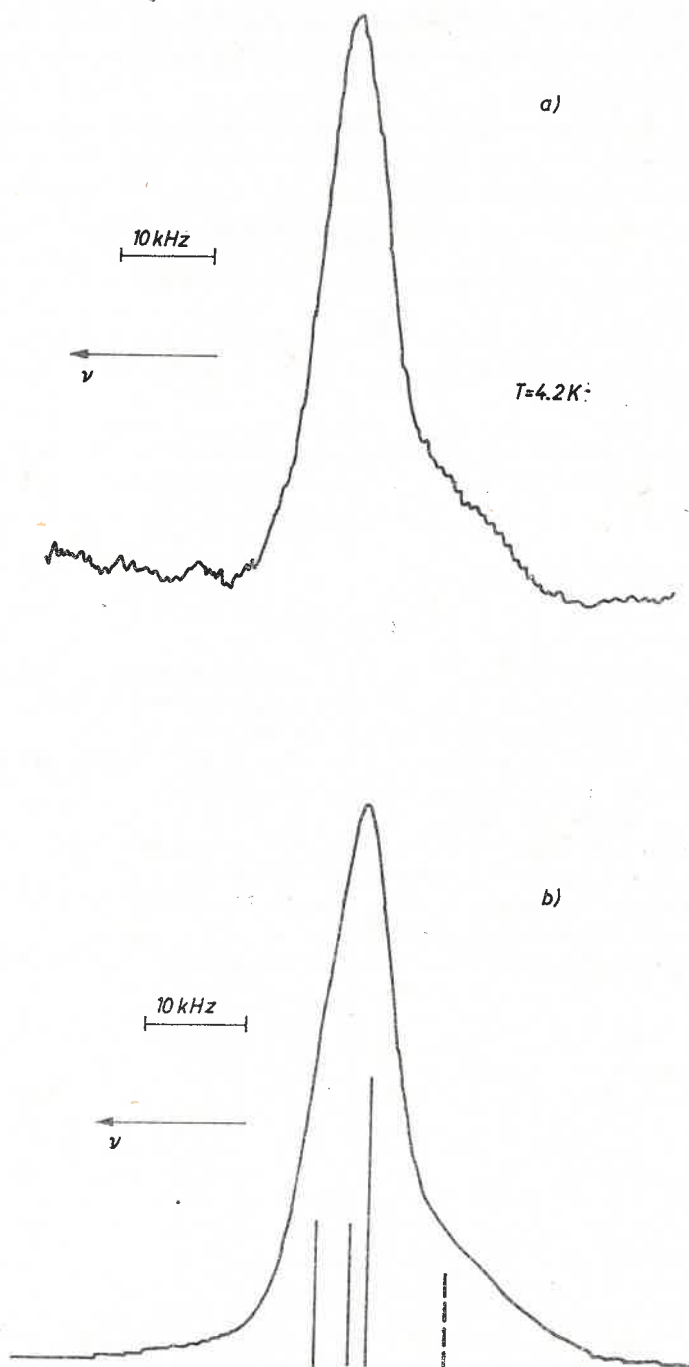
Fig. 5a. ^{35}Cl NQR absorption spectrum of solid HCl at 4.2 K, b. Computer-simulated absorption spectrum (60% Lorentzian line-shape). Higher-frequency component: $\Delta\nu = 2.8$ kHz, relative intensities 1:1:2, separations 3.8 kHz and 1.9 kHz. Lower-frequency component: $\Delta\nu = 7$ kHz, relative intensity 0.6

Because of the large line width of the individual components of the spectrum, no detailed information can be obtained regarding indirect spin-spin interactions and the field gradient asymmetry.

Indirect spin-spin interaction plays a more important role in the case of bonds between heavier atoms. For HCl, after Leavitt et al. [11], J amounts to barely about 80 Hz. No value is available for the asymmetry parameter of the HCl crystal. Nonetheless the analysis of the previous section shows that the influence of η on the fine structure of the spectrum is but slight $\left(\text{the shift in levels proportional to } d \sin^2 \frac{\alpha}{2} \text{ is but of the order of some tens of Hz}\right)$. These extremely subtle variations are much smaller than those due to intermolecular interactions, which are of the order of 0.2 kHz, and are inaccessible to analysis because of the considerable linewidth.

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