Line Shapes of the ^{35}Cl Nuclear Quadrupole Resonance in $KClO_3$, $AgClO_3$, $Ba(ClO_3)_2 \cdot H_2O$, and $Cu(ClO_3)_2 \cdot 6H_2O$

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The nuclear quadrupole resonance (NQR) of ^{35}Cl in $KClO_3$, $AgClO_3$, $Ba(ClO_3)_2 \cdot H_2O$, and $Cu(ClO_3)_2 \cdot 6H_2O$ at room temperature has been measured by using a spectrometer system capable of reproducing with fidelity the line shape. The line-shape parameters were determined from the observed spectrum. All the line shapes of the four chlorates are of an intermediate character between Gaussian and Lorentzian. The line-width in K and Ag salts seems to originate from the inhomogeneity of the electric-field gradient, itself a result of the imperfection of the crystal. In Ba salt, it was found that the line-width is determined by the magnetic dipole-dipole interaction between chlorine and protons in the water of crystallization. The Lorentzian is the superior component of the line shape in Cu salt. This is explained in terms of the anharmonicity of the torsional oscillation of the ClO_3^- group.

Most of the works on the NQR line shape have dealt with the line-width rather than with the actual line shape. This is also the case in the investigations of NQR in chlorates. Wang[1] studied the temperature change of the full half-width in $NaClO_3$ and found that the width increases with a decrease in the temperature. Zeldes and Livingston[2] observed the full width between the flex of the second derivative of the spectrum in $NaClO_3$, $KClO_3$, and $Ba(ClO_3)_2 \cdot H_2O$, and found the sharpest line in $KClO_3$. Grechishkin[3] measured the full half-width in $Ba(ClO_3)_2$, $KClO_3$, and $NaClO_3$ by using a super-regenerative spectrometer, which does not generally give the actual line shape. More precise observations have been reported by Koi and his co-workers[4,5,6] on the Br NQR line in $NaBrO_3$ and $KBrO_3$ using a regenerative spectrometer. However, no precise line-shape study has been done in metal chlorate. We have now determined the line-shape parameters in several chrorates by using a spectrometer capable of reproducing the line shape with fidelity.

Experimental

The NQR line was detected by utilizing a Kushida-type regenerative oscillator[7] with a magnetic field modulation of a 200 Hz on-off field. The spectrum was recorded on a chart by means of a lock-in detection technique, together with pip marks at 1 kHz intervals. In order to obtain an undistorted line shape, the rf level was kept as weak as possible, the sweep rate was 2 kHz/min, and the time constant, 0.3 sec. Details of the spectrometer system have been given in a previous paper.[8] During the observation, the temperature of the sample was maintained within 0.01 K, which corresponds to the shift of the resonance frequency of ~0.05 kHz. The accuracy of the temperature measurement was ±0.5 K. The chlorates were prepared in the usual way.[9]

Line-shape Analysis

A block diagram of the process of the line-shape analysis from the observed spectrum is shown in Fig. 1, together with the line-shape parameters to be determined. The analysis was performed by means of a NEAC 2230 computer at Kanazawa University.

The In-put Data consisted of the reading of the out-put voltage on the recorded chart with a constant frequency interval (order of 10^{-2} kHz), the number

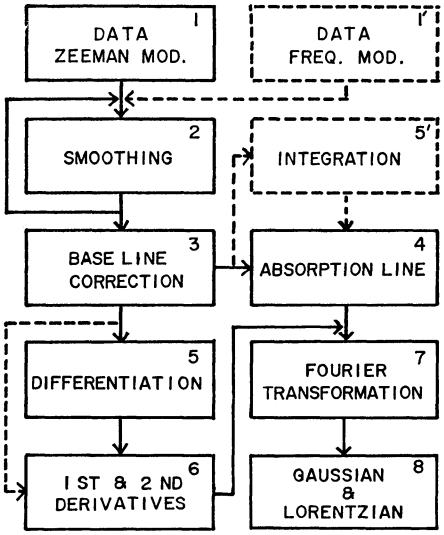

Fig. 1. Block diagram of the process of line shape analysis.
1, 1') Intensity of observed spectrum
Numbers of sample point
Frequencies of initial and final points
Frequency interval
2) Sensitivity improvement when poor S/N ratio.
3) When base line drift occures.
4) Area (M_0)
Peak intensity ($g(\nu_0)$)
Full half-line width ($\Delta\nu_{1/2}$)
First, second and fourth moments (M_1, M_2 and M_4)
6) Peak frequency (ν_0)
Width between maximum slope ($\Delta\nu_{msl}$)
Derivative half intensity (g'_{max})
8) Full half-line widths of Gaussian ($\Delta\nu_G$) and Lorentzian ($\Delta\nu_L$)

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of sample points (200~300), and the frequency at initial point.

Smoothing and Differentiation. When the observed spectrum has a poor S/N ratio, a least-squares smoothing technique (convolution method)[10] is employed to determine the smoothed spectrum. The m-th derivative of the original spectrum can also be obtained by a similar technique. Details of the technique were given by Savitzky and Golay.[11] The smoothing interval chosen is smaller than half of the full line-width at half-maximum intensity, seventeen sample points being included in this interval. Under these conditions, the line distortion error is expected to be smaller than 1%.[10] When a small base-line drift occurs, the true absorption spectrum can be obtained by subtracting the drift from the observed spectral intensity on a chart. The drift was assumed to be linear; by means of the least-squares method, the linear equation was determined using the ten data points, which consisted of two blocks of five successive sample points from both terminals of the frequency in the observed spectrum.

Separation of Gaussian and Lorentzian. Assuming the observed absorption curve to be a convolution of Gaussian and Lorentzian shape (Voigt profile), the full half-widths of each component ($\Delta\nu_G$ and $\Delta\nu_L$) can be determined by the Fourier transformation of the spectrum.[12] Using the least-squares method to fit the logarithm of cosine-transform of the observed spectrum to a quadratic function of the time, the linear and quadratic coefficients give the values of $\Delta\nu_L$ and $\Delta\nu_G$ respectively.

The reliability of the process and the results of the analysis were confirmed by checking the consistency between the observed value, $\Delta\nu_{1/2}$, and the calculated one, $\Delta\nu_{1/2}{}^C$. According to the steps:

$$\text{(i)}\quad a = \Delta\nu_L/[(\ln 2)^{-1/2}\Delta\nu_G],\quad \text{(ii)}\quad a \xrightarrow[\text{Table}]{\text{Posener's}} \omega,$$

$$\text{(iii)}\quad \Delta\nu_{1/2}{}^c = \Delta\nu_G\omega/(\ln 2)^{1/2},$$

the $\Delta\nu_{1/2}{}^C$ value was calculated from the $\Delta\nu_G$ and $\Delta\nu_L$ values by using the relationship between the a and ω parameters in the table[13] of the Voigt profile.

A Gaussian function was examined in order to check the error in the processes shown in Fig. 1. An excellent reproducibility of the line-shape parameters was obtained, as is shown in Table 1.

Results and Discussions

For all the chlorates, the S/N ratio of the observed spectrum was 10~20 even when using a slow sweep and a short time constant. An example is given in Fig. 2, in which the original spectrum and the true absorption line after smoothing and the base-line-drift correction are compared. The absorption line shapes of the four chlorates were almost symmetrical. The values of the first moment were smaller than ±0.1 kHz. The relative intensities of the chlorates of K and Ag were larger than those of Ba and Cu. The results of the measurement are summarized in Table 2. The full width between the half-maximum intensities ($\Delta\nu_{1/2}$), the full width between maximum slopes ($\Delta\nu_{msl}$), and second and fourth moments increase in the order (K, Ag), Ba, and Cu salts. The $\Delta\nu_L$ and $\Delta\nu_G$ values for each chlorate are also given in Table

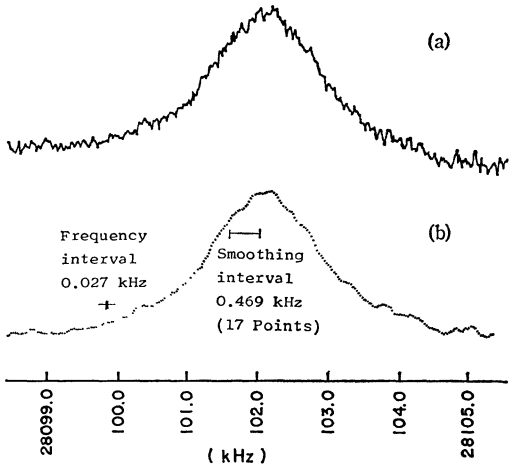

Fig. 2. (a) Observed resonance spectrum in $KClO_3$ (sweep rate 2 kHz/min, time constant 0.3 sec). (b) Spectrum after smoothing and base line correction.

Table 1. Reliability of the process of line shape analysis

Assumed function: Gaussian		Theoret	Calcd
$g(\nu)=g(\nu_0)\exp[-(\nu-\nu_0)^2\ln 2/(1/2\,\Delta\nu_{1/2})^2]$	ν_0	30000.000	30000.000_4
$\nu_0=30000.000$ kHz	M_0	2.1286	2.1289
$\Delta\nu_{1/2}=2.000$ kHz	M_2	0.721	0.720
$g(\nu_0)=1.000$	M_4	1.55	1·54
Data points 159	$g(\nu_0)$	1.000	1.000_1
Smoothing interval 0.85 kHz	$g(\nu_0+1/2\,\Delta\nu_{1/2})$	0.500	0.500_1
Differentiation interval 0.25 kHz	$g'(\nu_0+1/2\,\Delta\nu_{msl})$	0.7142	0.7113
	$\Delta\nu_{msl}$	1.698	1.70
	$\Delta\nu_G$	2.000	1.999_3
	$\Delta\nu_L$	0	0.000_7

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TABLE 2. SPECTRAL PARAMETERS OF OBSERVED LINES

	$KClO_3$	$AgClO_3$	$Ba(ClO_3)_2 \cdot H_2O$	$Cu(ClO_3)_2 \cdot 6H_2O$
T (K)	297	297	300	300
ν_0 (kHz)	28102.03±0.10	28847.93±0.10	29335.80±0.10	29118.58±0.10
$\Delta\nu_{1/2}$ (kHz)	1.66±0.10	2.00±0.10	2.80±0.10	3.29±0.10
$\Delta\nu_{msl}$ (kHz)	1.51±0.10	1.34±0.10	1.87±0.10	2.53±0.10
M_2 ((kHz)^2)	0.87±0.3	1.6 ±0.1	2.3 ±0.5	3.4 ±0.5
M_4 ((kHz)^4)	3±1	10±3	19±7	36±7
$\Delta\nu_L$ (kHz)	0.26±0.1	0.9 ±0.5	1.3 ±0.2	2.3 ±0.2
$\Delta\nu_G$ (kHz)	1.8 ±0.1	1.6 ±0.3	2.0 ±0.1	1.4 ±0.2
$\Delta\nu_{1/2}^C$ (kHz)	1.9	2.1	2.8	3.0
Number of experiments	4	6	4	3

TABLE 3. COMPARISON OF CHARACTERISTIC PARAMETERS

Parameters	Gaussian	Lorentzian	$KClO_3$	$AgClO_3$	$Ba(ClO_3)_2 \cdot H_2O$	$Cu(ClO_3)_2 \cdot 6H_2O$
$\Delta\nu_{1/2}/\Delta\nu_{msl}$	1.177	1.732	1.1	1.5	1.5	1.3
$g(\nu_0)/(g'_{max}\Delta\nu_{msl})$	0.824	1.333	0.63	0.86	0.84	0.92
$M_0/(g(\nu_0)\Delta\nu_{1/2})$	1.064	1.571	1.18	1.22	1.25	1.35
$M_0/(g'_{max}\Delta\nu_{msl})$	1.033	3.628	1.2	2.1	2.9	3.5
a	0	∞	0.12	0.47	0.51	1.32

2, together with the values of $\Delta\nu_{1/2}^C$. The excellent agreement between $\Delta\nu_{1/2}$ and $\Delta\nu_{1/2}^C$ indicates that the values of $\Delta\nu_L$ and $\Delta\nu_G$ for the four chlorates we obtained are reliable. Thus, it was found that each of the resonance lines of the four chlorates has an intermediate character between Gaussian and Lorentzian. In K salt, the line shape is close to Gaussian. On the other hand, a large amount of Lorentzian contributes to the line shape in Cu salt. Several spectral parameters are compared in Table 3, in which a relation similar to that seen in Table 2 is found.

The possible mechanisms of the line broadening are as follows: (1) quadrupole spin-lattice relaxation, (2) magnetic dipole-dipole interaction, and (3) field fluctuation due to the crystal strain. From (1) a Lorentzian shape would result, and from (2), a Gaussian, if there are many interacting neighbours. The line shape due to (3) depends on the nature of the strain. However, the second and the third mechanisms are assumed to give a single Gaussian shape. Koi[5] found that the main cause of the line-width of the $NaBrO_3$ crystal is the magnetic dipole interaction and that the contribution from the relaxation to the line-width is very small, since the ratio of the line-width for the ^{79}Br and ^{81}Br isotopes is equal to 0.94, agreeing closely with 0.928, the ratio of their magnetic dipole moments. Koi *et al.*[6] also reported that, in $KBrO_3$, the crystal strain is primarily responsible for the observed Br NQR line-width. Hashi[14] found that the free-induction-decay curve on Br NQR in $NaBrO_3$ has a Gaussian shape and that its decay time, T_2^*, is mostly determined by the distribution of the electric-field gradients in the crystal due to strain, imperfections, or temperature gradient. For $KClO_3$ and $AgClO_3$, the line shape we observed was almost Gaussian. The mechanism which contributes to the line-width is probably due to mechanism (2) and/or (3). Weber[15] observed that the free induction signals of the Zeeman components, the α and α' resonances, exhibit an increased decay lifetime relative to the lifetime in the zero-field resonance. It was found that the observed increase agrees with the predicted value obtained from the second moment, $\langle\Delta\nu^2\rangle = 0.0127$ (kHz)^2, due to the magnetic dipole interaction, calculated by the equations of Abragam and Kambe.[16] The observed second moment in $KClO_3$ was greater than the calculated one by one order of magnitude. A similar calculation of the second moment in $AgClO_3$ gave the value of $\langle\Delta\nu^2\rangle = 0.0058$ (kHz)^2. calculated by using the crystal parameters of $AgClO_3$[17] by means of NEAC 2230. In $AgClO_3$ as well as in $KClO_3$, the calculated second moment is considerably smaller than the observed one. Even the second moment expected from the value of $\Delta\nu_G$ does not agree with the calculated one. It can, therefore, be concluded that the mechanism which contributes to the $\Delta\nu_G$ values in $KClO_3$ and $AgClO_3$ might be mainly due to the random distribution of the electric-field gradient originating from the strain in the crystal. Using the crystal parameters of $Ba(ClO_3)_2 \cdot H_2O$,[18,19] we found that the line-width, $\Delta\nu_G$, corresponding to the calculated second moment, is 2.5 kHz and that it is mainly determined by the protons in the water of crystallization. In contrast to K and Ag salts, the rough agreement between the calculated line-width and the observed one indicates that the dominant effect on the Gaussian width in Ba salt is the magnetic

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dipole interaction between the chlorine nucleus and the proton. Although the crystal parameters are not known in $Cu(ClO_3)_2 \cdot 6H_2O$, it is considered that the observed line-width also originates from the dipolar interaction, as in the case of Ba salt, since many protons in the water of crystallization can give a broad line-width.

It is reasonable to consider that the Lorentzian width is attributable to the lifetime in the energy states of the nuclear spin system. A general theory of line shape was developed by Freed and Fraenkel[20] in terms of a relaxation matrix theory. They have shown that a composite line arising from a set of degenerate nuclear-spin states should, in general, consist of a sum of superimposed lines of the Lorentzian shape with different widths rather than a single line with an overall Lorentzian shape. However, as a limiting case, a single Lorentzian line is still obtained when the torsional oscillation in the crystal is represented a simple model in which, in am olecular frame, the by field gradient has a cylindrical symmetry around the oz axis (since the asymmetry parameter in chlorates has the value of almost zero, all the chlorates satisfy this condition); the motion of this frame is the rotation of oz by a small angle, θ, around a position of stable equilibrium, oZ, in a plane perpendicular to the axis, oX, of the laboratory frame. The time-dependent perturbation responsible for the broadening of the NQR line is thus given by:[21]

$$H_1(t) = A\left\{-\frac{1}{2}(\theta^2-\overline{\theta^2})[3I_z^2-I(I-1)] - \frac{3}{4}(\theta^2-\overline{\theta^2})(I_+^2+I_-^2) - 3\theta(I_zI_y+I_yI_z)\right\} \quad (1)$$

where $A=e^2qQ/4I(2I-1)$ However, it is easy to prove that, for half-integral spins, the two transitions, $m\rightarrow(m-1)$ and $-m\rightarrow-(m-1)$, are actually uncoupled, all the off-diagonal elements of the relaxation matrix being zero for the Hamiltonian $H_1(t)$. Each $m\rightarrow(m-1)$ transition is thus a simple line that has the shape of a single Lorentzian. For $I=3/2$, the line width, $1/T_2$, is expressed in terms of the spectral density functions of the random functions, $\theta^2(t)-\overline{\theta^2}$ and $\theta(t)$. The non-adiabatic terms in Eq. (1) also cause a spin-lattice relaxation, the decay time (or relaxation time, T_1) of which is expressed in terms of the same spectral density functions as in the case of T_2. In view of the fact that the quadrupole resonance frequency is small relative to the reciprocal of the correlation time for the random functions, the spectral density is assumed to be independent of the frequency. By using a damped oscillator model for the effect of the thermal bath, when the frequency distribution of the torsional oscillation is relatively sharp, the relation between the Lorentzian width, $1/T_2$, and the reciprocal of the spin-lattice relaxation time, $1/T_1$, is given by:[22]

$$1/T_2 = (7/2)(1/T_1) \quad (2)$$

In ionic crystals the additional relaxation due to crystal lattice vibrations should be considered. Chang[23] developed a general theory of quadrupole spin-lattice relaxation in solids based on the interaction of the quadrupole moment of the nucleus with the fluctuating crystalline electric-field gradient produced by thermal lattice vibrations of neighboring electronic charges. Although the theory was confirmed by the measurement[24] of the temperature dependence of T_1, Weber[15] found that the measurement of T_1 does not provide a critical test of the correctness of the model and that the Chang theory is inadequate for the ^{35}Cl relaxation in ClO_3^- groups, whereas the Bayer theory is consistent with the measurement of the individual transition probabilities corresponding to $\Delta m=\pm1$ and $\Delta m=\pm2$ by using a selective excitation experimental technique.

If the observed line-width for a Lorentzian component were determined by the torsional oscillation of the ClO_3^- ion in $KClO_3$, we might obtain the spin-lattice relaxation time, T_1, as about 4 msec, which is shorter by a factor of 1/5 than the reported value,[15] $T_1=21$ msec, at 300 K. It seems that the present c. w. experiment gives a much broader Lorentzian width than the one to be expected from the transient measurements. This discrepancy is probably due to the following factors: (1) A single mechanism of broadening, *i.e.*, the torsional motion, was considered. (2) Simple assumptions were used to derive Eq. (2), which was then used to obtain the line-width. (3) In the transient experiment, a large departure from the thermal equilibrium was achieved. On the other hand, the c. w. measurement was carried out without saturation. (4) The distribution of the electric-field gradient due to the strain and the imperfection in the crystal, which determine the major part of the line-width, was assumed to be Gsussian. In Ba salt, a similar discrepancy was obtained. We can not discuss Ag and Cu salts in detail because of the lack of the T_1 values. However, it should be noted that in Cu salt the superior component of the line shape is not Gaussian, but Lorentzian. If the Lorentzian width originates from spin-lattice relaxation due to the torsional oscillation of the ClO_3^- group, T_1 is found to be 0.5 msec, which is much shorter than that of $KClO_3$. This may be explained as follows. The relaxation mechanism due to torsional oscillation is mainly the transition process of $\Delta m=\pm2$, as is shown by the Bayer theory. When the temperature increases and the torsional frequency ν_t decreases, the $h\nu_t/kT$ factor becomes much smaller than unity and the transition probability corresponding to $\Delta m=\pm2$ becomes large. This situation is achieved when the anharmonicity of torsional oscillation can not be neglected;[9] from it the large temperature dependence of the torsional frequency of the ClO_3^- group has been found

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in Cu salt. Since the temperature at which the linewidth measurement was carried out is relatively close to the melting point, 65°C, a vigorous lattice motion can be expected. Thus, the transition probability or the spectral function corresponding to $\Delta m=\pm 2$ must have a large value, and a large lifetime broadening can thus be expected. More detailed discussions will be possible when the temperature dependence of the line shape is investigated experimentally.

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