A Chlorine NQR Study of Trichlorides of Group V Elements

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(Received June 19, 1970)

The NQR frequency of ^{35}Cl has been observed in polycrystalline PCl_3, $POCl_3$, $AsCl_3$, and $SbCl_3$ at 77°K and above. In all cases, the resonance frequency decreases at higher temperatures. The temperature coefficient of the resonance frequency is analyzed according to a modified Bayer-type treatment. A qualitative examination of the experimental results, including Robinson's results for $BiCl_3$ at 83 and 299°K, reveals that the strength of the intermolecular interactions in the solids of these trichlorides decreases in this order: $BiCl_3 > SbCl_3 > AsCl_3 > PCl_3$. The resonance was found to "fade-out" at temperatures below the melting point for the solids of PCl_3 and $POCl_3$, while the resonance was observed up to the melting point for the other compounds. The origin of this phenomenon is discussed.

As to the nuclear quadrupole resonance (NQR) of chlorine in trichlorides of the Group V elements, there have already been a number of investigations by several workers.[1-7] In the earlier studies, however, the measurements were made at only a few temperatures. Recently, though, Chihara *et al.*[8] measured almost continuously the NQR frequencies of chlorine and antimony in solid antimony trichloride in the range from 20°K to about 150°K.

The first theoretical elucidation of the temperature variation of resonance frequencies was given by Bayer,[9] who attributed the phenomenon to the influence of lattice vibration on the electric-field gradient tensor under a simple model with a one-dimensional torsional mode. This theory was later extended generally by Kushida[10] and Wang[4] separately. According to these treatments, the NQR frequencies are connected to the mean square amplitude of each normal vibration through both the electric-field gradient tensor and the asymmetry parameter. On the assumption that the mean energy of a normal mode is equal to that of the corresponding Planck oscillator, the resonance frequency may be said to be related explicitly to the temperature and the moment of inertia for the vibration concerned. Kushida *et al.*,[11] furthermore, discussed the dependence of the NQR frequency on the pressure as well as on the temperature.

In this investigation, the measurements of the NQR frequencies of ^{35}Cl in phosphorous, phosphoryl, arsenic, and antimony trichloride were carried out at 77°K and above at intervals of a few degrees. No reference to the temperature dependence of the NQR frequency of ^{35}Cl in phosphorous and phosphoryl trichloride has been found in previous works.

In all the compounds studied in this paper, the principal axes of the electric-field gradient tensor at a chlorine nucleus do not coincide with those of the moment of inertia of the molecule concerned. A treatment generalized for such a case is applied to the analysis of the temperature dependence of the NQR frequencies of ^{35}Cl in phosphorous trichloride. Some discussions of the torsional motions and the intermolecular interactions in the solid are given on the basis of the experimental results.

Experimental

The NQR frequencies of ^{35}Cl were measured with a super-regenerative spectrometer which was externally quenched and frequency-modulated.[12] For the frequency modulation, a 80 Hz sine wave was used. The quenching frequency was varied from 35 KHz to 70 KHz. The resonance frequencies were measured visually; that is, an NQR signal was compared directly on an oscilloscope screen with that from a standard frequency generator (National VP-828A), which was itself calibrated by means of a digital frequency counter (National VP-415 M). The accuracy of the frequency measurements is considered to be ±2 KHz.[13] Although the super-regenerative spectrometer used was not well suited for observing linewidths, the linewidths were estimated by recording the signals through a lock-in amplifier.

The resonance frequencies were measured at 77°K and above in liquid nitrogen and in various liquid baths. The temperature was determined by using two copper-constantan thermocouples, each in contact with the upper or the lower side of the sample tube. The accuracy of the temperature measurements may be considered to be better than ±1°K.[14]

Commercial compounds (Wako Pure Chemical Industries, Ltd.) were used without further purification. They were packed in glass tubes with an outside diameter of 18 mm.

Results

Phosphorous Trichloride. The resonance frequencies of ^{35}Cl due to two nonequivalent chlorine sites

1) R. Livingston, *Phys. Rev.*, **82**, 289 (1951).
2) H. G. Dehmelt and H. Krüger, *Z. Phys.*, **130**, 385 (1951).
3) R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).
4) T. C. Wang, *Phys. Rev.*, **99**, 566 (1955).
5) H. G. Robinson, *ibid.*, **100**, 1731 (1955).
6) S. Ogawa, *J. Phys. Soc. Jap.*, **13**, 168 (1958).
7) G. E. Peterson, Thesis, University of Pittsburgh, (1962).
8) H. Chihara, N. Nakamura, and H. Okuma, *J. Phys. Soc. Jap.*, **24**, 306 (1968).
9) H. Bayer, *Z. Phys.*, **130**, 227 (1951).
10) T. Kushida, *J. Sci. Hiroshima Univ.*, **A19**, 327 (1955).
11) T. Kushida, G. B. Benedek, and N. Bloembergen, *Phys. Rev.*, **104**, 1364 (1956).
12) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Solid State Physics, Suppl. 1, Academic Press, New York (1958), p. 90.
13) By comparing our measurements with those already reported, we estimated the accuracy of our frequency measurements.
14) In Ref. 8, Chihara *et al.* tabulated the resonance frequencies of ^{35}Cl in antimony trichloride in the low-temperature region (from 21.5°K to 178°K). By comparing our data with theirs, we deduced the accuracy of our temperature measurements.

(designated as ν_1 and ν_2) were measured at temperatures above 77°K. The signals could be observed up to about 165°K. Above this temperature, the resonance was found to fade out, while this compound melts at 179°K. The temperature dependences of ν_1 and ν_2 are shown in Fig. 1. The line-width of ν_2 was almost constant between 77°K and about 150°K. Above this temperature, though, the width increased rapidly.

Phosphoryl Trichloride. Although the compound melts at 272°K, two NQR signals (designated as ν_1 and ν_2) were found to fade out at temperatures above about 200°K. By immersing the sample in chlorobenzene bath (228°K), the NQR signals were searched for over the frequency region of 20 MHz to 33.5 MHz. No signals was found under these conditions. As is shown in Fig. 2, ν_1 and ν_2 decrease parallel with an increase in the temperature. The linewidth of the ν_2 was found to increase gradually as the temperature increased. The width at 187°K was about three times as large as that at 77°K.

Arsenic Trichloride. Three resonance frequencies of ^{35}Cl (designated as ν_α, ν_β, and ν_Γ) could be measured at temperatures between 77°K and the melting point of the compound (257°K). Their temperature dependences are shown in Fig. 3.

Antimony Trichloride. The resonance frequencies of ^{35}Cl due to two nonequivalent chlorine sites (designated as ν_1 and ν_2) could be measured up to the melting point of the compound (346°K). Our data were in good agreement with those of Chihara *et al.*[8] The linewidths of the ν_1 and ν_2 at 77°K were found to be almost equal to the corresponding values at room temperature.

Bismuth Trichloride. We could not observe the NQR signals of ^{35}Cl in this compound. The reason for our failure might perhaps be traced to the purity of the sample.

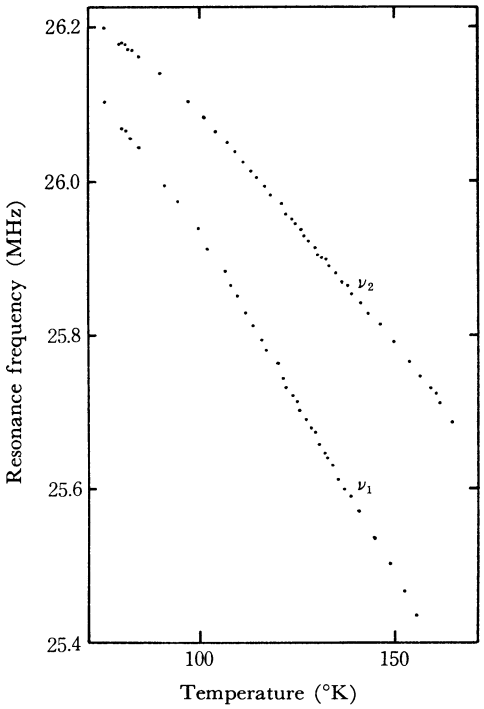

Fig. 1. Temperature dependence of ν_1 and ν_2 in PCl_3.

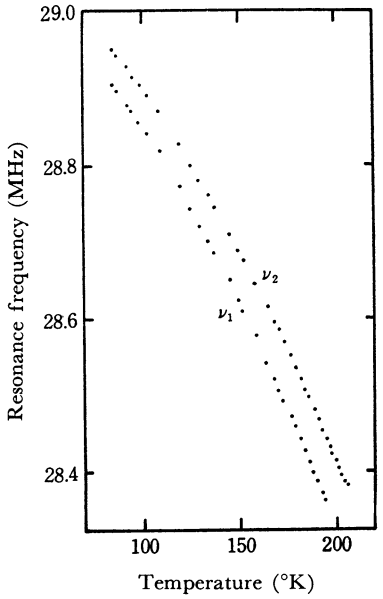

Fig. 2. Temperature dependence of ν_1 and ν_2 in $POCl_3$.

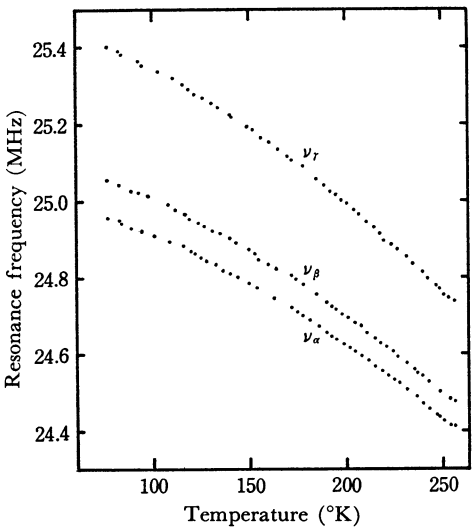

Fig. 3. Temperature dependence of ν_α, ν_β, and ν_Γ in $AsCl_3$.

Theoretical

When the principal axes of the field gradient (x, y, and z) coincide with the inertial axes (X, Y, and Z) around which the torsional motions may take place, the z component of the field gradient seen at a nucleus in the vibrating molecule (q) can be related to that in the static molecule (q_0) by Wang's expression;[15]

$$q = q_0\{1 - \tfrac{3}{2}(\langle\theta_X^2\rangle + \langle\theta_Y^2\rangle) + \tfrac{1}{2}\eta(\langle\theta_Y^2\rangle - \langle\theta_X^2\rangle)\}, \quad (1)^{16}$$

where $\langle\theta_i^2\rangle$ is the average square torsional displace-

15) T. C. Wang, *Phys. Rev.*, **99**, 566 (1955).

16) As has already been pointed out by Chihara *et al.* (Ref. 8), a slight correction must be made in the right-hand side of Wang's original expression.

Table 1. The frequency (ω_i) and the mean square amplitude ($\langle\theta_i^2\rangle$) of the torsional motion in phosphorous trichloride

T (°K)	ω_1	ω_2 (cm^{-1})	ω_3	$\langle\theta_1^2\rangle$	$\langle\theta_2^2\rangle$ (10^{-3} rad^2)	$\langle\theta_3^2\rangle$
93	57±7	29±1	39±5	3.8±1.9	13.6±1.0	4.5±1.0
143	50±6	27±1	35±5	7.5±1.7	24·5±1.0	8.4±2.3

ment about an axis, i, and η, the asymmetry parameter. This expression can not be applied immediately to the analysis of the field gradient at the chlorine nucleus in an MCl_3 molecule in the absence of the coincidence between the principal axes of the field gradient and inertial axes. Therefore, one must modify Eq. (1) to obtain an expression valid for such a situation.[17]

Now, let q' represent the field gradient at the chlorine nucleus along an M–Cl bond direction (designated as the z axis of the field-gradient tensor) in an MCl_3 molecule. For the sake of simplisity, the field gradient is assumed to be axially symmetric (*i.e.*, $\eta=0$) and the symmetry of the MCl_3 molecule is assumed to be C_{3v}. As the principal axes of the moment of inertia, we take the system of axes (X_1, X_2, and X_3) shown in Fig. 4, in which the X_3 axis is chosen perpendicular to the plane of three chlorine atoms, and the X_2 axis, parallel with the Cl(2)–Cl(2) direction.

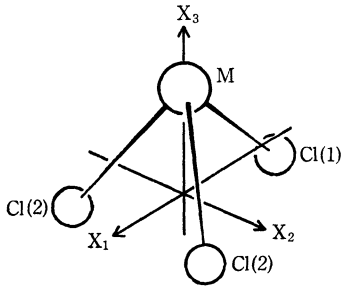

Fig. 4. The orientation of the coordinate system in the MCl_3 molecule.

A torsional motion around an X_i axis makes the z axis fluctuate by an angle of $c_i\theta_i$, where θ_i is a torsional displacement around the X_i axis, and c_i, a constant specified by the molecular geometry. As a first-order approximation, the total effect of the torsional motions around three inertial axes (X_i) on the field gradient at a chlorine nucleus may be written as follows:

$$q' = q_0'\{1 - 3/2 \sum_i \sin^2 \alpha_i \langle\theta_i^2\rangle\}, \quad (2)$$

where α_i is the angle between X_i and the z axis. Hence, the temperature-dependent frequency (ν') is related to the frequency of the stationary molecule (ν_0') by:

$$\nu' = \nu_0'\{1 - 3/2 \sum_i \sin^2 \alpha_i \langle\theta_i^2\rangle\}. \quad (3)$$

If the torsional motion is approximated by a quantum mechanical harmonic oscillator, the mean square displacement ($<\theta_i^2>$) is;

$$\langle\theta_i^2\rangle = \hbar/A_i\omega_i[1/2 + 1/\{\exp(\hbar\omega_i/kT) - 1\}], \quad (4)$$

where ω_i is the torsional frequency, and A_i, the moment of inertia associated with the torsional motion about the X_i axis.

The asymmetry parameter of the field gradient at a chlorine nucleus in $SbCl_3$ was found to be large,[18] and that in $BiCl_3$ seems likely to be large because of a strong intermolecular bond formation to be discussed later. In $AsCl_3$ there are three kinds of resonance frequencies; this make it difficult to regard the symmetry of the molecule as trigonal. Therefore, the assumptions included in the derivation of Eq. (2) or (3) are not valid for the cases of $SbCl_3$, $BiCl_3$, and $AsCl_3$ because of the large asymmetry parameter or the destruction of the trigonal symmetry. Since, however, as will be discussed later, the inter-molecular interactions in the solid of PCl_3 seem to be quite weak, the assumptions mentioned above may be valid for the case of this molecule.

The results of the analysis of the temperature dependence of ν_1 and ν_2 in PCl_3 according to Eqs. (3) and (4) are shown in Table 1. Unfortunately, we could not determine all the parameters definitely, although their values are considered to be reasonable.

Discussion

Although the crystal structure of the compounds studied in this work are, for the most part, unknown, here, we shall attempt a qualitative discussion of the intermolecular interactions in their crystals.

Two or three resonance frequencies are observed in each compound studied. The separation ($\Delta\nu$) between the multiple lines in each compound is shown in Table 2. According to Robinson's results,[5] the separation ($\Delta\nu$)

Table 2. The frequency separation ($\Delta\nu$) between non-equivalent sites in MCl_3 molecules at 77°K

Compound	$\Delta\nu$ (MHz)
$POCl_3$	0.05
PCl_3	0.10
$AsCl_3$	0.40[a]
$SbCl_3$	1.61
$BiCl_3$	3.68[b]

a) A separation between the highest resonance frequency and the mean of the lower two.
b) See Ref. 5.

17) I. Tatsuzaki and Y. Yokozawa, *J. Phys. Soc. Jap.*, **12**, 802 (1957).

18) T. Okuda, A. Nakao, M. Shiroyama, and H. Negita, This Bulletin, **41**, 61 (1968).

found for $BiCl_3$ is about 3.68 MHz at 83°K. A less drastic splitting occurs in $SbCl_3$. The separation ($\Delta\nu$) found for this compound is about 1.61 MHz at 77°K. Allen[19] pointed out that splittings greater than 0.5 MHz must be attributed to a different type of chemical bonding to the chlorine atoms. In fact, Peterson,[7] in his X-ray study of $SbCl_3$, found that one of the Sb–Cl bond lengths within a molecule is 2.30 Å, and the other two, 2.325 Å. Futhermore, the two nearest intermolecular Sb–Cl distances are 3.41 Å, which is smaller than the van der Waals distance (4 Å). Chihara *et al.* reasonably explained both the large separation ($\Delta\nu$) and the difference in the temperature dependence of the two lines of $SbCl_3$ in terms of this intermolecular-bond formation. That is, the intermolecular-bond formation mentioned above diminishes the electron density of the p_x or p_y orbitals of chlorine atoms participating in the bond formation and, therefore, their resonance frequencies. The decreases in this electron density and the resonance frequency due to the intermolecular-bond formation are proportional to the degree of the intermolecular overlap, which should tend to decrease as the molecular librations increase in amplitude at higher temperatures. The direct temperature effect, which tends to decrease the resonance frequency at higher temperatures, counteracts the above effect; their compromise determines the actual temperature coefficient of the resonance frequency.

If the formation of intermolecular covalent bonds similar to that found in $SbCl_3$ is possible in the crystal of $BiCl_3$, it accounts for the large separation ($\Delta\nu$) and the positive temperature coefficient found for $BiCl_3$. Both the fact that the separation ($\Delta\nu$) of $BiCl_3$ is considerably larger than that of $SbCl_3$ and the fact that one of the two lines in $BiCl_3$ exhibits a positive temperature coefficient suggest that the strength of the intermolecular covalent bonds in $BiCl_3$ is stronger than that in $SbCl_3$.

Because of the intermolecular interactions, the quadrupole coupling constant (eQq) of the solid determined from the pure quadrupole spectra may differ as much as 10% from that of gas determined from the hyperfine structure of the rotational spectra in the microwave region. Comparisons between the eQq values of PCl_3 and $POCl_3$ in the gaseous and solid states are given in Table 3, together with the values of some other molecules.

TABLE 3. COMPARISON OF eQq IN GAS AND SOLID

Compound	eQq gas (MHz)	eQq solid (MHz)	r(gas/solid)	Ref.
PCl_3	53.3	52.40	1.017	20
$POCl_3$	55.4	57.97	0.955	20
CH_3Cl	75.13	68.40	1.098	19
CH_2Cl_2	78.3	72.42	1.081	19
CF_3Cl	78.05	77.58	1.006	19

19) H. C. Allen Jr., *J. Phys. Chem.*, **57**, 501 (1953).
20) C. R. Nave, T. L. Weatherly, and Q. Williams, *J. Chem. Phys.*, **49**, 1413 (1968).

Since the difference in the eQq values in Table 3 and the $\Delta\nu$ values in Table 2 are rather small for PCl_3 and $POCl_3$, the intermolecular interactions in their solid states are considered to be weak.

The three M-Cl bonds within an MCl_3 molecule may be equivalent in its gaseous state, while in its solid state the intermolecular interactions destroy the equivalence. Therefore, the separation ($\Delta\nu$) between multiple lines may be a measure of the intermolecular interactions. In general, the melting point of a crystal reflects the degree of the intermolecular interactions. The relation between the melting point and the $\Delta\nu$ among these trichlorides is shown in Fig. 5. An expected correlation between them is found;

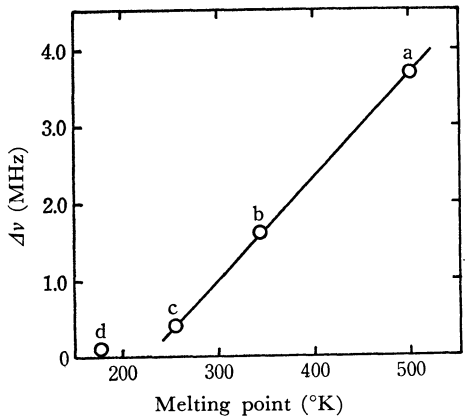

Fig. 5. Melting point versus $\Delta\nu$ plots: (a), $BiCl_3$; (b), $SbCl_3$; (c), $AsCl_3$; (d), PCl_3.

this indicates that the strength of the intermolecular interactions decreases in this order: $BiCl_3 > SbCl_3 > AsCl_3 > PCl_3$.

As the strength of the intermolecular interactions becomes weaker, the magnitude of the mean-square amplitudes ($<\theta_i^2>$) increases; consequently, the absolute values of their temperature coefficients ($|d<\theta_i^2>/dT|$) may be expected to increase. Furthermore, it may

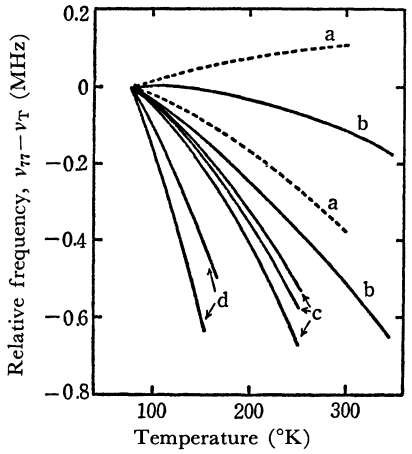

Fig. 6. Relative frequency (difference between the resonance frequency at 77°K (ν_{77}) and that at higher temperature (ν_T)) of ^{35}Cl in MCl_3 molecule as a function of temperature: (a), $BiCl_3$ (Estimated from the data at 83° and 299°K reported by Robinson.); (b), $SbCl_3$; (c), $AsCl_3$; (d), PCl_3.

be seen from Eqs. (1) and (2) that the absolute value of the temperature coefficient of the resonance frequency ($|d\nu/dT|$) is proportional [to that of the mean-square amplitudes ($|d<\theta_i^2>/dT|$). Therefore, if the strengths of intermolecular interactions are assumed to become weaker from material to material in this order: $BiCl_3>SbCl_3>AsCl_3>PCl_3$, it seems reasonable that the absolute values of the mean temperature coefficient of the resonance frequency of chlorine in the MCl_3 molecule increase in this order: $PCl_3>AsCl_3>SbCl_3>BiCl_3$, as may be seen from Fig. 6.

A fade-out phenomenon analogous to that found for PCl_3 and $POCl_3$ has been observed for some other solids[21-23] which had phase transitions associated with internal or molecular reorientations in the solids. From the fact that the fade-out apparently occurred only in a solid where internal or molecular rotation was either definitely known to occur or was very likely, it had been considered that such motions were responsible for the fade-out.[22] Although no reference to such motions in the solids of PCl_3 and $POCl_3$ has been found in previous works, the fade-out found for them may be due to molecular rotation, which is expected to occur as a result of the weak intermolecular interactions. One of the mean-square amplitues of torsional motions found for the solid PCl_3 is about 13.6×10^{-3} rad^2 at 93°K. According to Chihara *et al.*,[8] that of the solid $SbCl_3$ is about 10×10^{-3} rad^2 at the same temperature. This indicates a rather high degree of torsional motion in solid PCl_3 at lower temperatures.

Structual information on the solid triiodides of the Group V elements is available.[24] From a structural point of view, it is impossible to regard the solid of the triiodide of arsenic, antimony, or bismuth as a molecular crystal; this is because of a layer-structure formed by the sharing of the edges of the MI_6 octahedra. On the other hand, in the solid of PI_3 the existence of the intermolecular bonds is not expected from its crystal structure. It is not unreasonable to consider that this trend in the triiodide series occurs also in the trichloride series. This confirms the above conclusion that, in the solid of PCl_3, the strength of the intermolecular forces is quite weak, whereas Lucken[25] estimated that the phosphorous trichloride was isomorphous with the antimony trichloride, in which the strong intermolecular forces exist. If $BiCl_3$ crystalizes with the BiI_3 structure, it is difficult to explain the large separation ($\Delta\nu$) found for $BiCl_3$, because in the BiI_3 structure all the metal-halogen bonds are expected to be equivalent. Therefore, it is tempting to conclude from the similarity of the resonance spectra and their temperature dependence that $BiCl_3$ and $SbCl_3$ are isostructural with each other.

The authors wish to express their thanks to Professor Mikio Takeyama and Dr. Yoshio Kamishina for their valuable discussions and suggestions on the fabrication of the equipment. One of the authors (M.H.) also wishes to Professor Ryôiti Kiriyama for his continual encouragement and interest.

21) H. C. Allen, Jr., *J. Amer. Chem. Soc.*, **74**, 6074 (1952).
22) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **32**, 548 (1960).
23) H. C. Meal and H. C. Allen, Jr., *Phys. Rev.*, **90**, 348 (1953).
24) R. W. G. Wyckoff, "Crystal Structures", **2**, Chap. VB.
25) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants", Academic Press, New York (1969), p. 274.