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Nuclear Quadrupole Resonance in Studies on Molecular Compounds

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The review describes and gives a systematic account of data on the application of the nuclear quadrupole resonance method in studies on donor-acceptor complexes. Particular attention is paid to factors responsible for the changes in the principal parameters of nuclear quadrupole resonance spectra.
The bibliography includes 87 references.

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I. INTRODUCTION

The formation of a donor–acceptor bond between two valence-saturated molecules can be regarded as the result of charge transfer from the donor to the acceptor molecule [1]. The transfer of an electron from a higher, as regards energy, occupied molecular orbital (MO) of the donor to a lower vacant molecular orbital of the acceptor is accompanied by a change in electron distribution and a corresponding change in the electric field gradient at a particular atomic nucleus of the complex. Therefore the nuclear quadrupole resonance (NQR) method is very effective in studies on molecular compounds. Its application is interesting also because the field gradient is significantly influenced by various steric factors, in addition to the charge distribution in the molecule. Starting in 1953, when the first two NQR spectra of donor–acceptor complexes were published [2], the number of publications on charge-transfer complexes has steadily increased every year. However, very frequently quadrupole resonance data are non-systematic and their interpretation very contradictory.

Since in the vast majority of studies the effect of complex formation on the quadrupole spectrum of the acceptor was investigated, the type of the acceptor served as a basis for the subdivision of the available data into different sections. The type of the acceptor is determined by the type of the orbital to which the electron is transferred: for π-acceptors it is the π-electron system of aromatic and unsaturated compounds, for σ-acceptors (I_2, ICl, RX, etc.) it is a σ-molecular orbital (usually antibonding), and for ν-acceptors (metal halides, organometallic compounds) it is a vacant orbital of the central atom. In the discussion of the experimental data much attention has been devoted to the analysis of those spectra which had not been fully analysed from the standpoint of chemical structure in the original papers.

The review is not concerned with problems of self-association and intramolecular coordination since the same molecule then behaves simultaneously as the donor and the acceptor. Nor are data included on the quadrupole splittings of the NMR spectra of deuterium in hydrogen bonds. A review on this topic has been recently published [3].

2. THE NUCLEAR QUADRUPOLE RESONANCE METHOD

Nuclei with spin $I \geqslant 1$ typically have a non-spherical distribution of the positive nuclear charge. A measure of the deviation from the spherical distribution is the nuclear quadrupole moment Q. The quadrupole moment is positive when the charge ellipsoid is extended in the direction of the spin and negative when the ellipsoid is compressed in this direction. In the interaction between the quadrupolar nucleus and an inhomogeneous electric field due to the electrons surrounding it, there arise energy levels associated with definite orientations of the nucleus relative to the principal axes of the tensor of the electric field gradient. Thus the difference between the levels and hence the frequency of the transition depend on the quadrupole moment of the nucleus and the electric field gradient q. The frequencies of the transitions between the levels corresponding to different orientations of the nuclear spin lie in the radiofrequency range.

These transition frequencies are a source of information about the electronic structure of the molecules. With a suitable choice of the system of coordinates, the field gradient tensor q is defined by three components:

$$q_{xx} = \frac{\partial^2 V}{\partial x^2}, \quad q_{yy} = \frac{\partial^2 V}{\partial y^2}, \quad q_{zz} = \frac{\partial^2 V}{\partial z^2}.$$

It is assumed that q_{ZZ} is the largest component and q_{XX} the smallest. All three components are related by the Laplace equation

$$q_{xx} + q_{yy} + q_{zz} = 0. \qquad (1)$$

For an axially symetrical field ($q_{XX} = q_{YY}$), the energy levels are given by the simple expression

$$E_m = \frac{eQq_{zz}}{4I(2I-1)}[3m^2 - I(I+1)], \qquad (2)$$

where $m = I, I-1, \ldots, -I+1, -I$ is the magnetic quantum number of the nucleus and characterises the orientation of the spin in the external field. Since the square of m appears in the equation, the energy levels (with the exception of $m = 0$ for integral spins) are doubly degenerate. The selection rule for transitions between levels

is of the type $\Delta m = \pm 1$ and the transition frequency is given by

$$\nu_{m+1,m} = \frac{3eQq_{zz}}{4I(2I-1)} \frac{2|m|+1}{h}. \quad (3)$$

The quantity eQq_{ZZ}/h (or eQq_{ZZ} in frequency units, usually MHz) is called the quadrupole interaction constant.

On the other hand, when there is no axial symetry, i.e. $q_{XX} \neq q_{YY}$, the expressions for the energies become more complex and include an asymmetry parameter $\eta = |q_{ZZ} - q_{YY}|/q_{ZZ}$. For example, for nuclei with $I = 3/2$,

$$E_{\pm 1/2} = \frac{eQq_{zz}}{4}\left(1 + \frac{\eta^2}{3}\right)^{1/2}, \quad (4)$$

$$E_{\pm 3/2} = -\frac{eQq_{zz}}{4}\left(1 + \frac{\eta^2}{3}\right)^{1/2}. \quad (5)$$

The frequency of the corresponding transition,

$$\nu = \frac{eQq_{zz}}{2}\left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad (6)$$

depends simultaneously on two parameters: eQq_{ZZ} and η. When η has not been determined by the Zeeman effect, a certain indeterminacy appears in the interpretation of data on the quadrupole resonance of the nuclei. For halogen atoms $\eta < 0.2$, which gives rise to only slight changes in frequency. For this reason, it is assumed that η for halogens is either zero or has a definite value, adopted on the basis of structural data. For the majority of other quadrupole nuclei, at least two frequencies are observed in the spectra, from which it is possible to calculate both eQq_{ZZ} and η. Evidently there must be a fully defined relation between these two parameters and the electronic structure of the molecule.

The charge e at a distance r from the nucleus gives rise to a field gradient at the latter:

$$q_{zz} = e\frac{3\cos^2\theta - 1}{r^3}, \quad (7)$$

where θ is the angle between the direction of the radius vector $\bar{r}$ and the z axis. For an electron in an atom, the field gradient depends on the symmetry of its orbital ψ:

$$q_{zz} = e\int \psi^2 \frac{3\cos^2\theta - 1}{r^3} dv, \quad (8)$$

where dv is a volume element.

Since the s orbital is spherically symetrical, its electrons do not contribute to the field gradient at the nucleus. For the same reason, the field gradient due to filled electron shells is zero. The contributions to the gradient by d and f electrons are insignificant for transition elements, and are in most cases neglected. The principal contribution to the field gradients comes from the p electrons of the valence shells. If the gradient due to one p_Z electron is denoted by q_0 (or q_{at}), then, according to Eqn. (1), we have for an axially symetrical field

$$q_{xx} = q_{yy} = -\frac{1}{2}q_{at}, \quad (9)$$

i.e. the contribution to the field gradient by p_X and p_Y electrons is smaller by a factor of 2 than the contribution by p_Z electrons.

In an examination of the changes in the field gradient of an atom in a chemical bond, it is extremely convenient to estimate the gradient in terms of the population N of the p states (here the z axis coincides with the direction of the σ bond):

$$q_{zz} = \left(\frac{N_x + N_y}{2} - N_z\right)q_{at} = U_p q_{at} \quad (10)$$

The quantity U_p denotes "the number of non-balanced p electrons". The quantity q_{at} is usually determined from atomic spectra or by the atomic beam method. When the gradients are replaced by quadrupole interaction constants, Eqn. (10) can be written in the form

$$eQq_{zz} = U_p(eQq)_{at}. \quad (11)$$

Examination of the free chlorine atom as an example shows that two unshared pairs of its p electrons yield $N_X = N_Y = 2$ and the valence electron gives $N_Z = 1$. Then, according to Eqns. (10) and (11), $eQq_{ZZ} = eQq_{at}$. The chlorine atom in chemical compounds, usually the more electronegative species, attracts an additional charge. Then $N_Z = 1 + i$ (i is the degree of ionic character of the bond) and $eQq_{ZZ} = (1 - i)eQq_{at}$. In sp-hybridisation the contribution to the field gradient by the electron in the p_Z orbital diminishes $(1 + i)s$ owing to its partial s character. However, $3s^2$ electrons acquire a certain porportion of p_Z character and make a contribution $2s$ to the field gradient. As a result, the gradient diminishes and

$$eQq_{zz} = (1-i)(1-s)eQq_{at}. \quad (12)$$

In aromatic and unsaturated compounds the participation of one of the unshared pairs of p electrons in the conjugation system entails a decrease of the p_X or p_Y electron density at the chlorine atom and a corresponding decrease of the quadrupole interaction constant:

$$eQq_{zz} = [(1-i)(1-s) - \pi]eQq_{at}. \quad (13)$$

Eqn. (13) shows that the field gradient in the molecule depends on three parameters: i, s, and π. This gives rise to some indeterminacy in the interpretation of the NQR spectra. In many cases a knowledge of the asymmetry parameter may help significantly. By definition, $\eta = |q_{XX} - q_{YY}|/q_{ZZ}$ is a direct measure of the difference between the populations of the p_X and p_Y orbitals. Therefore the asymmetry parameter may provide information about the double bond character. Quite often it is possible to estimate some of these three parameters from structural considerations or results obtained by other methods. Usually however, as with many other techniques, the relevant information is obtained by comparing the data within the limits of a single series or several series of compounds.

Measurements of quadrupole spectra are possible only for substances in the solid state, since in the gas or liquid molecular rotation averages out the field gradient and there is no splitting of quadrupole levels. Therefore the interpretation of the data may be somewhat complicated by the influence of the crystal lattice. However, similar difficulties are usually encountered also in studies by other methods (the solvent effect, etc.). It has been shown [4] that the effect of the crystal lattice does not as a rule exceed 2% of the measured frequency, while for a series of compounds with similar structures the standard deviation is about 0.3%.

In a description of the method as a whole one must emphasise particularly its high sensitivity to changes in the structural parameters of the molecules. A more detailed description of the essential features of the method and its applications can be found in a number of monographs and reviews [5-9].

3. FREQUENCY SHIFTS AND THE SPLITTING OF THE NUCLEAR QUADRUPOLE RESONANCE SPECTRA OF CHARGE-TRANSFER COMPLEXES

As mentioned above, the formation of a donor–acceptor type of complex is due to a partial charge transfer from

the donor to the acceptor molecule. The charge transferred, the distribution corresponding to it, and the accompanying changes in the electronic structure of the interacting molecules, give rise to fairly significant changes in the field gradient at each atom of the complex.

Furthermore, new steric interactions may arise and those existing previously may change on complex formation, which naturally entails additional changes in the field gradient. The indeterminacy introduced by the crystal field is of course still present. The combination of all these factors can give rise to a very complicated pattern of NQR spectroscopic effects associated with complex formation. Therefore it is useful to carry out a preliminary analysis of the effects of the individual factors and to determine under what conditions each of them operates and what role it plays.

We shall examine the role of charge transfer or the electronic factor. The wave function of the ground state of the complex D.A can be represented as follows [1,10]:

$$\psi_N = a\psi_0(D \cdot A) + b_1\psi_1(D^+A^-). \quad (14)$$

Using this approximation, relations have been obtained [11] between the changes in the field gradient Δq_{zz}, on the one hand, and the degree of charge transfer b^2 and its density c^2 at the given atom, on the other:

$$\Delta q_A = \frac{b^2}{1+S^2}\sum_t c_{At}^2 q_t \text{ for the acceptor} \quad (15)$$

$$\Delta q_D = -\left(1 - a^2 + \frac{b^2S^2}{1+S^2}\right)\sum_r c_{Dr}^2 q_r \text{ for the donor} \quad (16)$$

where S is the overlap integral of the interacting molecular orbitals and t the atomic orbital of the atom investigated, participating in the formation of the donor–acceptor bond. We may recall that $q_S = 0$, $q_{p_Z} = q_{at}$, $q_{p_X} = q_{p_Y} = -q_{at}/2$ and the quantities q_d and q_f may be neglected. We shall now consider the application of Eqn. (15) to acceptors of various types (σ, π, v). For simplicity, we shall for the moment confine ourselves to halogen-containing molecules. In the first place, Eqn. (15) shows that the change in the gradient as a result of charge transfer is directly proportional to the degree of charge transfer b^2. The direction of the shift may be predicted beforehand even without calculating the electron distribution. For σ acceptors (I_2, ICl, CCl_4, $CHCl_3$, etc.), an increase of the σ-electron density of the molecule is accompanied by an increase of the population of the p_Z orbital of the halogen and consequently a decrease of the field gradient. In the simplest case of a diatomic σ acceptor (I_2, ICl, IBr, etc.) Eqn. (15) yields a simple expression for the relative change in the field gradient or, putting $\eta = 0$ in Eqn. (6), the relative frequency shift:

$$\frac{\Delta q_{zz}}{q_{zz}} = \frac{\Delta\nu}{\nu} = -\frac{b^2}{2(1+S^2)}. \quad (17)$$

For π acceptors (chloranil, picryl chloride, etc.) charge transfer to the π orbital increases the population of the p_X orbital of the halogen atom, which increases its field gradient. Since $q_{p_X} = -q_{at}/2$, we find, after substituting Eqn. (15) in Eqn. (13), that the field gradient at the halogen atom of the acceptor molecule increases as a result of charge transfer by an amount

$$\Delta q_{zz} = \frac{b^2}{2}c_A^2 q_{at}. \quad (18)$$

The subscript t may be omitted, since the p_X orbital is non-hybridised.

As already stated, the p-electron density is closely linked to the asymmetry parameter η. Then the degree of charge transfer can be related, to an adequate degree of approximation, to the change in the asymmetry parameter $\Delta\eta$ by the expression [12]:

$$\Delta\eta = -b^2c_A^2. \quad (19)$$

Eqns. (18) and (19) yield a direct relation between the changes in the characteristics of the NQR spectra and the degree of charge transfer for π acceptors. The corresponding relations for σ and π donors have been given by one of the present authors [12].

The analysis of the shifts is more complex for v acceptors. The formation of complexes by v acceptors involves in the vast majority of cases a complete rearrangement of the entire electron system of the molecule and the appearance of one or several additional vacant orbitals. The rearrangement of molecular geometry naturally involves changes in the M–X bond parameters (amount of ionic character, double bond character, etc.). Therefore, exception in certain cases, a detailed analysis of the change in the field gradient is possible only on the basis of a detailed calculation for each specific complex. The entire process may be represented approximately as consisting of two stages: direct rearrangement of the acceptor molecule MX_n and charge transfer to the vacant orbital produced, in accordance with the distribution of the charge. One can assume with reasonable certainty that, within the limits of a restricted range of complexes of the same acceptor with different donors, the change in electron distribution solely due to the rearrangement of the electron system will be approximately the same for all the complexes. Then the variation from complex to complex within the limits of this series can be fully attributed to the differences in the degree of charge transfer. An increase in the degree of charge transfer will favour an increase in electron density in the σ system of the acceptor and hence a decrease of the field gradient at the atoms X. This is the qualitative aspect of the problem. On the other hand, as already stated, the quantitative relation between the quadrupole shift and charge transfer can be revealed only by detailed calculations. However, one may suppose that this relation is fairly complicated. Sometimes, the valence bond method may be used to analyse the NQR spectra of complexes having similar compositions and structures, particularly when there is a possibility of observing the NQR spectra not only due to X atoms but also due to the central atom.

In the molecule of an n donor the coordination due to the unshared electron pair causes a shift of electron density towards the atom involved in the formation of the dative bond. When the group R contains a halogen atom X, this shift is accompanied by decrease of the ionic character of the C–X bond, which in turn leads to a high-frequency shift of the NQR spectrum of the halogen.

Thus in the general case the direction of the NQR frequency shift due to the electronic factor for both donors and acceptors is determined by the orbital involved in complex formation. On the other hand, the magnitude of the shift depends on the degree of charge transfer and the nature of charge distribution.

We shall consider how steric factors affect NQR spectra. On formation of a complex, the coordinating centres of the interacting molecules can approach one another to within distances ranging from the sum of the van der Waals radii (weak complexes) to the sum of the covalent radii (stable complexes). Both the structure of the interacting molecules themselves and their relative positions in the

complex play a major role in the spectroscopic effects of complex formation [12,13]. The effect of steric factors can be ultimately divided into three types. Firstly, steric factors can prevent the mutual approach of the donor and acceptor molecules, restricting the possibility of charge transfer. Then, even when the donor has pronounced dative properties, the degree of charge transfer may be slight. This means that in this case steric factors affect electronic factors, whose relation to the field gradient has already been examined. Secondly, steric interactions can distort the geometrical structure of the molecules: they may cause changes in bond length, distort the valence angles, etc. There will be corresponding changes also in the field gradient of the atoms. Thirdly, steric effects can lead to the deformation of the electron shells of the atoms investigated due to polarisation. The last two factors are not related to the degree of charge transfer and are of independent importance. The combination of all three factors can alter significantly from complex to complex even within the limits of the same series. For this reason, their effect on the field gradient is specific for each concrete case.

Thus the change in field gradient as a result of complex formation is determined by two principal factors: electronic effects and steric interactions. On the other hand, both factors affect one another and, on the other, they compete with one another. It may be supposed that, depending on the intensity of the donor–acceptor interaction, the electronic factor will predominate in the NQR spectra of the stable complexes and the geometrical factor will predominate in those of weak complexes. The influence of the combination of the two factors leads to a very complex pattern of spectroscopic shifts which must be duly taken into account in the analysis of the NQR data.

Apart from the frequency shift, an important characteristic of the NQR spectra is their multiplicity. When the molecule contains several identical atoms with quadrupole nuclei, their frequencies may be expected to be different. Such splitting of the spectrum can be caused by differences in the electronic state of the atoms (chemical non-equivalence), steric effects, and the effect of the crystal field. The splitting due to crystal field effects is as a rule within the limits of the usual 2% range, while the splitting due to the chemical non-equivalence can be very considerable, depending on the type of electron distribution in the molecule.

This makes it possible, on the one hand, to predict the nature of the splitting in the spectrum of a complex from its electron distribution and, on the other hand, to draw conclusions from the type of splitting concerning the geometrical and electronic structure of the complex. An approximate analysis of this type has been made [12,14] for the octahedral *cis*- and *trans*-complexes $MX_4.2D$ (where X = halogen) (Fig. 1). Using molecular orbitals of symmetry O_h, the authors showed that in the *trans*-complexes all four halogen atoms have the same σ-electron density and are chemically equivalent. Therefore the splitting in the NQR spectra of the octahedral *trans*-complexes is possible only owing to the crystal field effects. Fig. 1*a* shows the hypothetical form of the spectrum of such a complex. Analogous calculation for the *cis*-complex shows that the σ-electron density for the two positions of the halogen atom (equatorial and axial) is different. Therefore considerable splitting, due to the chemical non-equivalence of these positions, should be observed in the NQR spectra of such complexes (Fig. 1*b*). Yet another interesting consequence of this calculation is noteworthy, namely that, for the same degree of charge transfer, the average shift of the NQR spectrum of the halogen in the *cis*- and *trans*-complexes is different. This must be taken into account in a comparison of the properties of donors (treated as bases) in complexes of different structures. In the simplest case the type of splitting in the spectra due to chemical non-equivalence can be determined with the aid of the symmetry properties of the complex. In symmetry operations the molecular orbitals of the complex are transformed in accordance with the irreducible representations of its point group. Therefore in symmetry operations chemically equivalent atoms will be interchanged. Hence it is not difficult to determine the number of non-equivalent positions of the halogen atom.

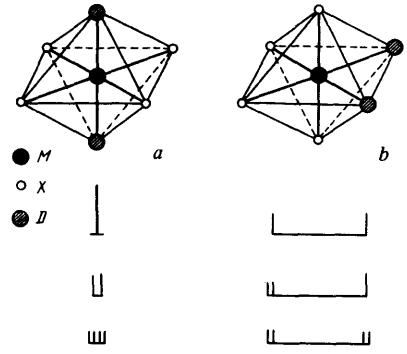


Figure 1. Schematic representation of the splitting in the NQR spectra of the octahedral complexes $MX_4.2D$: *a*) *trans*-structure; *b*) *cis*-structure.

In an analysis of the splitting in the spectra particular attention must be paid to the effect of steric factors. The role of the deformation of the angles and bonds in spectral splitting can be so marked that its importance in some cases can approach or even exceed that of chemical non-equivalence. However, as for the frequency shifts, the effect of steric factors on the splitting is highly specific for each concrete case.

4. π-ACCEPTOR COMPLEXES

Among π acceptors, the NQR method was used to study the complexes of polyhalogenobenzenes [13,15], chloranil [15,16], and picryl chloride [12,17,18]. The studies were based only on chlorine-35 frequencies.

Charge transfer in complexes of this type increases the electron density in the π system of the acceptor and consequently the spectroscopic shift should occur at high frequencies. The degree of charge transfer in the π complexes is slight and usually lies in the range 1–6%. [19] For this reason, even under conditions of complete localisation of the transferred charge at the halogen atom the quadrupole frequency shift will not exceed 5%. Hence it is easily seen that in the complexes of these acceptors steric interactions will have a dominant effect on the NQR spectra.

The effect of the geometrical structure of the molecules (or the geometrical factor) on the shift of the quadrupole

spectra on complex formation was first demonstrated for the complexes of halogenobenzenes [13]. Calculation by Hückel's method [20] showed that halogenobenzenes have almost identical and very weak acceptor properties. According to X-ray diffraction analysis [21], the distance between the components of the complex is not reduced as compared with the sum of the van der Waals radii of the components. Both these findings indicate that in this case the usual intermolecular interactions predominate. This view is confirmed also by a series of physicochemical experiments [22,23].

Table 1. ^{35}Cl NQR spectra of the complexes $C_6F_5Cl.D$.

Donor	$\nu_{^{35}Cl}$, MHz
—	39.410
Benzene	38.717
Mesitylene	38.68
Chlorobenzene	39.36
Aniline	38.64
Triethylamine	39.284
Toluene	39.16

Table 1 shows that in five chloropentafluorobenzene complexes with various bases [13] the chlorine-35 frequency shifts are independent of the dative properties of the donors, a measure of which is provided by the ionisation potentials, and are determined mainly by the geometrical structure of the molecules. Thus the ionisation potentials of mesitylene and benzene (8.39 eV [24] and 9.25 eV [25]) are significantly different, but the symmetry types of both molecules are similar and the chlorine-35 frequency shift is virtually identical in both cases. In all the remaining complexes the molecular structure of the donors is extremely varied and the frequency shifts show significant differences. This suggests, in the first place, that in the complexes of chloropentafluorobenzene the degree of charge transfer is small and, in the second place, that molecular geometry plays a dominant role in the spectroscopic effects.

The nature of a slight low-frequency shift is still obscure. One can only note that the extremely short spin–lattice relaxation times for these complexes indicate that their benzene rings rotate (although at frequencies lower than those observed by NQR). Such rotation may lead to the averaging of the field gradient and hence to a lowering of the frequency.

The complexes of chloranil with mesitylene and hexamethylbenzene are more stable. The distance between the components of the complex is somewhat smaller than the sum of the van der Waals radii [26] and the degree of charge transfer is approximately 3%. [19] The observed shifts of the quadrupole spectra of these complexes occur at high frequencies, as was to be expected, but are very small (0.075 MHz [15] and 0.107 MHz [16] respectively). However, the available experimental data are too few to arrive at any definite conclusions.

A more systematic investigation of the effect of the electronic and geometrical factors on the quadrupole frequency shift has been made [12,18] for complexes of picryl chloride with aromatic donors (Table 2).

Picryl chloride can be very conveniently investigated by the NQR method. The two nitro-groups in the *ortho*-positions relative to the chlorine atom are displaced from the plane of the ring and make an angle of 80–90° with it [27]. The chlorine atom is to some extent protected from the direct steric effect of the donor molecule. When account was taken of the corresponding donor symmetry, this made possible a number of interesting conclusions concerning the effect of various factors on the NQR frequency shift.

Table 2. ^{35}Cl NQR spectra of picryl chloride complexes with aromatic donors.

No.	Donor	ν, MHz	$\Delta\nu$, MHz	Remarks
1	—	39.385	+0.193	
2	Benzene	39.578	+0.193	
3	Fluorobenzene	39.683	0.298	
4	Chlorobenzene	39.956	0.571	
5	Bromobenzene	39.988	0.613	
6	Toluene	40.075	0.690	*Anti*-isomer
		39.662	0.277	*Syn*-isomer
7	Iodobenzene	40.250	0.865	
8	Phenol	40.544	1.159	
9	Nitrobenzene	39.466	0.081	
10	*p*-Xylene	39.425	0.040	
11	*p*-Iodotoluene	39.431	0.046	
12	*p*-Cresol	39.501	0.166	
13	*p*-Bromotoluene	39.606	0.221	
14	*p*-Chlorotoluene	40.152	0.767	*Anti*-isomer
		39.907	0.522	*Syn*-isomer
15	*p*-Fluorotoluene	40.040	0.655	
16	Mesitylene	40.383	1.002	
17	Durene	39.970	0.585	
18	Pentamethylbenzene	40.264	0.879	
19	Naphthalene	39.935	0.550	
20	Anthracene	39.802	0.417	
21	Phenanthrene	39.914	0.529	

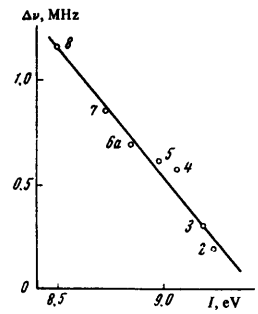


Figure 2. Variation of the ^{35}Cl NQR frequency shift for picryl chloride in complexes with monosubstituted benzene derivatives as a function of the ionisation potential of the donor (the points are numbered in accordance with Table 2).

In complexes with monosubstituted benzenes the symmetry of the donor molecules is identical and therefore one may assume that the steric interactions are also approximately the same. It has been shown for such complexes that the shift of the chlorine-35 quadrupole frequency of the acceptor varies linearly with the ionisation potential of the donor (Fig. 2). Since the degree of charge transfer in a series of complexes of the same acceptor is linearly related to the ionisation potential of the donor [28], the nature of this correlation confirms the linearly of Eqn. (15), i.e. the linearity of the relation between the quadrupole frequency shift and the degree of charge transfer.

In complexes with *para*-substituted toluenes the symmetry of the donors can also be regarded as identical. However, the presence of the *para*-substituent intensifies the effect of the steric interaction. There are two most probable positions of the *donor* molecule in the complex depending on the orientation of the CH_3 group in relation to the bulky picryl chloride group (*syn*- or *anti*-).

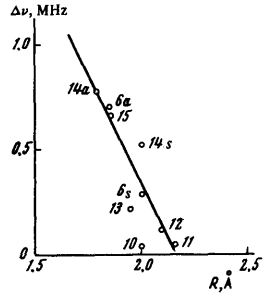


Figure 3. Variation of the ^{35}Cl NQR frequency shift for picryl chloride as a function of the van der Waals radius of the *para*-substituent in complexes with *para*-derivatives of toluene [the points are numbered according to Table 2; *a*—anti-conformation; *s*—syn-conformation].

Table 2 shows that in the majority of complexes there is only one conformation, believed[18] to be the *anti*-conformation. The doublet structure of the spectrum in many cases indicates the existence of both conformations.

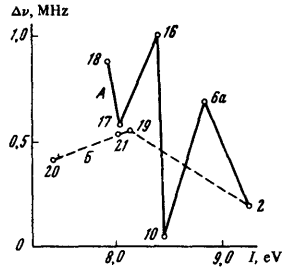


Figure 4. Variation of the ^{35}Cl NQR frequency shift for picryl chloride as a function of the ionisation potential of the donor in complexes with polymethylbenzenes (A) and condensed aromatic systems (B) (the points are numbered according to Table 2).

Furthermore, with increase of the bulk of the *para*-substituent, the distance between the components of the complex also increases, which reduces the degree of charge transfer. Therefore an increase of the bulk of the *para*-substituent in the donor molecule should cause a fall of the quadrupole frequency shift. Fig. 3 shows the variation of the quadrupole frequency shift with the van der Waals radius of the *para*-substituent. Evidently the relation is fairly well approximated by a straight line.

The effect of the molecular structure of the donor on the shift is well illustrated by the spectra of the complexes of picryl chloride with polymethylbenzenes and condensed aromatic systems (Fig. 4). With increase in the number of methyl groups in the donor molecule, the ionisation potentials of the donor decreases, but the effect of its molecular symmetry is so great that the shift does not show a definite variation from complex to complex, although its general direction is maintained. The same tendency is observed also in the spectra of the complexes of picryl chloride with polycyclic aromatic systems.

Thus the investigations show that (1) after exclusion of the effect of the geometrical factor the linearity of the relation between the quadrupole frequency shift and the degree of charge transfer is confirmed and that (2) in the presence of the combined effect of the electronic and geometrical factors the role of the latter may be very significant.

5. σ-ACCEPTOR COMPLEXES

As already stated, charge transfer to an antibonding σ orbital of the acceptor leads to a low-frequency shift in the quadrupole spectrum of the halogen. The magnitude of this shift is determined by the distribution of the transferred charge. Since in the majority of complexes of this type the degree of charge transfer is small, the frequency shift should depend significantly on the geometrical factor.

Table 3. ^{81}Br NQR spectra of the complexes $Br_2.D$.

Donor	$\nu_{^{81}Br}$, MHz	Δν, MHz
—	319.509	—
Benzene	319.616	+0.107
Fluorobenzene	319.469	−0.040
Chlorobenzene	319.483	−0.026
Bromobenzene	317.803	−1.704
	215.92*	−8.69
Dioxan	314.77	−4.74
Acetone	318.336	−1.173
Ethyl ether	320.499	+0.990

*Bromine-81 in bound C_6H_5Br.

Among complexes of σ acceptors, those of Br_2 with various *n* and π donors have been most thoroughly investigated[29–32]. Table 3 shows that, with the exception of the bromine complexes with benzene and ethyl ether, the observed low-frequency shifts are usually small and lie in the range 0.01–4%. In the spectra of the complexes $Br_2.C_6H_6$ and $Br_2.O(C_2H_5)_2$ small high-frequency shifts were observed. Comparison of the data shows that the shifts are not determined by the dative properties of the donors. As for the complexes of π acceptors, steric interactions play a dominant role in the spectroscopic effects. An attempt was made[32] to compare the dative properties of the donors with the quadrupole interaction constants of bromine atoms calculated by Eqn. (6) from the experimental frequencies for various arbitrarily specified asymmetry parameters. However, the attempt was

unsuccessful because of the specificity of the steric factors.

For the complex $Br_2.C_6H_5Br$, observations were also made of the ^{81}Br NQR frequencies for the bromine atom in the aromatic system. The low-frequency direction of the shift agrees with expectation and the magnitude of the shift is 4%. In this case complex formation involves the unshared pair of electrons of the bromine atom and not the π-electron system of the ring [33]. The magnitude of the shift determines directly the decrease of electron density at the p_X orbital of the bromine atom as a result of the charge transfer. The charge transfer was estimated [32] as 8% from the relative change of the field gradient $\Delta q_{zz}/q_{zz(obs)}$. However, according to Eqn. (18), in such an estimate it is more valid to employ q_{at} instead of $q_{zz(obs)}$, since the population of the $3p_X$ orbital is influenced neither by the degree of s-hybridisation nor the amount of ionic character of the C–Br bond, on which q_{zz} depends. Generally speaking, this inaccuracy is of secondary importance in a rough estimate but may be significant in more accurate calculations. The use of q_{at} yields an estimate of about 5% for the degree of charge transfer. On the other hand, the degree of charge transfer determined from the shift of the spectrum of the Br_2 acceptor is 2%. The discrepancy between the fractions of charge transferred found for the donor and the acceptor may be accounted for by the involvement in complex formation of the vacant d orbitals of the bromine atoms in the Br_2 molecule. A similar hypothesis was also made for the complex of carbon tetrabromide with p-xylene [34,35]. The involvement of d orbitals favours a decrease of the p_Z-electron density and consequently a high-frequency shift of the quadrupole spectrum of the bromine atom.

A remarkable feature of the spectra, characteristic of all bromine complexes, has also been noted [32]: the frequencies of both bromine atoms in the acceptor molecules fully coincide, without any signs of a broadening of the band. This type of phenomenon implies that their chemical and crystallographic environments are fully equivalent. X-Ray diffraction studies showed [36–39] that the complexes of bromine with benzene, acetone, and dioxan have a chain structure. It may be supposed that a chain structure obtains also in all other cases, since otherwise signs of crystallographic splitting should be observed.

The complexes of I_2, ICl, and IBr with various donors are widely known and have been fairly thoroughly investigated by other methods. X-Ray diffraction analysis has shown [40] that the length of the I–X bond in the complexes is much greater than in the initial compound, while the I...D distances are smaller than the sum of the van der Waals radii of the coordinating atoms. For a large series of complexes with amines, the degree of charge transfer has been estimated by various methods [41,42] as 20–50%. According to these data, a decrease of the frequencies in the NQR spectra by about 10–25% was to be expected. However, contrary to expectation, experiments showed [43,44] that eQq_{zz} for ^{127}I in complexes of this kind increases.

The suggested low degree of charge transfer [43,44] is inconsistent with the above results from other methods. It is also difficult to accept that, with the observed increase of eQq_{zz} (from 2156 MHz for I_2 to 3000–3100 MHz for I_2.D, where D = pyridine), a charge transfer of 20–50% plays an insignificant role. It is more realistic to suppose that in these complexes charge transfer is accompanied by sp^3d-hybridisation of the iodine atom [42]. We shall consider the effect of sp^3d-hybridisation and charge transfer on eQq_{zz} in greater detail. For simplicity, we shall confine ourselves to the complex I_2.D, where the ionic character of the I–X bond may be neglected. Five sp^3d-hybrid wave functions of the iodine atom are of the following form [45]:

$$\sigma_1 = \frac{1}{\sqrt{6}}(s - d_{z^2} + 2p_x),$$

$$\sigma_2 = \frac{1}{\sqrt{6}}(s - d_{z^2} - p_x + \sqrt{3}\,p_y),$$

$$\sigma_3 = \frac{1}{\sqrt{6}}(s - d_{z^2} - p_x - \sqrt{3}\,p_y), \qquad (20)$$

$$\sigma_4 = \frac{1}{2}(s + d_{z^2} + \sqrt{2}\,p_z),$$

$$\sigma_5 = \frac{1}{2}(s + d_{z^2} - \sqrt{2}\,p_z).$$

The σ_1, σ_2, and σ_3 orbitals are occupied by unshared electron pairs, the σ_4 orbital is involved in the formation of a covalent bond, and σ_5 is an acceptor orbital. After the summation of the electron densities of the p_X, p_Y, and p_Z orbitals, it is readily seen [Eqn. (10)] that the field gradient due to the sp^3d-hybrid valence shells of iodine is $\frac{3}{2}q_{at}$ and charge transfer leads to its decrease. Hence the degree of charge transfer in the complexes investigated is about 40–50%, which agrees fairly well with the previous results based on the dipole moments and infrared spectra.

In the complexes of carbon tetrachloride and carbon tetrabromide with various donors electrons are transferred to an antibonding σ orbital of the acceptor molecule. As already stated, this should be accompanied by a low-frequency shift of the halogen spectra. The available data for the complexes CCl_4.D [15,29,46,47] are non-systematic and contradictory and therefore will not be discussed. The spectra of CBr_4 complexes with a number of π donors [29,48] consist of 2–3 lines located in most cases in the same frequency range as the spectra of the initial compounds. Using X-ray diffraction data, the low-frequency lines in the spectra of the complexes were assigned [49] to the bromine atoms in the immediate vicinity of the aromatic system. The attempts to compare their frequencies with the ionisation potentials of the donors were unsuccessful. It is believed that this may be caused by intermolecular reorientation of the donor in the complex and by the difference between the Ar...Br distances.

In the complexes $AsI_3.3S_8$, $SbI_3.3S_8$, $SnI_4.2S_8$, and $SnI_4.4S_8$ [50–53] coordination also involves the iodine atoms and not the central metal atom [54–56]. They too can be classified as complexes with acceptors of the σ type.

The large changes in the quadrupole interaction constants of iodine-127, antimony-121, and antimony-123 and in the arsenic-75 frequencies in the complexes $AsI_3.3S_8$ and $SbI_3.3S_8$ originate not from charge transfer but from a rearrangement of the crystal lattice when the individual compound is converted into the complex. Thus the crystals of pure AsI_3 have a layer structure with six adjacent I atoms surrounding one ^{75}As atom. On the other hand, in the complex the AsI_3 molecule has a pyramidal structure. The changes in the gradient following such rearrangement are of course appreciable. The changes in the iodine-127 quadrupole interaction constants in the remaining complexes are very slight and their interpretation is difficult.

Thus the investigation of the NQR spectroscopic effects of complex formation by σ acceptors suggests that (1), since the degree of charge transfer in these complexes is low, the geometrical factor plays the principal role in the

spectroscopic effect and (2) there is a general tendency towards a low-frequency shift as a result of charge transfer.

6. THE HYDROGEN BOND

The hydrogen bond is also of the donor–acceptor type [1]. Protic acids usually behave as proton donors in the hydrogen bond. Thus they can be regarded as electron acceptors of the σ type. Using the generally adopted hypotheses concerning the nature of the hydrogen bond, this makes it possible to maintain a common approach to the analysis of the quadrupole shifts. Among systems with hydrogen bonds, complexes of certain halogen-containing acids (CCl_3COOH, $CHCl_3$, HCl, HBr) with various donors have been investigated by the NQR method [15,17,46,47,58].

The transmission of the effect of complex formation to the halogen atoms of the acceptors, which are usually remote from the coordinating centre, is achieved by an inductive mechanism and leads to an increase of the ionic character of the R–X bond. For this reason, the quadrupole spectra of the halogen-containing acids should exhibit a low-frequency shift.

The hydrogen bonds in dilute solutions are frequently investigated using acids capable of self-association. In the solid state such acids form polymeric structures when the same molecule behaves simultaneously as a donor and an acceptor. On addition of a base to such an acid (in studies by the NQR method the pure components are usually mixed), a dynamic equilibrium is established in the liquid between the self-associated species and the complex. On crystallisation both forms of associated species are maintained and the NQR spectrum shows simultaneously the frequencies of the self-associated species as well as the complex, altered by the steric and crystal field effects. It is very difficult to analyse in detail and assign the frequencies in such spectra. For this reason, it is more convenient to employ an average frequency shift in the analysis of the results. The average frequency shift will be greater, the more basic is the donor. Although this approach is very approximate, the results may be of definite interest.

A large number of molecular compounds of trichloroacetic acid with oxygen-containing substances have been investigated [59]. The multiplicity of the NQR spectra of trichloroacetic acid in these compounds is higher than in the spectrum of the initial acid and the limits of the frequency range are greatly extended. These changes were fully attributed [59] to crystal effects ignoring the possibility of charge transfer. However, trichloroacetic acid is a fairly powerful acceptor and therefore the role of hydrogen bonds may be significant. As a rule, the second component added to trichloroacetic acid was either another acid or a base. Since in the mixtures there is a possibility of the formation of associated species with a wide variety of compositions, it is interesting to examine in the light of the above considerations the distribution of the mean frequencies along the frequency scale for mixtures of both types. Fig. 5 shows such a distribution as a function of $N(\nu_{av})$. As was to be expected, the average frequencies of the complexes with bases are displaced to the low-frequency region, while those with acids remain the same as the mean frequency of the initial trichloroacetic acid (40.010 MHz).

A similar behaviour is possible also for weak acids incapable of self-association (for example, chloroform). In this case, the wek acidity favours a greater degree of dissociation of the complexes and therefore the spectrum may show together with the frequencies of the complex those of the initial acid. However, with increasing basicity of the donor, the low-frequency shift of the average frequency should increase. This tendency is observed in the spectra of the complexes of chloroform with various donors [15,46,47,58]. The chlorine-35 shifts of bound chloroform in all the complexes investigated are of the low-frequency type and are usually in the range 1 to 2.5%. A more detailed analysis is difficult, since the donors investigated have various frequencies and it is difficult to estimate the role of the geometrical factor. One can only note that on going from aromatic to oxygen-containing donors and from the latter to amines, the average low-frequency shift increases.

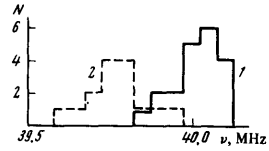


Figure 5. Frequency distribution for [^{35}Cl]trichloroacetic acid in molecular compounds with acids (1) and bases (2).

Interesting results were obtained from the NQR spectra of complexes of HCl with chlorine-containing amines [60–64]. Hydrogen chloride is close to the ionic state in such complexes and therefore the frequencies of its chlorine atoms should be close to zero, the possibility of their observation being limited in consequence. The frequencies of the chlorine present in the donors were observed in the spectra. In complexes of HCl with aliphatic amines there are high-frequency shifts in accordance with the decrease of the ionic character of the C–X bond, their magnitude reaching about 10%.

Table 4. NQR spectra of the hydrochlorides of *p*-halogenoanilines (p-$XC_6H_5NH_3)^+Cl^-$.

Compound	ν_X, MHz	$\Delta\nu/\nu$, %
p-$IC_6H_4NH_2$	261.14	
	521.15	
(p-$IC_6H_4NH_3)^+Cl^-$	288.28	
	572.15	+10.1
p-$BrC_6H_4NH_2$	221.862	
(p-$BrC_6H_4NH_3)^+Cl^-$	232.043	+4.6
p-$ClC_6H_4NH_2$	34.146	
(p-$ClC_6H_4NH_3)^+Cl^-$	35.448	+3.8
(p-$ClC_6H_4NH_3)^+Br^-$	34.572	+1.8

In HCl complexes with *p*-halogenoanilines the effect of complex formation is transmitted to the halogen atoms in two ways. The ionic character of the C–X bond decreases via an inductive mechanism and a high-frequency shift should be observed. However, in complex formation the conjugation between the *p*-electrons of the ring and the unshared pair of the nitrogen atom is broken and the

unshared pair now participates in complex formation. As a result, the conjugation between the halogen and the ring increases. The enhanced double bond character is indicated by the increase of the asymmetry parameter of the iodine atom to 7% in *p*-iodoanilinium chloride compared with pure *p*-iodoaniline ($\eta = 3\%$).[64] The increase of the conjugation between the halogen and the ring reduces the p_x electron density at the halogen, which should favour a low-frequency shift in the spectrum.

It has been shown[62-64] (Table 4) that the inductive effect prevails and the relative high-frequency shifts increase in the sequence Cl < Br < I. Comparison of the chlorine frequencies of *p*-chloroaniline in complexes with HCl and HBr shows that their H–Cl and H–Br bonds retain a certain amount of covalent character.

Thus the data quoted demonstrate that all the factors which operate in σ-acceptor complexes apply to hydrogen bonds. On the one hand, the self-association and dissociation phenomena hinder the interpretation of the NQR data and on the other serve as an additional source of information concerning the role of hydrogen bonds in solids.

7. *v*-ACCEPTOR COMPLEXES

The complexes of metal halides have been most completely investigated by the NQR method. In the vast majority of cases the frequencies of the halogen atoms bound to the central atom were studied. As a rule they show low-frequency shifts which are interpreted as due to an increase of the ionic character of the M–X bond. When the central atom has a quadrupolar nucleus, there is a possibility of a more complete study of the changes in the electronic structure of the acceptor molecule as a result of complex formation. Since the third section of this review dealt with a preliminary examination of the nature of the shifts and splittings in the spectra of *v*-acceptor complexes, we can proceed directly to a discussion of the experimental results. These can be conveniently arranged in order of the increasing Periodic Group number of the central atom.

Among Group II metal halides, 1:1 complexes of mercury chloride and bromide with various *n*-donors have been investigated by the NQR method[65,66] (Table 5). The relative low-frequency shifts of $HgCl_2$ chlorine-35 in the complexes are quite considerable, amounting to 7–15%. The complexes $HgCl_2$.D in the solid state consist of polymeric structures comprising trigonal bipyramids linked via the edges, with the Hg atom in the centre and the donor molecule in the equatorial phase[67]. The same chlorine atom is equatorial relative to one bipyramid and axial relative to another. Therefore the splitting in the NQR spectra of complexes of this kind may be due only to crystal field effects. If one assumes that the change in the parameters of the Hg–X bonds following the change in the hybridisation of the mercury atom is the same for all complexes, the quadrupole frequency shift should be proportional to the degree of charge transfer. Indeed Table 5 shows that a decrease of the ionisation potential of the donor entails an increase of the average shift of the $HgCl_2$ chlorine-35 quadrupole frequency. It is difficult to expect a rigorously linear relation, since the geometrical factor plays a very significant role, but the general tendency is maintained.

For the complexes $HgBr_2$.D, both low-frequency and high-frequency shifts are observed. It is difficult to expect that only the geometrical factor is responsible for the 8% high-frequency shift in the spectra of the $HgBr_2$.dimethoxyethane complex. The change in the double bond character of the Hg–Br bond may also play a very significant role.

Table 5. ^{35}Cl and ^{81}Br NQR spectra of the complexes HgX_2.D.

No.	Complex	ν_X, MHz
1	$HgCl_2$	22.522 22.874
2	Dimethylformamide.$HgCl_2$	20.208 20.456
3	Dimethoxyethane.$HgCl_2$	21.326
4	Dimethylsulphoxide.$HgCl_2$	19.878 19.494
5	Dioxan.$HgCl_2$	21.196
6	Tetrahydrofuran.$HgCl_2$	20.584 19.272
7	$HgBr_2$	122.90 130.93
8	Dimethyl sulphoxide.$HgBr_2$ (2:1)	128.08 134.78 141.45 141.84
9	Dimethoxyethane.$HgBr_2$	141.23 140.40
10	Dimethylformamide.$HgBr_2$	122.87 134.60 136.00

Among compounds in Group III elements, the NQR spectra of complexes of aluminium chloride and bromide and also gallium chloride with *n*-donors have been investigated[2,12,68,70,71]. The only available spectrum, of the complex of $AlCl_3$ with ethyl ether[2], does not yield any definite conclusions concerning the structure, since so far the ^{35}Cl NQR spectrum of pure aluminium chloride has not been obtained. In all the aluminium bromide spectra investigated[68] appreciable low-frequency shifts of the quadrupole frequencies of the bromine atoms were observed (Table 6). Comparison of the spectra shows that in the spectrum of the complex $AlBr_3$.pyridine, which is more stable than the complexes $AlBr_3$.OR'R'' and therefore gives rise to a higher degree of charge transfer[60], there is a more pronounced low-frequency shift. Complexes of aluminium bromide with ether are of interest also from another point of view. The splitting in the NQR spectra of $AlBr_3$ in complexes with ethers of various structures indicates the occurrence of significant steric interactions between the hydrocarbon groups of the ether and the bromine atoms of the $AlBr_3$ molecule. The type of this interaction is such that, an increase in the bulk of the group increases the quadrupole frequency of the adjacent bromine atom compared with that of the bromine atom adjacent to a smaller group.

Among the halide complexes of Group III elements, those of gallium chloride with a number of *n*-donors have been investigated in greatest detail[70,71]. Both chlorine-35 and gallium-69 (central atom) frequencies were found in the NQR spectraof these complexes. The variation of the NQR frequencies within the limits of a series of complexes investigated are very considerable: 16–18.5 MHz for chlorine-35 and 0–25 MHz for gallium-69. Unfortunately, the main paper on the subject[70] does not give the numerical results of the measurements and all data are presented as plots of νCl against νGa, νCl against $-\Delta H$, and νGa against $-\Delta H$, where $-\Delta H$ is the heat of complex formation in the gas phase. Nor are the relations

obtained discussed from the standpoint of the chemical structure. Although lack of concrete data restricts the interpretation of the NQR spectra obtained, the observed correlations permit a number of interesting conclusions.

Table 6. ^{81}Br NQR spectra of the complexes $AlBr_3.D$.

Donor	ν_{av}, MHz
	92.00
Ethyl ether	83.49
Phenetole	85.73
Phenyl ether	86.33
Dimethyl sulphide	81.62
Pyridine	82.22

The relations between νCl and $-\Delta H$ and between νGa and $-\Delta H$ obtained by the author (Fig. 6) show that an increase in the strength of the donor–acceptor bond, i.e. an increase in the degree of charge transfer, entails a low-frequency shift of the frequencies of both the halogen and the central atom. Furthermore, the presence of such relations confirms directly the earlier conclusion that the effect of charge transfer on the NQR spectroscopic shift predominates over the effect of steric factors in complexes of υ acceptors.

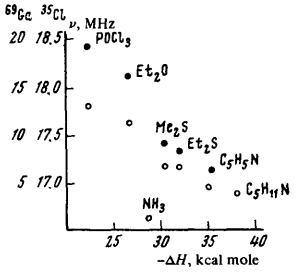


Figure 6. Variation of the average ^{35}Cl (o) and ^{69}Ga (o) NQR frequencies with the energy of the donor–acceptor bond in the complexes $GaCl_3.D$ (Figure taken from Tong [70]).

The correlation between the chlorine-35 and gallium-69 frequencies, presented by the author in a graphical form and in the form of the equation

$$\nu_{Cl} = 16.326 + 0.826\,\nu_{Ga},$$

is of considerable interest. The equation permits the estimation of the type of distribution of the transferred charge in the $GaCl_3$ acceptor molecule. Assuming that the sp^3-hybridisation of the gallium atom remains unchanged, the equation can be reformulated as follows:

$$\Delta e_{3Cl} = 2.5\,\Delta e_{Ga},$$

where Δe_3Cl is the overall change in electron density at all three chlorine atoms as a result of charge transfer and ΔeGa is the analogous change at the gallium atom. This equation characterises the distribution of the transferred charge in the $GaCl_3$ acceptor molecule, i.e. 2/7 of the charge is localised at the central Ga atom and 5/7 is distributed among the three chlorine atoms. These results are notable because they refer to one of the first experimental estimates of the distribution of the transferred charge.

Above it was shown (Section 2) that the multiplicity of the spectra of the complexes may be used to investigate their geometrical structures. In addition to a theoretical examination of this problem, Babushkina et al. [4] made an experimental study of a number of hexaco-ordinated tin tetrachloride complexes. By comparing the experimental splitting of the chlorine-35 spectra with the theoretical scheme for the complexes $MX_4.2D$ with various geometrical structures, the structures of a number of octahedral $SnCl_4.2D$ complexes were established, Some of these complexes were investigated also by other workers [2, 46,65,72].

Table 7. ^{35}Cl NQR spectra of the complexes $SnCl_4.2D$.

Complex	ν, MHz	Structure
$SnCl_4 \cdot 2\,(C_2H_5)_2O$	19.438	*trans-*
	19.473	
$SnCl_4 \cdot CH_3O\,(CH_2)_2OCH_3$	19.620	*trans-*
$SnCl_4 \cdot CH_3O\,(CH_2)_4OCH_3$	19.428	*trans-*
	20.160	
$SnCl_4 \cdot 2POCl_3$	19.035	*cis-*
	19.807	
	21.146	
$SnCl_4 \cdot 2C_2H_5OH$	17.498	*cis-*
	17.750	
	20.120	
	20.568	
$SnCl_4 \cdot C_6H_5NO_2$	20.832	*cis-*
	20.952	
	23.152	
	23.208	
	23.336	

The complexes $SnCl_4.2C_2H_5OH$, $SnCl_4.2POCl_3$, and $SnCl_4.C_6H_5NO_2$ have been assigned the *cis*-structure (Table 7). On the basis of the average low-frequency shift, the dative properties of the donors can be arranged in the series $C_2H_5OH > POCl_3 > C_6H_5NO_2$. The complexes $SnCl_4.2(C_2H_5)_2O$, $SnCl_4.CH_3OCH_2CH_2OCH_3$, and $SnCl_4.CH_3O(CH_2)_4OCH_3$ have the *trans*-configuration and the last two complexes have a chain structure in the solid state (Fig. 7). Since the complexes $SnCl_4.RO(CH_2)_2OR$ have the *cis*-structure in solution, it was concluded that the *cis*-form isomerises to the *trans*-form when the complexes are crystallised from solutions.

The literature data [73–75] on the structures of certain complexes confirm these results. High-frequency shifts of the $POCl_3$ chlorine-35 transition have been found for the complex $SnCl_4.2POCl_3$. On average they amount to 4%. The shifts indicate that, on formation of the complex with $SnCl_4$, the ionic character of the P–Cl bond diminishes by 2.1%.

The structure of the octahedral complexes of antimony pentachloride of type $SbCl_5.D$ is very close to that of the octahedral complexes of tin tetrachloride. Their symmetry belongs to the point group C_{4v}. Consequently 4 of the 5 chlorine atoms should be equivalent (equatorial atoms). The non-equivalent (axial) atom is in the *trans*-position in relation to the donor molecule. Accordingly,

when steric factors and the crystal field effects are disregarded, the ^{35}Cl NQR spectra of the complexes $SbCl_5.D$ should consist of 2 lines with an intensity ratio of 4 : 1.

The spectra of two antimony pentachloride complexes ($SbCl_5.CH_3CN$ and $SbCl_5.POCl_3$) have been obtained[72,76]. As was to be expected, the ^{35}Cl NQR spectrum of the $SbCl_5$ molecule in the complex with acetonitrile consists of two lines with an intensity ratio of 4 : 1 and a splitting of 1.5 MHz. The frequency assignment gives rise to no doubt in this case. The steric effect of the donor molecules in the complex $SbCl_5.POCl_3$ on the quadrupole frequencies of the equatorial chlorine atoms in $SbCl_5$ is so great that the resulting splitting exceeds the frequency difference caused by the chemical non-equivalence. For this reason, in order to assign the frequencies, it was necessary to investigate[76] their temperature variation.

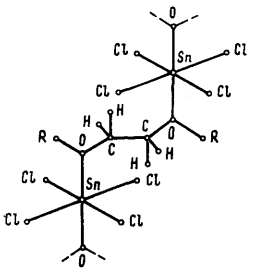


Figure 7. Structure of the complex $SnCl_4.RO(CH_2)_2OR$.

The chlorine-35 frequency shifts together with the quadrupole interaction constants of antimony-121 and antimony-123 (spins of 5/2 and 7/2 respectively) make it possible to estimate the degree of charge transfer and the type of its distribution in the acceptor molecule. For simplicity we shall assume that, when the sp^3d-hybridisation of the antimony atom changes to sp^3d^2-hybridisation, the amount of ionic character of the Sb–Cl bond is unaltered. Then the increase of electron density at the chlorine atoms can be fully attributed to charge transfer. The overall charge transfer is about 35%. Using the hybrid orbitals, it is possible to calculate that the increase of the charge at the antimony atom as a result of complex formation is approximately 5 and 10% respectively for $SbCl_5.CH_3CN$ and $SbCl_5.POCl_3$. Thus the overall degree of charge transfer is about 40–45% for both complexes. It is interesting to note that the charge transferred is preferentially localised at the chlorine atoms, probably due to their high electronegativity.

As for the complexes of antimony pentachloride, the presence of two isotopes (antimony-121 and antimony-123) permits the determination of eQq_{ZZ} and η for antimony trichloride and tribromide in complexes with various aromatic bases[47,65,76–85]. Extensive experimental data have revealed the following trends in the changes of quadrupole spectra on formation of the complexes $SbX_3.D$ and $2SbX_3.D$: (1) the shift of eQq_{ZZ} for antimony is in most cases towards higher frequencies; (2) for 2 : 1 complexes, eQq_{ZZ} is usually higher than for 1 : 1 complexes; (3) for 1 : 1 complexes, some parallelism in the increase of eQq_{ZZ} with increase of the ionisation potential of the donor is observed; (4) the average $SbCl_3$ chlorine-35 frequencies in the complexes are slightly displaced to the low-frequency region relative to the frequency of the initial $SbCl_3$; in antimony tribromide complexes such shifts are hardly ever observed; (5) in most of the $2SbX_3.D$ complexes the two acceptor molecules are non-equivalent.

The interpretation of the changes in eQq_{ZZ} in these complexes is very complicated, since on complex formation the partially sp^3-hybridised atomic orbitals of antimony become in addition partially d-hybridised. Neglecting the d-hybridisation, the authors[79–84] interpret the decrease of eQq_{ZZ} by electron transfer to the p_X or p_Y atomic orbitals of antimony and the increase by transfer to the p_Z orbital. However, this interpretation is not unique. In the first place, direct transfer of electrons to the p_X, p_Y, or p_Z orbitals is impossible, since three of the sp^3-hybrid orbitals participate in the formation of Sb=Cl bonds and the fourth is occupied by an unshared electron pair. Moreover, sp^3d-hybridisation leads to a change in the distribution of electron density between the s, p, and d orbitals. For a sufficiently high degree of d-hybridisation, the contribution to eQq_{ZZ} due to such redistribution may be very considerable. Therefore neglect of d-hybridisation can lead to an incorrect interpretation of the experimental data.

The overall change in eQq_{ZZ} on complex formation can probably be regarded as a result of the operation of two principal effects (excluding the steric and crystallographic effects): sp^3d-hybridisation with a corresponding change in the populations of the p orbitals and charge transfer to the vacant orbital.

It has been shown by infrared spectroscopy[86] that the complex $2SbCl_3.C_6H_6$ has C_{2v} symmetry. From this point of view, and also taking into account the maximum repulsion between the "ligands" and the unshared pair of the antimony atom, sp^3d_{XY}-hybridisation is most appropriate[45]. Then an increase of the degree of d-hybridisation hardly alters the p_Z character of the unshared electron pair and reduces significantly the populations of the p_X and p_Y orbitals. Consequently a change in hybridisation leads to an increase of eQq_{ZZ} [see Eqn. (10), remembering that the sign of q_{at} for antimony is the opposite of that for the halogen]. Charge transfer to the vacant hybrid orbital corresponds to an increase of p_X- and p_Y-electron density and leads to a decrease of eQq_{ZZ}. This view appears to be more appropriate for the explanation of the available experimental data. One may assume that in complexes of the same acceptor, for example $SbCl_3$, the degree of d-hybridisation is approximately the same and leads to the same increase of eQq_{ZZ}. Then, following an increase in the degree of charge transfer, eQq_{ZZ} in this series of complexes will diminish. Such a tendency is observed very distinctly in the complexes $SbCl_3.D$; when the ionisation potential of the donor falls, the degree of charge transfer increases and eQq_{ZZ} diminishes. In a complex $2SbX_3.D$ the degree of charge transfer to one of the acceptor molecules will of course be smaller than in a complex $SbX_3.D$ and therefore eQq_{ZZ} for D will, of course, be greater. The increase of the antimony field gradient in most of the complexes and the slight low-frequency shifts in the quadrupole spectra of the halogens suggests a low degree of charge transfer in these complexes. Steric factors would then, of course, play a very significant role. Despite the large number of experimental data, a more detailed analysis of the effects of the electronic and steric factors in these complexes is still difficult.

An attempt has been made[86] to establish the steric structure of the complex $2SbCl_3.C_6H_6$ by the Zeeman analysis of the quadrupole spectra. It was shown that the

geometry of both $SbCl_3$ molecules is distorted only slightly. The relative positions of all three molecules in the complex can probably be elucidated in detail by X-ray diffraction analysis.

As for the antimony trichloride complexes, only slight chlorine-35 frequency shifts were observed in the complexes $AsCl_3.Ar$.[65,85] By analogy with the splitting of the chlorine-35 frequencies and the splitting of the spectra of antimony trichloride complexes, the authors established that the structure of the $2AsCl_3.D$ complexes investigated is analogous to that of the corresponding complexes $2SbCl_3.D$.

While in the above investigations the spectroscopic shifts of the acceptors for various dative properties of the donors were mainly compared, Rogers and Ryan[72] attempted to use the frequency shifts of the donors to compare the acceptor properties of certain metal halides. According to the $POCl_3$ chlorine-35 shift in the complexes $MX_n.POCl_3$, the acceptor properties of the metal chlorides vary in the sequence $SbCl_5 > FeCl_3 > SnCl_4 > TiCl_4$. After appropriate development, it will probably be possible to use this method for the determination of the electron affinities of acceptors.

Thus the effect of complex formation by v acceptors on NQR spectra is as follows.

1. The change in the field gradient at the central atom is determined mainly by two factors—the change in the hybridisation of the valence shell and in the degree of charge transfer. In most cases the effect of electronic factors is considerable, while steric factors play a secondary role.

2. The frequencies of the quadrupole spectra of the halogens are displaced towards lower values as a result of an increase of the ionic character of the M–X bond. This shift is higher, the greater is the degree of charge transfer. An appreciable effect of steric factors is characteristic of weak complexes.

3. The type of splitting in the spectra is largely determined by the symmetry of the complex formed. This splitting is caused by the chemical non-equivalence of the halogen atoms in the complex. The magnitude and nature of the splitting can serve as an additional source of information about the electronic and steric effects in the complexes investigated.

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The results of the investigations demonstrate in the first place that the shift of the NQR frequencies for the complexes is closely related to the degree of charge transfer. Although there is as yet no direct experimental proof of this relation, theoretical studies and many indirect experimental data suggest that this relation should be of the type of direct proportionality. The type of splitting in the spectrum is determined by the distribution of electron density in the molecule and the symmetry of the complex. Steric effects can, on the one hand, obscure the effects of electronic factors and, on the other hand, they can serve as an additional source of information about the steric structure of the complexes in the crystal.

Summarising the results of the investigations, we should note that, despite the small number of studies, NQR has proved useful as a very effective method for the investigation of molecular compounds. It is effective because NQR is directly related to the distribution of electron density among the bonds in the molecule. Even slight changes, as regards energy, in electron distribution are reflected in NQR spectroscopic parameters. From this point of view, the NQR method is very promising for chemical structure analysis.

The temperature variation of the frequencies and the asymmetry parameters is of great interest for the investigation of charge-transfer complexes. Recent studies have shown that these relations can yield information about the intra- and inter-molecular motions in crystals.

The review does not deal at all with the problem of the effects of complex formation on the spin–lattice (T_1) and spin–spin (T_2) relaxation times. The number of studies in this field is so far small. This branch of NQR spectroscopy has been scarcely applied in the study of molecular compounds.

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