Correlation of NQR and Chemical Bond Parameters *

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Nuclear quadrupole resonance is an effective spectroscopic method to investigate the charge
density distribution in solids. The range of compounds which may be investigated is wide, reaching
from a crystal lattice built up by an ordered arrangement of neutral molecules in the crystalline
material to ionic crystals and to metallic solids.

First the correlations between NQR quantities and bond parameters which become apparent
from the molecular orbital picture will be discussed, e.g. Hammett σ, $\varkappa$-parameter, ionic character i,
s-character, ionicity, electronegativity in their connection to NQR. Then, the correlations of NQR
frequencies, respectively nuclear quadrupole coupling constants, with bond lengths and bond angles
are considered.

Cross correlations, e.g. of NQR frequencies with bond distances, bond distances with vibrational
frequencies, and vibrational frequencies with NQR frequencies are discussed as are pK_A dependen-
cies of NQR parameters. The connection of $e\,\Phi_{zz}\,Q\,h^{-1}\,(^{14}N)$ in pharmaceuticals with their biolog-
ical activity is pointed out.

Introduction

There are many approaches to chemistry, the branch
of science which synthesizes and analyses molecules,
the chemical items. Chemists are faced with a multi-
branched (multidimensional) countable infinite set of
items, and each day the set grows by thousands of
them. The problem of the science "Chemistry" is, to
understand the relations, the elective affinities be-
tween the items which govern their phenomenology.
The ideal object of the theory of chemistry is, to find
the unified theory, the unified model of chemistry.
Presently it is, however, impossible to reach such a
goal; but to try paths towards it is our task. At the
time being, it ends up in a numerical solution of the
Hamiltonian, for each item a separate set of informa-
tion, based on results decoupled from functional inter-
dependences. The recognition of elective affinities, ex-
trapolating and interpolating "neighboring" items,
this is very difficult on such a basis. The other extre-
mum is the purely empirical way of collecting data
and compiling them in huge data banks which contain
all the information for anybody who primarily
whishes to be informed but not to know about the
backbone.

We think that a way in between is the only one to
get a system in the countable set of chemical items. It
is the experiment to recognize patterns in the sea of
information and to try to rationalize such patterns
according to laws based on first principles. Such a way
was followed up in chemistry since a long time. It is
the way to correlate elective affinities and items within
a functional dependence.

The discovery of the experimental access to hyper-
fine interactions between the nuclear electric quadru-
pole moment $e\,Q$ and an electric field gradient tensor
$\tilde{\Phi}_{ii}$, $i = x, y, z$, in solids by Dehmelt and Krüger [1–3]
and by Pound [4] in 1950 was immediately transferred
as a spectroscopic method to applications in the field
of Chemistry. Both experimental approaches, [1] and
[4], are today of equal importance in solid state chem-
istry, and the solid state is a necessary experimental
condition but by no means the crucial question. Pure
nuclear quadrupole resonance, NQR, [1] and nuclear
quadrupole interactions, studied in nuclear magnetic
resonance as a fine structure of the NMR spectrum [4]
are solely different in the experimental approach.
Large nuclear quadrupole interaction energies lead to
energy level separations of several MHz and up. Then
NQR is the preferable choice of experiment. In the
case of small nuclear quadrupole interaction energies
– level splittings of < 1 MHz – a drastic change in the
Boltzmann distribution of level population by appli-
cation of strong magnetic fields $\boldsymbol{B}_0$ to nuclear mag-
netic moments $\boldsymbol{\mu}$ in the solid and thereby a creation of
the situation $\mu\,B_0 \gg e\,\Phi_{zz}\,Q\,h^{-1}$ [4] is superior to

NQR. In the product describing the nuclear quadrupole coupling constant (NQCC), $e\Phi_{zz}Qh^{-1}$, e is the unit charge, Q the nuclear electric quadrupole moment, h the Planck constant, and Φ_{zz} the main principal axis of the electric field gradient tensor (EFGT) $\tilde{\Phi}_{ii}$, $i = x, y, z$. The continuous progress in the development of high field superconducting magnets should push the study of weak nuclear quadrupole interactions in future.

The reason for applying NQR and the study of the quadrupole induced fine structure of NMR, QFS-NMR, as a spectroscopic method to chemistry is obvious. The energy level scheme and therefrom the observable energy differences are connected in a very simple way with the basic observables of quantum chemistry, the electron distribution $\varrho(x, y, z)\,d\tau$.

$$e\Phi_{zz}Qh^{-1} \propto \int_0^\infty \varrho(x, y, z)\,d\tau/r^3. \qquad (1)$$

The knowledge of $\varrho(x, y, z)\,d\tau$ is the key to the understanding of chemical bond, and no other spectroscopic method besides microwave spectroscopy gives such a direct access to it than NQR. The determination of the electric field gradient tensor is the result of both methods. Therefrom the charge distribution will be derived, and vice versa, see (1).

Here, we are not concerned with microwave spectroscopy, which is restricted to the gaseous phase and to rather simple chemical items out of the infinite set.

Speaking about NQR, we restrict ourselfes to the solid state. The information on nuclear quadrupole interactions one gaines from matter in the liquid state or in the partially ordered liquid state (liquid crystals) we shall not discuss, besides their interesting potentialities for evaluating the acting electric field gradient tensors, EFGT's.

In the following, we shall consider first NQR as a spectroscopic method in the chemistry of molecules which are, for experimental convenience, condensed into the solid state. Then, the intermolecular forces in the solid state can be regarded as weak perturbations of the chemical bond in the individual molecules. Such an approximation is, from the viewpoint of thermodynamics, an allowed one. The molar enthalpies of sublimation (the lattice energy) $\Delta \bar{H}_s$ of crystals composed of uncharged, diamagnetic molecules are a few percent of the molar enthalpies $\Delta \bar{H}_f$ of molecule formation.

In a second step, we shall consider the answers NQR and QFS-NMR offer for solids built up from charged molecules and atoms (ions). Weak nuclear quadrupole interaction energies are observed and, in the limit of ionic crystals, $e\Phi_{zz}Qh^{-1}$ is solely determined by interionic fields. There is, of course, a continuous transition from one extreme situation to the other. Several orders of magnitude in the electric field gradient, EFG, main principal axis Φ_{zz} may be acting on a nucleus. For example we consider the iodine atom: $e\Phi_{zz}Qh^{-1}({}^{127}I)$ is in the order of a few MHz in AgI and of two GHz in solid iodine.

The literature on NQR and QFS-NMR is numerous. Extensive treatments of experimental and theoretical aspects of NQR are given by Das and Hahn [5] and by Lucken [6]. QFS-NMR is thouroughly discussed by Cohen and Reif [7]. Compilations of NQR data have been published by Semin, Babushkina, and Yakobson [8] and by Chihara and Nakamura [9].

Correlations of NQR and Intramolecular Bond Parameters

Before the work of Dehmelt and Krüger [1–3] and Pound [4], there was already a theoretical guide available to correlate NQR frequencies and nuclear quadrupole coupling constants, NQCC, to models of the chemical bond. This guide was given by Townes and Dailey in their pioneer work [10, 11]. Relaying on a Molecular Orbital "Ansatz" they developed a simple relation between the nuclear quadrupole coupling constant $e\Phi_{zz}Qh^{-1}$, the s-character s of a single bond the atom in question is forming with its partner, the ionic character i of this bond, and the double bond character π of the bond. An extensive discussion of the Townes-Dailey theory [10, 11] is given in [5, 6, 8]. In the case of carbon-halogen bonds (C–Cl, C–Br) one finds [12]

$$(e\Phi_{zz}Qh^{-1})_{\text{exp}}/(e\Phi_{zz}Qh^{-1})_{\text{at}}$$
$$= (1 - i - \pi)(1 - s) + \tfrac{1}{2}\pi(1 + c). \qquad (2)$$

The double bond character can be found from [13]:

$$\eta = (3/2)\,\pi(1 + c)(e\Phi_{zz}Qh^{-1})_{\text{at}}/(e\Phi_{zz}Qh^{-1})_{\text{exp}}. \qquad (3)$$

η is the asymmetry parameter of the EFG tensor, available from single crystal Zeeman split NQR experiments in Cl and Br NQR spectroscopy,

$$\eta = |\Phi_{xx} - \Phi_{yy}|/|\Phi_{zz}|. \qquad (4)$$

For Cl $(e\Phi_{zz}Qh^{-1})_{\text{at}}$ is 109.6 MHz and for bonds C–Cl the correction factor c is 0.15. Therefrom one
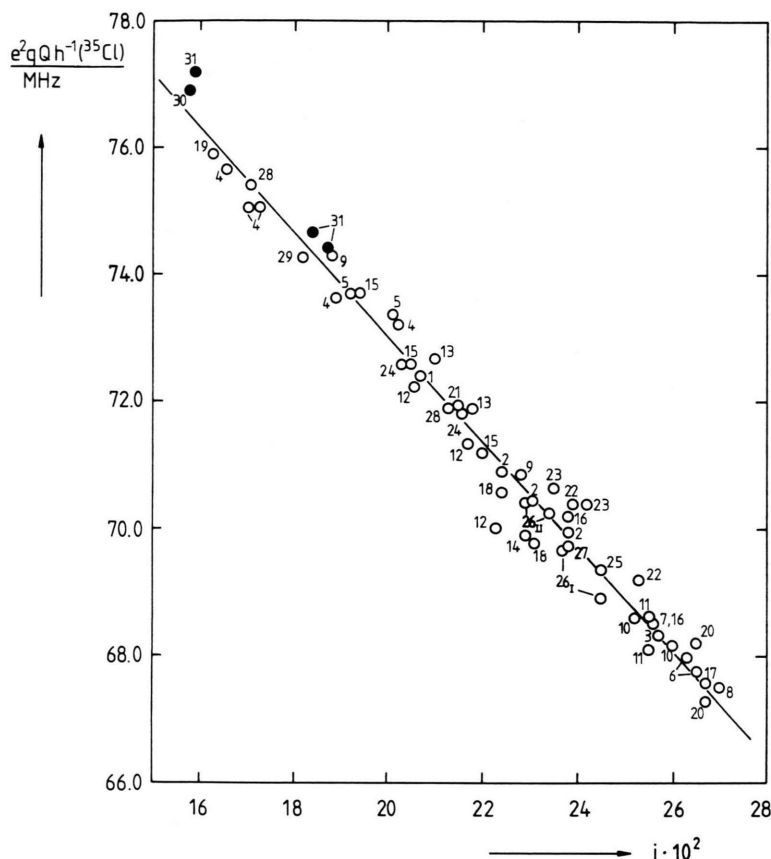
Fig. 1. Correlation between the nuclear quadrupole coupling constant of ^{35}Cl and the ionic character of the C–Cl bond in chlorobenzenes. The numbering corresponds to that in Table 1. The correlation is given by ($\Phi_{zz} \equiv eq$)

$$e\,\Phi_{zz}\,Q\,h^{-1}\,(^{35}Cl)/MHz = 89.559 - 82.5\,i.$$

finds

$$\pi = [(e\,\Phi_{zz}\,Q\,h^{-1})_{exp}/MHz]\cdot\eta/189.06 \quad (5)$$

and with (3)

$$i = 1 - 0.324\,\pi - [(e\,\Phi_{zz}\,Q\,h^{-1})_{exp}/MHz]/93.16. \quad (6)$$

An example for the correlation between the ionic character i and the NQCC of ^{35}Cl in benzene derivatives we show in Fig. 1. For 31 compounds, $e\,\Phi_{zz}\,Q\,h^{-1}(^{35}Cl)$ is plotted as a function of i; the relation is derived from the ^{35}Cl-NQR Zeeman experiment via (5) and (6). The numbers in Fig. 1 correspond to the numbers in Table 1. We here point out that the correlation shown in Fig. 1 is based on single crystal Zeeman NQR spectroscopy only.

There is a rather simple relation between the ionic character i of a single bond A–B and the electronegativity of the atoms involved, X_A and X_B [51]:

$$i = 1/2\,|X_A - X_B|. \quad (7)$$

Figure 2 shows the results for halogenides AB reported by Townes and Dailey [10] and by Gordy [51]. The

ionic character of the bond A–B was calculated by the authors from microwave spectroscopic data.

The relation (7) can be successfully applied in many cases if the electronegativities are kown. Several NQR-studies (experimental and theoretical) on the correlation between the ionic character i of a bond and the electronegativity difference of the partners are reported, e.g. for compounds MX_4, M = group IVa-element, B = halogen atom [52–54], see also [6], [8]. Not very advanced is the theory of group electronegativities. Anyway, tables of empirical data are scare. Since, however, the empirical correlations show that the ionic character of a bond A–R increases with the sum of the electronegativities of the atoms in a complex group R, it may be worthwhile to determine from an experimental NQR-ionicity correlation group electronegativities. Taking advantage of (7), Miyagawa [55] has correlated $e\,\Phi_{zz}\,Q\,h^{-1}(^{35}Cl)$ measured on aliphatic chlorohydrocarbons with calculated electric dipole moments μ and found a linear correlation

$$e\,\Phi_{zz}\,Q\,h^{-1}(^{35}Cl) = a + b\,|\mu|. \quad (8)$$

Table 1. $e\Phi_{zz}Qh^{-1}$ (^{35}Cl) (in MHz) and η(^{35}Cl) for chlorobenzene derivatives found from single crystal Zeeman-split NQR spectroscopy. All data used, were measured at room temperature. The double bond character π is calculated with the aid of (5), and then i by (6). Additionally the $\varkappa_i$-values (in MHz) [14, 15, 16] are listed. Not included are low temperature investigations on para-dichlorobenzene [17], ortho-dichlorobenzene [18], hexachlorobenzene [19], 1,2,3-trichlorobenzene [20], parachloroaniline [21], and parachlorobenzyl chloride [21].

No.	Substance		e^2qQh^{-1}	η	$\sum_i \varkappa_i$	$\pi \cdot 10^2$	$i \cdot 10^2$	Ref.
1	1,2,4,5-Cl$_4$C$_6$H$_2$		72.412	0.125	2.034	4.8	20.7 [a]	[22]
2	1,3,5-Cl$_3$C$_6$H$_3$		69.946	0.09	0.998	3.3	23.8 [a]	[23]
			70.450	0.11	0.998	4.1	23.1	
			70.920	0.12	0.998	4.5	22.4	
3	4-ClC$_6$H$_4$CO$_2$H		68.327	0.08	0.409	2.9	25.7	[24]
4	C$_6$Cl$_5$OH	Cl$^{(3)}$	75.689	0.167	3.858	6.7	16.6 [a]	[25]
		Cl$^{(4)}$	75.073	0.185	3.513	7.4	17.0	
		Cl$^{(2)}$	75.084	0.164	3.513	6.5	17.3	
		Cl$^{(1)}$	73.635	0.163	2.982	6.4	18.9	
		Cl$^{(5)}$	73.218	0.100	2.982	3.9	20.2	
5	C$_6$Cl$_4$(OH)$_2$	Cl$^{(1)}$	73.381	0.09	2.756	3.5	20.1 [a]	[26]
		Cl$^{(2)}$	73.713	0.13	2.756	5.1	19.2	
6	2,5-Cl$_2$C$_6$H$_3$NH$_2$	Cl$^{(2)}$	67.746	0.069	0.029	2.5	26.5 [a]	[27]
		Cl$^{(5)}$	67.971	0.066	0.314	2.4	26.3	
7	1,4-Cl$_2$C$_6$H$_4$		68.477	0.073	0.329	2.6	25.6 [a]	[28]
8	4-ClC$_6$H$_4$NH$_2$		67.507	0.049	−0.470	1.8	27.0	[28]
9	2,5-Cl$_2$C$_6$H$_3$NO$_2$	Cl$^{(2)}$	74.310	0.11	2.975	4.3	18.8	[29]
		Cl$^{(5)}$	70.864	0.09	1.266	3.4	22.8	
10	4-ClC$_6$H$_4$OH		68.183	0.071	0.249	2.6	26.0	[30]
			68.595	0.096	0.249	3.5	25.2	
11	4-Cl-3-CH$_3$C$_6$H$_3$OH		68.644	0.07	−0.143	2.5	25.5	[31]
			68.117	0.12	−0.143	4.3	25.5	
12	2,4,6-Cl$_3$C$_6$H$_2$OCH$_3$							
		p-Cl	70.019	0.21	1.186	7.8	22.3	[32]
		o-Cl	71.369	0.14	1.756	5.3	21.7	
		o-Cl	72.236	0.15	1.756	5.7	20.6	
13	3,4-Cl$_2$C$_6$H$_3$NO$_2$	Cl$^{(4)}$	72.683	0.08	2.143	3.1	21.0	[33]
		Cl$^{(3)}$	71.903	0.08	1.787	3.0	21.8	
14	4-Cl-2-NO$_2$C$_6$H$_3$O		69.914	0.17	1.186	6.3	22.9	[34]
15	2,4,6-Cl$_3$C$_6$H$_2$CN	Cl$^{(4)}$	71.208	0.130	1.476	4.9	22.0 [a]	[35]
		Cl$^{(2)}$	72.592	0.128	2.114	4.9	20.5	
		Cl$^{(6)}$	73.717	0.116	2.114	4.5	19.4	
16	2,4-Cl$_2$C$_6$H$_3$NHCOCH$_3$							
		Cl$^{(2)}$	70.199	0.07	1.256	2.6	23.8	[36]
		Cl$^{(4)}$	68.534	0.07	0.694	2.5	25.6	
17	5-Cl-2-OCH$_3$C$_6$H$_3$NH$_2$		67.574	0.065	0.096	2.3	26.7	[37]
18	2,6-Cl$_2$-4-NO$_2$C$_6$H$_2$NH$_2$		69.772	0.165	0.966	6.1	23.1 [a]	[38]
			70.578	0.155	0.966	5.8	22.4	
19	2,6-(NO$_2$)$_2$C$_6$H$_3$Cl		75.915	0.170	4.398	6.8	16.3	[39]
20	3-Cl-C$_6$H$_4$NHCOCH$_3$		68.196	0.03	0.373	1.1	26.5	[40]
			67.281	0.09	0.373	3.2	26.7	
21	3,5-Cl$_2$C$_6$H$_3$NO$_2$		71.948	0.105	1.436	4.0	21.5	[41]
22	2,5-Cl$_2$C$_6$H$_3$NHCOCH$_3$							
		Cl$^{(2)}$	70.405	0.04	1.086	1.5	23.9	[42]
		Cl$^{(5)}$	69.194	0.04	0.702	1.5	25.3	
23	2,5-Cl$_2$-4-NO$_2$C$_6$H$_2$NH$_2$							
		Cl$^{(2)}$	70.391	0.020	0.796	0.7	24.2	[43]
		Cl$^{(5)}$	70.656	0.055	2.883	2.1	23.5	
24	2,3,6-Cl$_3$C$_6$H$_2$OCOCH$_3$							
		Cl$^{(3)}$	71.824	0.1037	2.000	3.9	21.6 [a]	[44]
		Cl$^{(6)}$	71.977	0.1015	1.843	3.8	21.5	
		Cl$^{(2)}$	72.591	0.1423	2.720	5.5	20.3	
25	3-Cl-4-OCH$_3$C$_6$H$_3$NH$_2$		69.357	0.085	0.666	3.1	24.5	[45]
26	2,6-Cl$_2$C$_6$H$_3$NHCOCH$_3$(II)							
		Cl$^{(2)}$	70.435	0.1214	1.256	4.5	22.9 [a]	[46]
		Cl$^{(6)}$	70.244	0.1013	1.256	3.8	23.4	
(Phase I)		Cl$^{(2)}$	69.674	0.1293	1.256	4.8	23.7	
		Cl$^{(6)}$	68.890	0.1307	1.256	4.8	24.5	
27	1-Cl-3-NO$_2$C$_6$H$_4$		69.745	0.1091	0.937	4.0	23.8 [a]	[47]
28	1,2-Cl$_2$-3-NO$_2$C$_6$H$_3$							
		Cl$^{(1)}$	71.892	0.1287	2.143	4.9	21.3 [a]	[48]
		Cl$^{(2)}$	75.436	0.1525	3.852	6.1	17.1	
29	1-Cl-2,4-(NO$_2$)$_2$C$_6$H$_3$		74.287	0.1636	3.227	6.4	18.2 [a]	[49]
30	1,2,4,5-Cl$_4$-3,6-(NO$_2$)$_2$C$_6$		76.937	0.1207	4.723	4.9	15.8 [a]	[50]
31	1,3,5-Cl$_3$-2,4-(NO$_2$)$_2$C$_6$H							
		C$^{(1)}$	74.672	0.1097	3.310	4.3	18.4 [a]	[50]
		Cl$^{(3)}$	77.167	0.0969	4.502	4.0	15.9	
		Cl$^{(5)}$	74.422	0.1143	3.310	4.5	18.7	

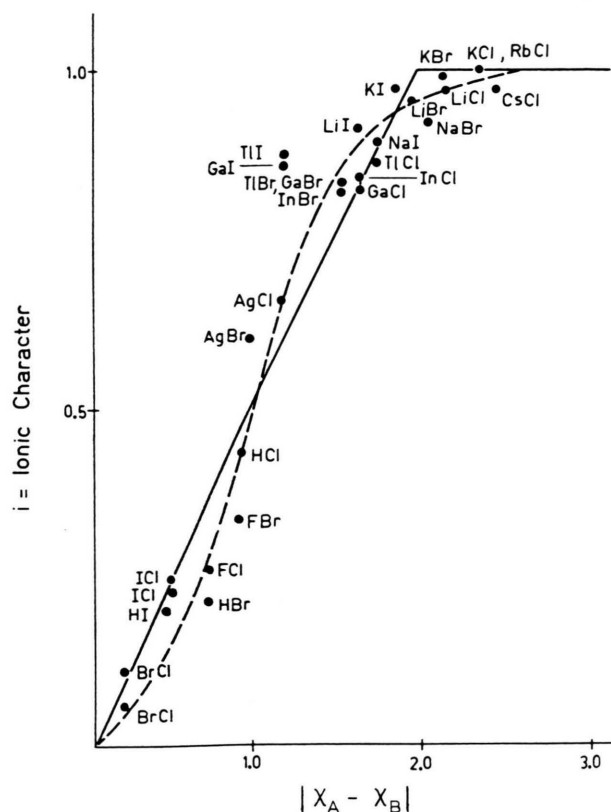[a] Crystal structure is reported in literature.

Fig. 2. Ionic character of the bond A−B in diatomic molecules as a function of the electronegativity difference $|X_A - X_B|$ of the partners A and B [10], [51].

Equation (8) is, however, only a first order approximation, as many correlations are. Modifications of this relation have been observed; they result from crystal field effects (see below) and, as with the melting points of alkanes, the influence of even-odd number of carbon atoms appears in ^{35}Cl-NQR [56, 57].

NQR and Hammett σ Parameters

Probably the most frequently applied correlation of NQR data with chemical bond parameters is the relation between the NQR frequency, respectively the NQCC, and the Hammett σ parameter. σ is determined from equilibrium, or from reaction rate constants K via

$$\log(K/K_0) = \Gamma \sigma \tag{9}$$

Γ is characteristic for the reaction under investigation (dissociation of an acid, saponification of an ester,

etc.). σ characterizes the substituent in a molecule. The Hammett model was originally put foreward for applications to substitutions on the aromatic ring and there to meta- and para-substitution. Meal [58], in the spring days of NQR, first correlated Hammett σ with the NQR frequencies and found a linear relation

$$\nu(^{35}\text{Cl}) = a + b\sigma \tag{10}$$

for monochlorobenzenes $\text{ClC}_6\text{H}_4\text{X}$. Bray [59, 60] extended the correlation to monobromobenzenes, and then it was generalized to polyhalogenobenzenes by Bray and his colleagues and by others [61–64]. For the large number of compounds

$$\nu(^{35}\text{Cl})/\text{MHz} = 34.826 + 1.024 \sum_i \sigma_i \tag{11}$$

resulted [61]. The interpretation of (11) is:

1) The change of $\nu(^{35}\text{Cl})$ (and $\nu(^{79,\,81}\text{Br})$, $\nu(^{127}\text{I})$, etc.) is characteristic for a certain substituent; it is constant and independent of the presence of other substituents on the benzene ring. The effect of multiple substitution is additive (additivity rule).

2) In contrast to the Hammett equation, the additivity rule holds for substituents ortho to the atom, which incorporates the NQR nucleus, too.

Biedenkapp and Weiss [14] have introduced substituent parameters which are derived directly from $\nu(^{35}\text{Cl})$

$$\nu(^{35}\text{Cl}) = \nu_0 + \sum_i \varkappa_i, \tag{12}$$

and applied (12) to a large number of benzene derivatives. The logic of such a definition of a correlation parameter lies in the fact that Hammett σ is derived from reaction rates, whereas the kappa values are true ground state parameters (NQR is a measurement on a ground state molecule, respectively solid). Extensions of the $\nu(\text{NQR})$-σ-relation for heterocyclic compounds and for aliphatic systems have been reported in [65–70].

In case of $I = 3/2$, from "common" NQR spectroscopy the frequency $\nu(I = 3/2)$ is the observable. Since for $^{35,\,37}$Cl and for $^{79,\,81}$Br single bonds R-halogen is the frequent connections, η is mostly < 0.2, and from

$$\nu(I = 3/2) = (1/2)\,e\,\Phi_{zz}\,Q\,h^{-1}\,(1 + \eta^2/3)^{1/2} \tag{13}$$

$\nu \approx (1/2)\,e\,\Phi_{zz}\,Q\,h^{-1}$ follows. For all other quadrupolar nuclei, $I = 1$ and $I \geqq 3/2$, $e\,\Phi_{zz}\,Q\,h^{-1}$ is available from the experiment on polycrystalline material.

The model of Taft, to divide σ in an inductive (σ_I) and a resonance (σ_R) term, and its application to NQR

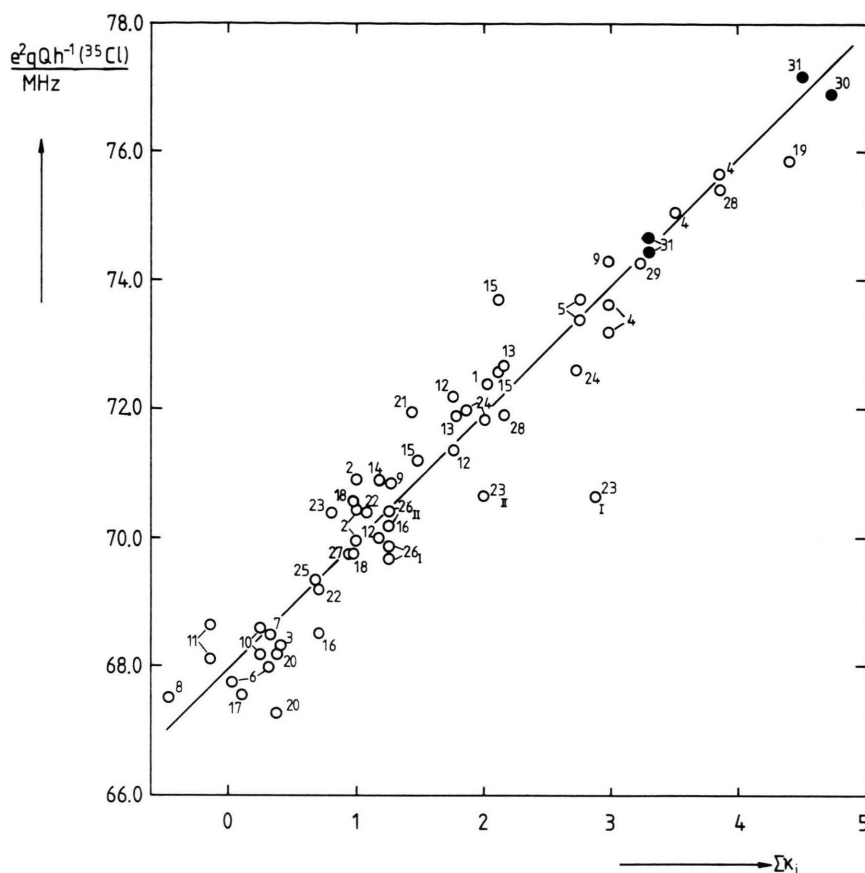Fig. 3. Nuclear quadrupole coupling constants $e\,\Phi_{zz}Q\,h^{-1}$ (^{35}Cl) of substituted chlorobenzenes vs. the substitution parameter $\varkappa_i$. The numbers given in the Figure correspond to the numbering in Table 1. The least squares fit gives ($\Phi_{zz} \equiv e\,q$)

$$e\,\Phi_{zz}Q\,h^{-1}(^{35}\text{Cl})/\text{MHz}$$
$$= 67.974 + 1.9\sum_i \varkappa_i .$$

is discussed in literature at lengths, see e.g. [14, 6, 8].

We have a look on an $e\,\Phi_{zz}Q\,h^{-1}$ (^{35}Cl)$-\varkappa_i$ correlation. For the compounds listed in Table 1, the $\varkappa_i$ values calculated from the data in [15, 16] are given, too. In Fig. 3 the $e\,\Phi_{zz}Q\,h^{-1}$ (^{35}Cl) are plotted vs. $\sum_i \varkappa_i$. The correlation found is quite satisfying. As in Fig. 1, the correlation given in Fig. 3 is based on single crystal Zeeman NQR spectroscopy.

It is interesting to compare Fig. 1 with Fig. 3. The striking feature is the stronger scattering of the data (the less satisfying correlation) shown in Fig. 3 compared to Fig. 1. Particularly the sum of the $\varkappa_i$ for compounds no. 20 and 23 (Table 1) is deviating from the correlation line. The cause may be twofold,

a) the $\varkappa_i$ for several substituents relay on a few measurements only and therefore the error may be large and

b) the $\varkappa_i$ for groups which have a rotational degree of freedom with respect to the aromatic ring may depend on a twist angle α with respect to this plane. The same arguments hold for the σ values.

The correlation $e\,\Phi_{zz}Q\,h^{-1} = f$(Hammett σ) is not restricted to single bond atoms, working quite well e.g. for nitrogen. This is shown in Fig. 4, where $e\,\Phi_{zz}Q\,h^{-1}$ (^{14}N) is plotted vs. $\sum \sigma_i$ for a considerable number of molecules. The numbered compounds in Fig. 4 are listed in Table 2.

In summary, we can say that nuclear quadrupole resonance frequencies (or $e\,\Phi_{zz}Q\,h^{-1}$) correlate well with empirical bond parameters, such as ionicity, electronegativity, Hammett σ, and the $\varkappa$-parameters.

NQR and Bond Geometry

As already discussed, the direct connection of the EFG tensor with another observable is the dependence of $e\,\Phi_{zz}Q\,h^{-1}$ on the charge distribution around the nucleus considered. The most simple outcome of (1) is, in "pure" ionic crystals, the point charge model which, however, has to be modified by the antishielding (Sternheimer factor). Nevertheless, Φ_{zz} is a func-
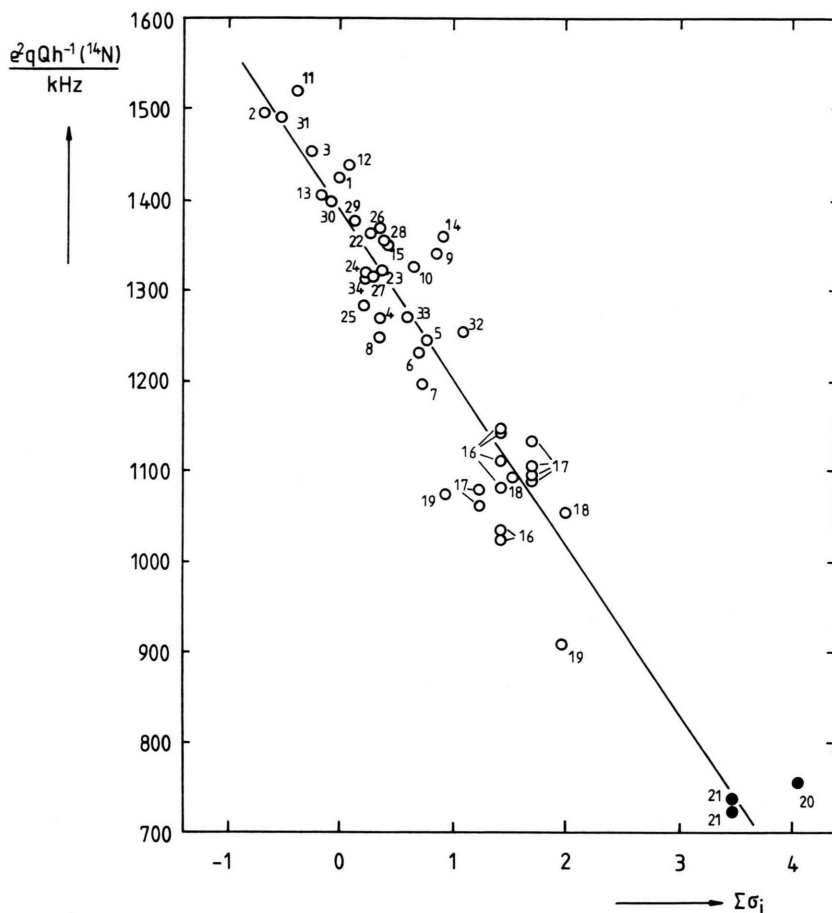
Fig. 4. Nuclear quadrupole coupling constant $e\Phi_{zz}Qh^{-1}(^{14}N)$ of substituted nitrobenzenes vs. Hammett-σ parameters. The numbers given in the Figure correspond to the numbering in Table 2. The least squares fit gives ($\Phi_{zz} \equiv eq$)

$$e\Phi_{zz}Qh^{-1}(^{14}N)/MHz = 1.388 - 0.18 \sum_i \sigma_i.$$

tion of the distance r of all the charges acting via the EFG at the nucleus, and $\Phi_{zz} = f(r^{-3})$.

It is appropriate to apply (1) to molecules condensed into a solid, too, and to relate simply the EFG (or in first approximation the NQR frequency) to the intramolecular distance $d(R-X)$, where X is the quadrupolar nucleus and R the rest of the molecule. In case X is a group of atoms, e.g. $-NO_2$, the orientation of this group with respect to R may also influence the acting EFGT.

NQR and Bond Distances

To correlate NQR with bond distances, the crystal structure of the compound under investigation must be known. This is a somewhat limiting condition; quite often the structure one is looking for is not available in literature. Furthermore, the difficulty lies in the accuracy of bond distance determinations. As an example,

we consider C—Cl bonds in the group $-CCl_3$ (sp³-carbon). In the molecule trichloroethylidene trichlorolactic ester (Chloralide), $Cl_3CCHOCOCHOCCl_3$, there are two CCl_3 groups; the six chlorines are crystallographically independent, that is, one finds six distances $d(C-Cl)$ [93]. They are observed in the range $175.8 \leqq d/pm \leqq 176.5$ (±0.4). $e\Phi_{zz}Qh^{-1}(^{35}Cl)$ at $T = 21$ °C is in the range $76.053 \leqq e\Phi_{zz}Qh^{-1}(^{35}Cl)/MHz \leqq 78.790$ (±0.006) [94]. It is easy to see that the spread in $d(C-Cl)$ is 0.7 pm $\pm$ 0.4 pm whereas the spread in $e\Phi_{zz}Qh^{-1}(^{35}Cl)$ is 2.737 ± 0.006 MHz. A correlation $e\Phi_{zz}Qh^{-1}(^{35}Cl) = f(1/d^3(C-Cl))$ was tried, but with very little success as can be seen in Figure 5.

It seems to be rather difficult, too, to correlate $d(C-Cl)$ in benzenoid systems with $\nu(^{35}Cl)$ or with $e\Phi_{zz}Qh^{-1}(^{35}Cl)$.

A different situation occurs if one considers bond distances $d(C-Cl)$ where C is a true sp²-carbon.

No.	Compound	$e\Phi_{zz}Qh^{-1}(^{14}N)$	$\eta(^{14}N)$	α	$\Sigma\sigma$	Ref.
1	$C_6H_5NO_2$	1425	0.404	0	0	[71, 72]
2	$4\text{-}(NO_2)C_6H_4NH_2$	1493	0.292	1.9	−0.66	[71, 73]
3	$3\text{-}(NO_2)C_6H_4NH_2$	1453	0.374	2.0	−0.15	[71, 74]
4	$3\text{-}ClC_6H_4NO_2$	1271	0.356	0	0.37	[71, 47]
5	$1,4\text{-}(NO_2)_2C_6H_4$	1246	0.326	11.0	0.78	[71, 75]
6	$1,3\text{-}(NO_2)_2C_6H_4$	1232	0.360	13.0	0.71	[71, 76]
7	$4\text{-}(NO_2)C_6H_4CO_2H$	1196	0.284	13.7	0.73	[77, 78]
8	$3\text{-}(NO_2)C_6H_4CO_2H$	1249	0.375	5.3	0.37	[77, 79]
				21.7		
9	$4\text{-}(NO_2)C_6H_4COCH_3$	1341	0.361	3.6	0.87	[77, 80]
10	$4\text{-}(NO_2)C_6H_4CN$	1327	0.363	10.3	0.66	[77, 81]
11	$4\text{-}(NO_2)C_6H_4OH$	1523	0.357	1.5	−0.37	[77, 82]
12	$3\text{-}(NO_2)C_6H_4OH$	1469	0.347	0.5	0.12	[77, 83]
13	$4\text{-}(NO_2)C_6H_4CH_3$	1406	0.408	3.0	−0.17	[77, 84]
13 a	$4\text{-}(NO_2)C_6H_4CH_3$	1340	0.408			[77 a, 84]
14	$2\text{-}(NO_2)C_6H_4OH$	1363	0.307	1.6	0.89	[77, 85]
15	$1,3,5\text{-}(CH_3)_3C_6H_2(NO_2)$	1353	0.163	66.4	0.41	[86, 87]
16	$1,3,5\text{-}(NO_2)_3C_6H_3$	1145	0.352	10.0	1.42	[88, 89]
		1140	0.359	10.0	1.42	
		1111	0.355	5.0	1.42	
		1083	0.351	3.0	1.42	
		1035	0.416	8.0	1.42	
		1024	0.250	28.0	1.42	
17	$2,4,6\text{-}(NO_2)_3C_6H_2CH_3$	1107	0.136	59.5	1.71	[88, 90]
	orthorhomb. phase	1134	0.167	50.9	1.71	
		1085	0.166	45.7	1.71	
		1095	0.200	41.3	1.71	
		1060	0.255	32.8	1.25	
		1079	0.284	22.3	1.25	
18	$1,3,5\text{-}(NO_2)_3\text{-}2,4\text{-}(CH_3)_2C_6H$	1054	0.120	75.2	2.00	[88, 90]
		1097	0.232	35.7	1.54	
19	$2,4\text{-}(NO_2)_2C_6H_3Cl$	910	0.222	41.9	1.97	[49, 49]
		1076	0.303	12.3	0.94	
20	$1,2,4,5\text{-}Cl_4C_6(NO_2)_2$	757	0.025	90.0	4.04	[50, 92]
21	$1,3,5\text{-}Cl_3C_6H\text{-}2,4\text{-}(NO_2)_2$	722	0.069	79.7	3.46	[50, 92]
		738	0.064	87.6	3.46	
22	$4\text{-}IC_6H_4NO_2$	1363	0.364		0.28	[71, −]
23	$3\text{-}(NO_2)C_6H_4CHO$	1324	0.366		0.36	[71, −]
24	$4\text{-}ClC_6H_4NO_2$	1321	0.406		0.23	[71, −]
25	$4\text{-}(NO_2)C_6H_4CHO$	1284	0.333		0.22	[71, −]
26	$3\text{-}(NO_2)C_6H_4COCH_3$	1369	0.391		0.38	[77, −]
27	$4\text{-}(NO_2)C_6H_4COOCH_3$	1315	0.406		0.31	[77, −]
28	$3\text{-}(NO_2)C_6H_4COOCH_3$	1357	0.389		0.39	[77, −]
29	$3\text{-}(NO_2)C_4H_4CH=CHCO_2H$	1378	0.402		0.14	[77, −]
30	$3\text{-}(NO_2)C_6H_4CH_3$	1400	0.400		−0.07	[77, −]
31	$2,6\text{-}(CH_3)_2\text{-}4\text{-}(NO_2)C_6H_2OH$	1492	0.319		−0.51	[77, −]
32	$2\text{-}Cl\text{-}4\text{-}(NO_2)C_6H_3CO_2H$	1254	0.330		1.10	[77, −]
33	$2\text{-}Cl\text{-}5\text{-}(NO_2)C_6H_3COOH$	1271	0.343		0.60	[77, −]
34	$2\text{-}Cl\text{-}4\text{-}(NO_2)C_6H_3CH_3$	1317	0.372		0.20	[77, −]

Table 2.
$e\Phi_{zz}Qh^{-1}(^{14}N)$, in kHz, and $\eta(^{14}N)$ for nitrobenzene derivatives. α is the twist angle of the NO_2-group with respect to the benzene ring. No. 13 a, 19−21 are based on single crystal QFS-NMR studies at room temperature, all other on NQR measurements at 77 K. The σ-values are taken from [16]. The first reference in the table belongs to the NQR- or QFS-NMR work, the second to crystal structure determinations.
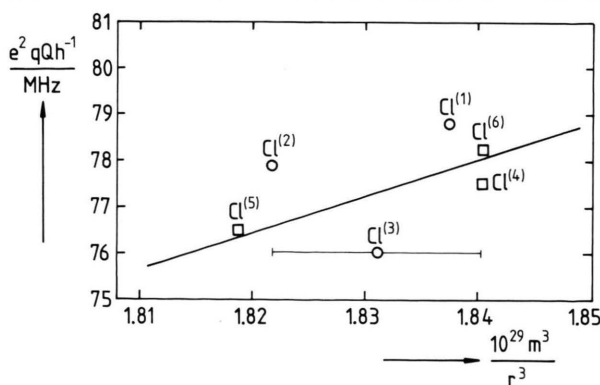

Fig. 5. $e\Phi_{zz}Qh^{-1}(^{35}Cl^{(1-6)})$ in trichloroethylidene trichlorolactic ester, $Cl_3C\underline{C}HOCOCOCHOCCl_3$, versus the reciprocal third power of the bond distances $d(C-Cl^{(1-6)})$. The mean error in d^{-1} is shown in the graph as an error bar ($\Phi_{zz}\equiv eq$).
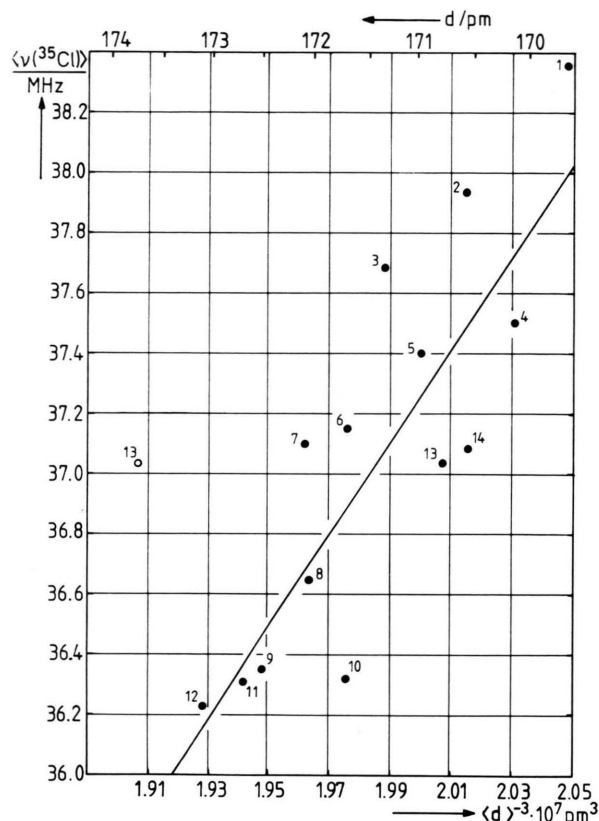
Fig. 6. Average ^{35}Cl NQR frequency $\langle v(^{35}\text{Cl})\rangle$ of chloro-cyclohexadienones vs. $1/d^3$(C–Cl) in these compounds. The open circle no. 13 corresponds to an early crystal structure determinaion. The filled circle no. 13 is found from a recent refinement of the crystal structure determination [96]. Compounds corresponding to the given numbers: 1) 2,3-dichloro-5,6-dicyano-p-benzoquinone; 2) 2,3,4,4,5,6-hexachloro-2,5-cyclohexadiene-1-one; 3) 2,3,4,4-tetrachloro-1-oxo-1,4-di-hydronaphthaline (β-TKN); 4) 2,3,5,6-tetrachloro-p-benzo-quinone (chloranil); 5) chloranil · perylene; 6) 2,5-dichloro-3,6-dihydroxy-p-benzoquinone; 7) 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthaline (α-TKN); 8) 2,4,4,6-tetrachloro-2,5-cyclohexadiene-1-one; 9) 2,4,4-trichloro-1,4-dihydronaphth-[1,8-cd]isothiazole-1,1-dioxide (TCNS); 10) 2,5-dichloro-p-benzoquinone; 11) 2,6-dichloro-p-benzoquinone; 12) 2,4,4,6-tetrachloro-3,5-dimethyl-2,5-cyclohexadiene-1-one; 13) 2,3-dichloro-1,4-napthoquinone (phase I); 14) 2,3-dichloro-1,4-naphthoquinone (phase II).

Several chlorocyclodienones have been studied and $v(^{35}\text{Cl})$ was correlated with d(C–Cl) [95]. A linear correlation results, shown in Fig. 6, which includes some very recent results.

In Fig. 6 there are two points (both with no. 13) shown for 2,3-dichloro-1,4-naphthoquinone (phase I, C_i^1-P$\bar{1}$). The breakdown of the correlation $v(^{35}\text{Cl}) = f(d^{-3}$ (C–Cl)) led us to a refinement of the crystal structure with good results [96]; the point no. 13 in

Fig. 6 nearer to the regression line results from the refinement of the crystal structure determination.

There are many correlation studies, halogen-NQR as a function of bond distances, on bonds R–X, where X is a halogen and R may contain carbon atoms, but not directly connected to the atom X. Scaife and his colleagues related d(R–X) to a number of radicals R [97] such as R–Cu^{II}–Cl [98] etc. NQR experiments on halogeno complexes of Cu^{II} and Zn^{II} are discussed in [99], bonds R–Hg–Cl are extensively treated in [100].

In compounds with halogen bound to group V atoms, Keat et al. [101] have studied the ^{35}Cl NQR as a function of d (P–Cl) in cyclophosphazenes. Ishihara [102] investigated complexes with SbCl$_3$ and found a relation between $v(^{35}\text{Cl})$ and d(Sb–Cl). The ^{35}Cl NQR frequencies in five-membered ring chelate derivatives of antimony pentachloride were related to d(Sb–Cl) by Gerard-Dion and Lucken [103]; they found a linear relation, $v(^{35}\text{Cl}) = a - b \cdot d$ (Sb–Cl).

From literature data of $v(^{127}\text{I})$, (transition $m = \pm 1/2 \leftrightarrow m = \pm 3/2$) in salts MI$_3$, a correlation of the distance d(terminal I–central I) in the I$_3$-ion and the NQR frequency was found by Yoshioka et al. [104].

The group of compounds most widely chosen by NQR spectroscopists for a variety of investigations, are the hexahalogeno compounds with the K$_2$PtCl$_6$ type crystal structure (or similar packing). Particularly Sn^{IV} as the central atom is favoured because an octahedral coordination appears also in molecular complexes SnX$_4$ · 2 L, where L is a neutral ligand. Additionally, the frequency range of ^{35}Cl NQR is in a convenient experimental range. Feshin et al. [105] found a correlation between the bond distances d (Ge–Cl) and v (^{35}Cl) in compounds Cl$_3$GeR, and Huggett et al. [106] have observed that in compounds M$_2$SnCl$_6$ and SnCl$_4$ · 2 L the distance d (Sn–Cl) correlates well with $v(^{35}\text{Cl})$, v (^{35}Cl) $= a - b \cdot d$ (Sn–Cl). In this correlation, the range of bond lengths was $231 \leq d$ (Sn–Cl)/pm ≤ 247. We have studied recently a large variety of compounds with bonds Sn–Cl [107]. The range of d (Sn–Cl) covered is $231 \leq d$ (Sn–Cl)/pm ≤ 272; hexachloro salts [SnCl$_6$]$^{2-}$, pentachloro salts (SnCl$_5$R)$^{2-}$, compounds [SnCl$_{4-x}$R$_x$] · 2 L, and molecules SnCl$_{4-x}$R$_x$ are included. The result is shown in Figs. 7 and 8. The correlation is quite satisfying. On comparing Fig. 7 with Fig. 8, we note that the least squares regression lines differ only little for a plot v (^{35}Cl) $= f(1/d^3)$ and v (^{35}Cl) $= \phi(d)$. This is understandable if one takes the short range of d(Sn–Cl)
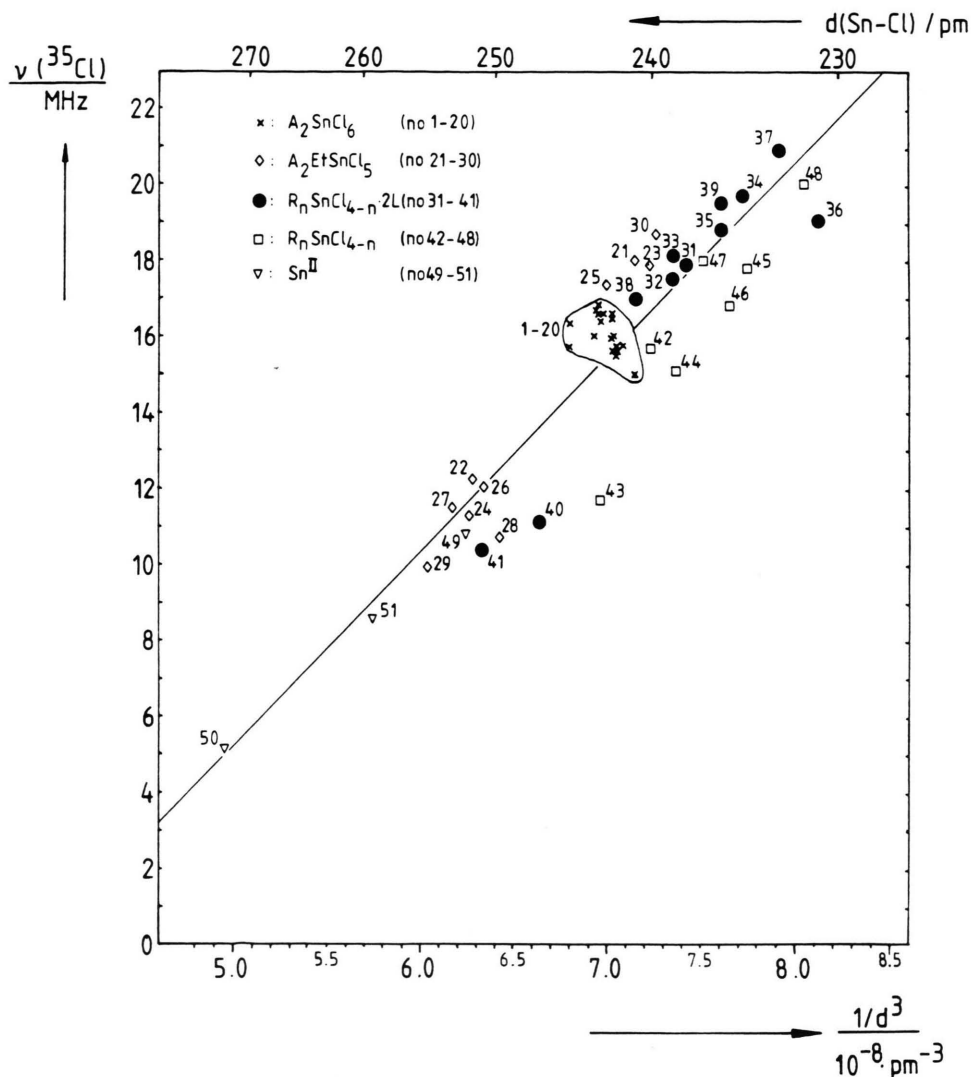
Fig. 7. ^{35}Cl NQR frequencies of compounds with bonds Sn–Cl vs. the bond distance $1/d^3$ (Sn–Cl). The symbols in the drawing mean: ×: A_2SnCl_6 (No. 1–20), A: 1) K; 2) NH_4; 3) Rb; 4) Cs; 5) $(CH_3)_4N$; 6) $A_2 = Ni(H_2O)_6$; 7) CH_3NH_3; 8) 9) $(CH_3)_2NH_2$; 10) $(CH_3)_3NH$; 11) $(C_2H_5)NH_3$; 12) $(C_2H_5)_3NH$; 13) $A_2 = H_3N(CH_2)_2NH_3$; 14) 15) $A_2 = H_3N(CH_2)_3NH_3$; 16) C_5H_5NH; 17) 4-ClC_5H_4NH; 18) 19) $A_2 = C_4H_{12}N_2 \cdot 3H_2O$; 20) $(C_6H_5)_2CNH_2$. ◇: $A_2EtSnCl_5$ (No. 21–30), A: 21) 22) $(CH_3)_4N$; 23) 24) C_5H_5NH; 25)–29) CH_3NH_3; 30) 4-$CH_3C_5H_4NH$. •: $R_nSnCl_{4-n} \cdot 2L$ (No. 31–39: $n=0$; No. 40, 41: $n=2$, $R = CH_3$); L: 31) HMPT; 32) DMSO; 33) $(C_6H_5)_3PO$; 34) $(CH_3)CN$; 35)–37) $POCl_3$; 38) 39) $SeOCl_2$; 40) DMF; 41) DMSO. □: R_nSnCl_{4-n} (No. 42–48): 42) $n=2$, $R = CH_3$; 43) $n=3$, $R = CH_3$; 44) $n=2$, $R = C_2H_5$; 45) $n=2$, $R = C_6H_5$; 46) $n=3$, $R = C_6H_5$; 47) $n=2$, $R = ClCH_2$; 48) $n=1$, $R = 3$-ClC_3H_6. ▽: Sn^{II} (No. 49–51): 49) $CsSnCl_3$; 50) $SnCl_2$; 51) $SnCl_2 \cdot 2H_2O$.

available into account. Unfortunately, the plot $v(^{35}Cl) = f(d^{-3})$ is, therefore, not a proof of (1).

The dependence $v(^{35}Cl) = f(d^{-3})$ for hexachlorotellurates is shown in Fig. 9 [108].

We have tried to understand on a quantitative basis such a simple relation as $v = a + b \cdot d^{-3}$. The EFG at the ^{35}Cl site in compounds of the K_2PtCl_6-type was calculated [109] on the basis of the Xα-method. The

outcome of the calculation can be interpreted in the following way: The EFG at the Cl-site is the sum of the intraionic $[XCl_6]^{2-}$ gradient and the lattice contribution. The main part is the intraionic one; the lattice part is of opposite sign. Increase of the lattice constant therefore increases the EFG and the frequency $v(^{35}Cl)$. In case of dominant ionic bond within the complex ion, as it is found in A_2MX_6, A = alkali metal
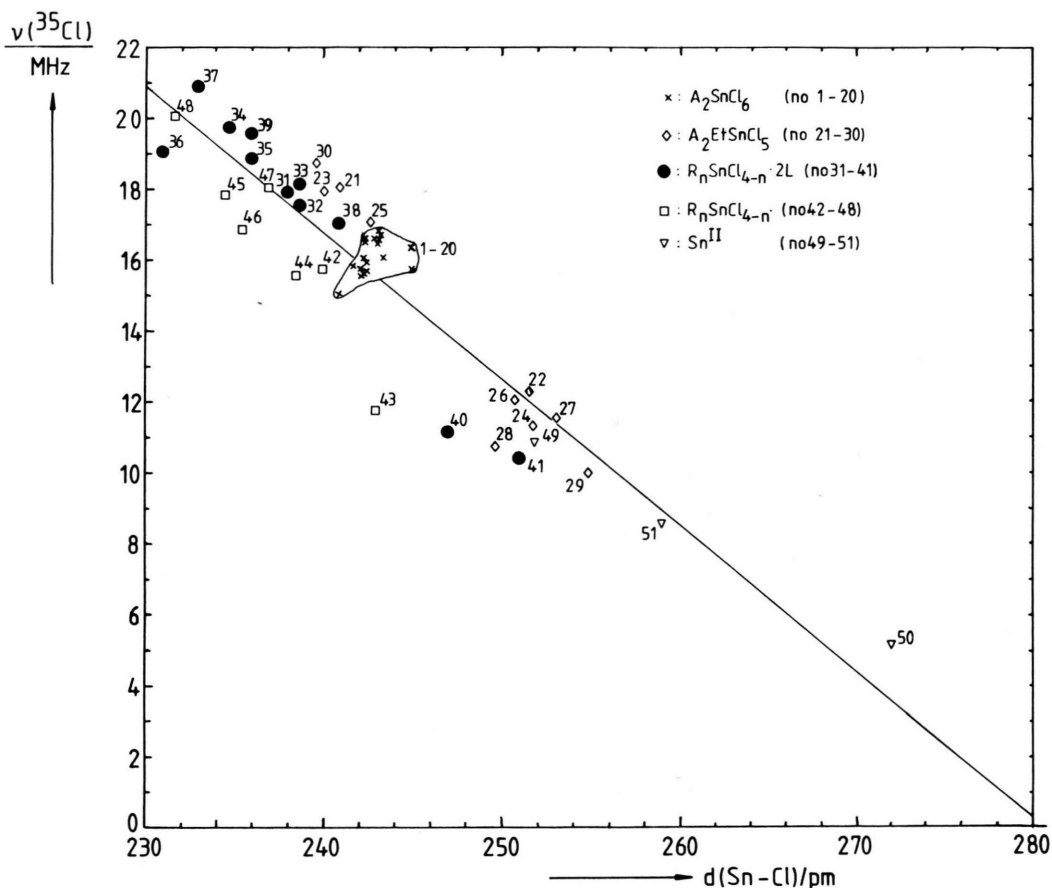
Fig. 8. ^{35}Cl NQR frequencies vs. $d(\text{Sn}-\text{Cl})$. The symbols in the Figure are explained in the legend to Figure 7.

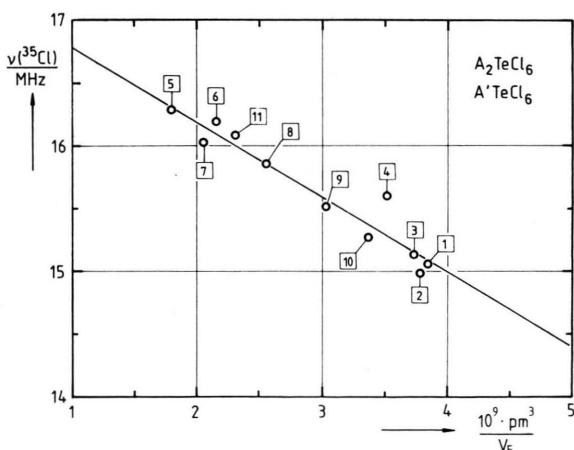Fig. 9. ^{35}Cl NQR frequencies vs. the reciprocal volume of the unit cell per formula unit, $1/V_F$, for hexachlorotellurates. The numbers in the Figure symbolize the following cations: 1) K^+; 2) NH_4^+; 3) Rb^+; 4) Cs^+; 5) $(CH_3)_4N^+$; 6) $(CH_3)_3NH^+$; 7) $(CH_3)_3S^+$; 8) $(CH_3)_2NH_2^+$; 9) $CH_3NH_3^+$; 10) $(H_3N(CH_2)_2NH_3)^{2+}$; 11) $C_5H_5NH^+$.

ion, $M = Cd^{II}$, $X = Br$, the total EFG at the halogen site decreases with increasing lattice constant [110].

Brill et al. [111] have correlated ^{35}Cl NQR frequencies and bond distances by scaling the results to the frequencies $\nu(^{35}Cl)$ in compounds with $[SnCl_6]^{2-}$ as anion. The result, including more recent data [108], is shown in Figure 10.

Information on $\nu(\text{NQR}) = f(\text{bond length})$ can be found in case of group IIIa halides and halogeno complexes, too. Both, the central atom M^{III} and the halogen ligand X give information via NQR. As examples we mention studies on the compounds $A_2InX_5 \cdot H_2O$, $A = K$, NH_4, Rb, Cs; $X = Cl$, Br [112, 113]. Replacing a smaller cation by a larger one, the halogen NQR frequencies $\nu(^{35}Cl)$, $\nu(^{81}Br)$ increase and $e\Phi_{zz}Qh^{-1}(^{115}In)$ decreases in accordance with the weighted contributions of the anion (intraionic) and the lattice contribution to the EFG. Yamada and Okuda [114] discussed the NQR results for the com-
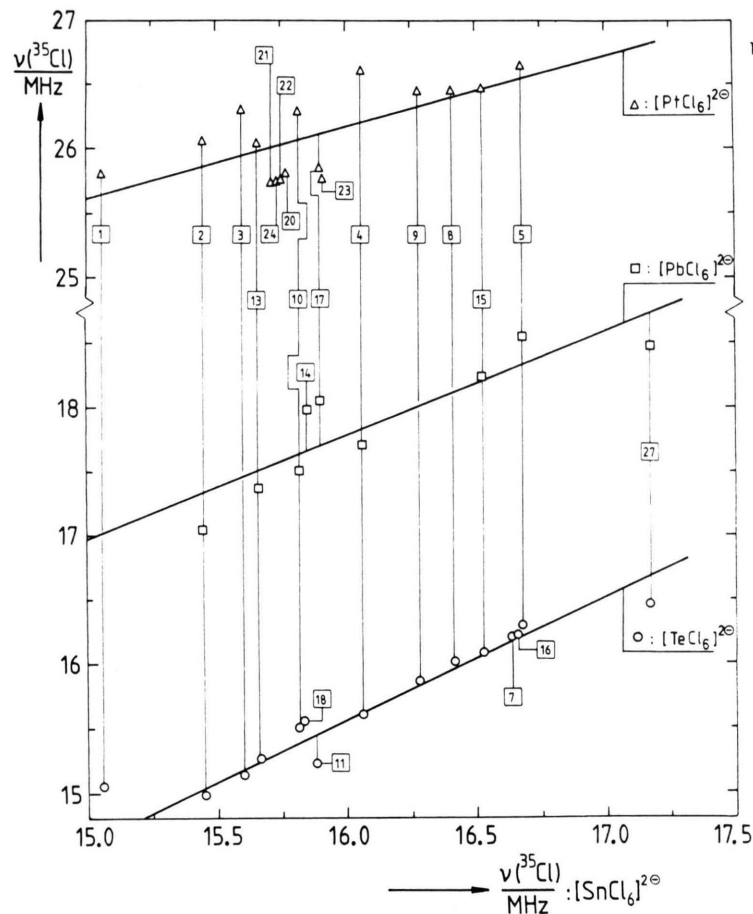
Fig. 10. Plot of the ^{35}Cl NQR frequencies of the hexachlorometallates (IV) $[MCl_6]^{2-}$, M = Te, Pb, Pt, versus the ^{35}Cl NQR frequencies of the corresponding hexachlorostannate, $[SnCl_6]^{2-}$. The numbering (1–5) of the data points corresponds with the numbers given in the legend to Fig. 9. 6) $(C_2H_5)_3(CH_3)N^+$; 7) $(CH_3)_3NH^+$; 8) $(CH_3)_3S^+$; 9) $(CH_3)_2NH_2^+$; 10) $CH_3NH_3^+$; 11) $C_2H_5NH_3^+$; 12) $(C_2H_5)_3NH^+$; 13) $(H_3N(CH_2)_2NH_3)^{2+}$; 14) $(H_3N(CH_2)_3NH_3)^{2+}$; 15) $(C_5H_5NH)^+$; 16) 4-ClC$_5$H$_4$NH$^+$; 17) $(C_3H_{12}N_2)^{2+}$; 18)–26) M(H$_2$O)$_6^{2+}$, M = Mg, Ca, Mn, Ni, Co, Cd, Zn, Fe, Cu; 27) 4-CH$_3$C$_5$H$_4$NH$^+$; etc.

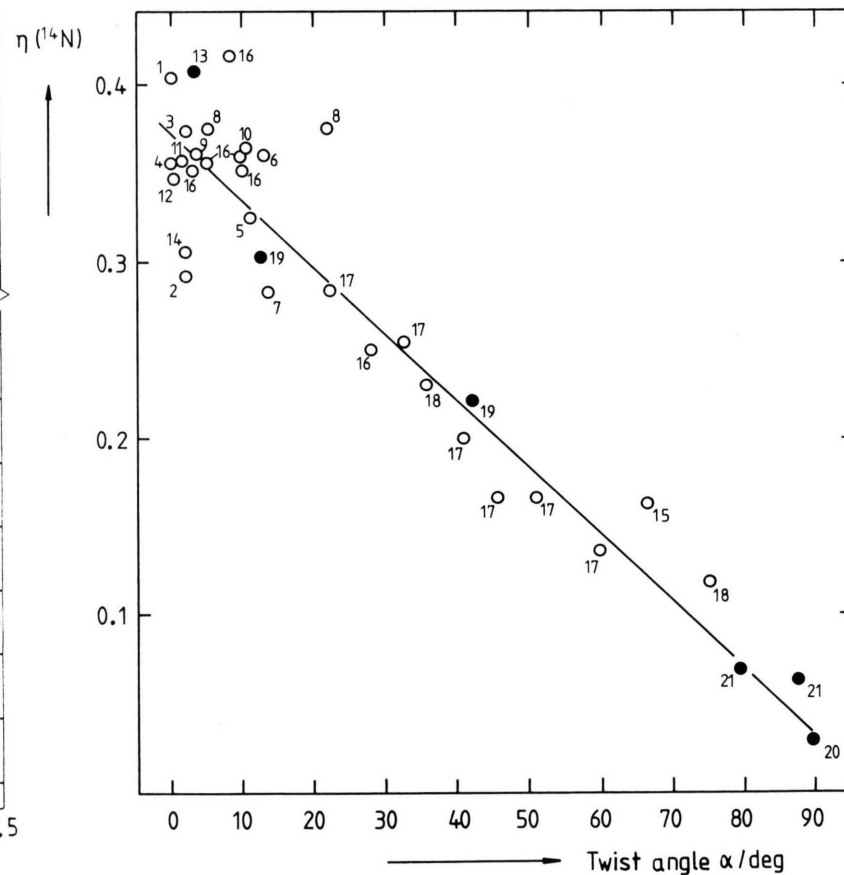Fig. 11. Asymmetry parameter $\eta(^{14}N)$ vs. the twist angle α in substituted nitrobenzenes (α = angle between the C$_6$-ring plane and the NO$_2$-plane). The numbering in the Figure corresponds to Table 2. The points 13, 19, 20, and 21 have been found from single crystal studies, QFS-NMR. The least squares analysis gives

$$\eta(^{14}N) = 0.374 - 0.004 \cdot (\alpha/\text{degree}).$$

pounds $A[Al_2Br_7]$, $A = K$, NH_4, $(CH_3)_4N$, $(C_2H_5)_4N$, and found a dependence of $v(^{81}Br)$ on the cation radius.

NQR and Bond Angles

In chemical bond, bond distances are one prominent property characterizing the bond. Bond angles, however play also an important role in molecules, complex ions, etc. Bond lenghts and bond angles (or more general atomic distances, atomic coordination and angles in the coordination spheres) rule the structures of organic and inorganic complex compounds. From NQR experiments, there is a wealth of information available on coordination chemistry. A monograph, published in 1987, covers the subject thoroughly [115] and we shall not go into the connection of NQR and coordination chemistry here. There is, however, one point we wish to stress.

For substituted nitrobenzenes, a reasonable number of crystal structure determinations is available which show a pronounced degree of freedom in the twist angle α (angle between the C_6 plane and the NO_2 plane). Strong thermal vibrations are observed for such NO_2 groups in X-ray diffraction, too. In the ideal case, like in nitrobenzene, the NO_2 group is in the plane of the benzene ring, as one expects from a resonance system. Bulky ortho neighbors of the NO_2 may force it to a twist. Marino and Connors [88] found a linear relation between the twist angle α and the asymmetry parameter $\eta(^{14}N)$ in nitrobenzene derivatives. In Fig. 11, we show a graph (including some recent data) of $\eta(^{14}N) = f(\alpha)$. The correlation is convincing, and in case of a few substituted polynitrobenzenes or in compounds with more than one formula unit in the asymmetric unit of the elementary cell the assignment $\eta(^{14}N) \leftrightarrow NO_2$ group was proven by single crystal measurements (QFS-NMR). These compounds are marked in Fig. 11 by filled circles.

The QFS-NMR experiments have shown [77a, 49, 50], that the main principal axis of the EFGT, Φ_{zz} at the ^{14}N site of the NO_2 group, is to an overwhelming extent parallel to the bond C–N connecting ring and NO_2 group. In the ideal case, twist angle $\alpha = 0$, Φ_{xx} at the nitrogen site is parallel to the C_6-ring plane and therefore parallel to the plane of the NO_2 group. With increasing twist angle α, Φ_{xx} stays neither parallel to the C_6-plane nor parallel to the plane NO_2 but lies somewhere in between. At $\alpha = 90°$, Φ_{xx} is again parallel to the ring plain and perpendicular to the NO_2 plane,
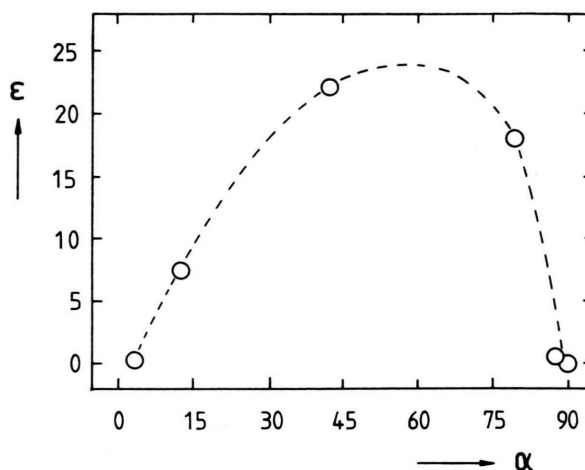

Fig. 12. Dependence of the angle ε (angle Φ_{xx}, C_6 plane) on the twist angle α. The data are from Table 2, No. 13, 19, 20, 21.

as observed in 2,3,5,6-tetrachloro-1,4-dinitrobenzene [50]. In a speculative way, we have drawn a curve relating the twist angle α and a twist angle ε, the latter one being defined as the angle between Φ_{xx} at the nitrogen site and the C_6 plane. This is shown in Figure 12. The correlation $\varepsilon = f(\alpha)$ may be an interesting object for a theoretical (and experimental) study.

Compounds, must probably useful to ensure the dependence $\varepsilon = f(\alpha)$ shown in Fig. 12, would be 3,5-dichloro-4-nitroaniline [91] and N,N-difluoroamino-2,4,6-trinitrobenzene [91a]. A twist angle of 64° has been reported for the dichloro nitroaniline and three different angles $\alpha = 28.20°$, $37.15°$, and $62.22°$ in the N,N-difluoroamino compound.

Correlation of NQR and other Bond Dependent Physical Properties of Molecules in the Solid State

The correlations of NQR results with properties of the chemical bond is part of the task of physical chemistry to find relations between physical properties and chemical bond parameters. In general, we may progress best by bring all the cross correlations available into the scenery.

A possibility of such a correlation parameter is the nuclear quadrupole splitting on tin-halogeno complexes found from Mössbauer experiments. Both, the EFG's at the Sn site and at the halogen site are available from a combined Mössbauer and NQR experiment. Investigations along this line are reported by Bryukhova et al. [116] and by Debye and Linzer [117].
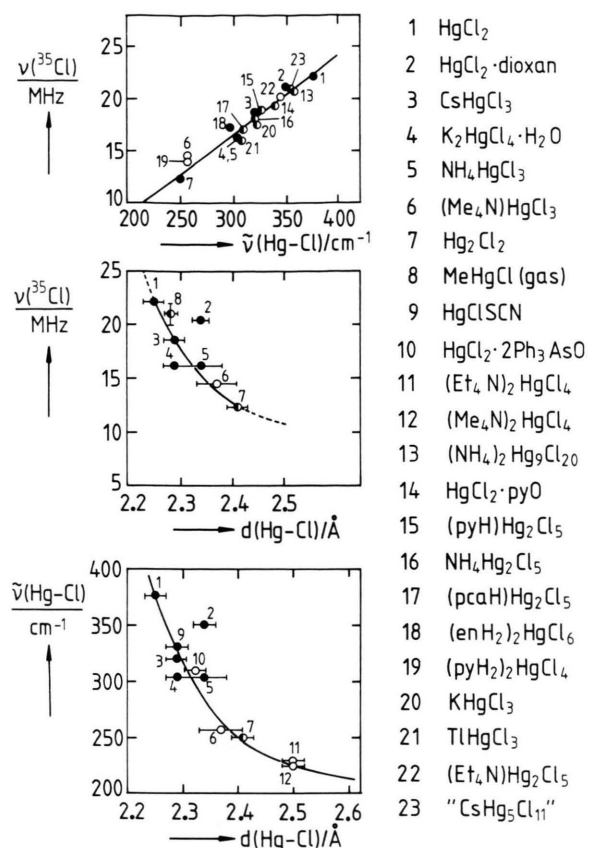
1	$HgCl_2$
2	$HgCl_2 \cdot$ dioxan
3	$CsHgCl_3$
4	$K_2HgCl_4 \cdot H_2O$
5	NH_4HgCl_3
6	$(Me_4N)HgCl_3$
7	Hg_2Cl_2
8	$MeHgCl$ (gas)
9	$HgClSCN$
10	$HgCl_2 \cdot 2Ph_3AsO$
11	$(Et_4N)_2HgCl_4$
12	$(Me_4N)_2HgCl_4$
13	$(NH_4)_2Hg_9Cl_{20}$
14	$HgCl_2 \cdot pyO$
15	$(pyH)Hg_2Cl_5$
16	$NH_4Hg_2Cl_5$
17	$(pcaH)Hg_2Cl_5$
18	$(enH_2)_2HgCl_6$
19	$(pyH_2)_2HgCl_4$
20	$KHgCl_3$
21	$TlHgCl_3$
22	$(Et_4N)Hg_2Cl_5$
23	"$CsHg_5Cl_{11}$"

Fig. 13. Correlation of the NQR frequencies (^{35}Cl) of mercury chloride complexes, a) with the Hg–Cl-stretching frequencies, b) with the bond distances d(Hg–Cl); c) correlation of stretching frequencies (Hg–Cl) and bond distances d(Hg–Cl).

Unfortunately, Mössbauer spectroscopy is somewhat limited by the number of suitable nuclei. Combined experiments $NQR(I_1)$–$NQR(I_2)$ are, however, possible for many systems. We have already mentioned the combination of In-NQR and halogen-NQR [112, 113] and of Al-NQR and halogen-NQR [114]. Other interesting "NQR-pairs" are As-Hal, Bi-Hal, Ga-Hal, B-Hal, etc. Hg-Hal would be an interesting pair in NQR on complexes; e.g. the bond distances Hg–Cl cover a wide range [100] and ^{201}Hg ($I = 3/2$) is accessible to the method as shown many years ago by Dehmelt et al. [118]. A further open problem in this context is the chemistry of gold-halogeno complexes (^{197}Au). The point of discussion here is, however, the cross correlation of NQR and information not gained from NMR-NQR.

A large body of information is available on the correlation of vibrational frequencies and chemical

bond. A convincing relation between the stretching frequencies and ^{35}Cl NQR frequencies was given by Scaife [100] for bonds R–Hg–Cl in $HgCl_2$ and mercuri-halogeno complexes. Figure 13 shows the cross correlation found.

To us it appears that particularly in complexes with coordination Hg-halogen one may find the wide range of distances d(mercury-Hal) one observes for d(Hg–Cl), reaching from the short bonds in $HgCl_2$ to the quite long ones in the complex salts, see Figure 13. This point is of interest because Fig. 13a shows that the relation $v(^{35}Cl)=f(d(Hg-Cl))$ is by no means linear. A linear relation exists, however, between $v(^{35}Cl)$ and $\tilde{v}(Hg-Cl)$.

The valence vibration frequency $\tilde{v}(C-Cl)$ of chloro hydrocarbons correlates in a linear way with the NQR frequency $v(^{35}Cl)$ as found by Gerdil [119]. For charge transfer complexes chloranil · X, the C=O stretching frequency in the chloranil part was related to $v(^{35}Cl)$ as was the stretching frequency $\tilde{v}(C-Cl)$. The correlation $v(^{35}Cl) \leftrightarrow \tilde{v}(C=O)$ is, in contrast to that in Hg–Cl complexes not linear [120], see also [121, 122].

A change in the charge distribution within a molecule by the effect of substitution or by the formation of molecular addition compounds should show up in the ionisation potential and in the polarographic half wave potential. The correlation NQR-ionisation potential was studied for π-π molecular complexes by Maksyutin et al. [123]. Semin et al. [124] and Grechishkin and Kyuntsel [125] studied the dependence of the NQR frequency $v(^{35}Cl)$ on the van der Waals radius of the donor molecule in such complexes. The half wave potential $U_{\frac{1}{2}}$ is, of course, connected with a charge transfer; the correlations found between the NQR frequencies ($v(^{35}Cl)$, $v(^{127}I)$) and $U_{\frac{1}{2}}$ is linear [126, 127].

The MO theory of NQR spectroscopy [10] as well as the Hammett σ relations to NQR, discussed above, have to do with charge transfer. Hydrogen bonded complexes are proton charge transfer complexes and one expects a correlation between the ΔpK_A of acidbase pairs and NQR frequencies. Typical examples are the compounds the medium strong acid trichloro acetic acid forms with bases [128]. A correlation $v(^{35}Cl)=f(\Delta pK_A)$ was pointed out by Maksyutin et al. [129]. Some more recent results are condensed in Fig. 14 [130].

Correlations of $v(^{35}Cl)$ with pK_A data are found in the literature also for $Cl_2HCCOOH \cdot X$ and for $Cl_{5-x}C_6H_xOH \cdot X$. The dynamics of the CCl_3 group
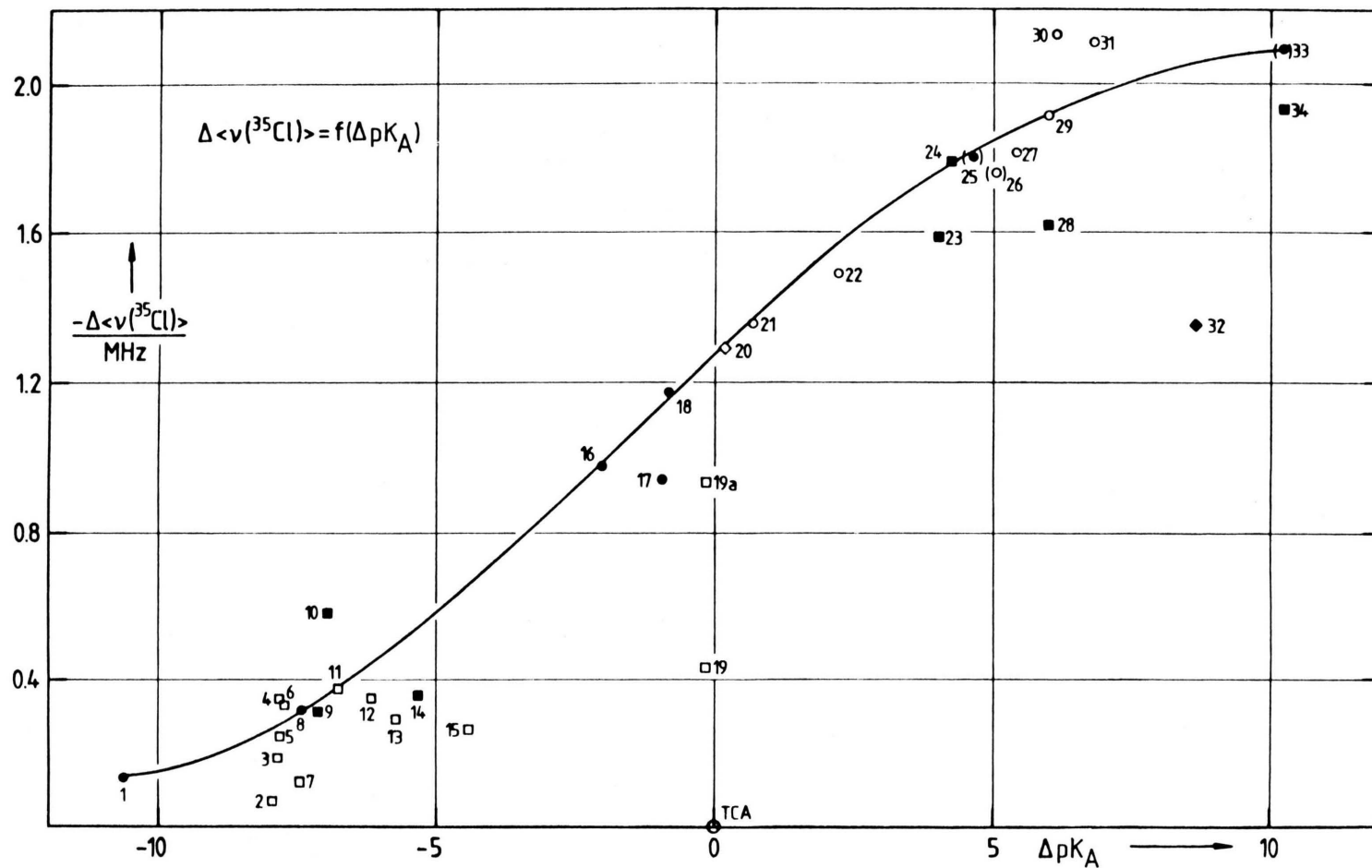
Fig. 14. Correlation of the ^{35}Cl NQR frequencies of compounds $Cl_3CCOOH \cdot X$ with the pK_A of the proton charge acceptor X. The ^{35}Cl NQR of the CCl_3 group is described by the mean frequency shift $\Delta \langle v (^{35}Cl) \rangle$ with respect to pure trichloro acetic acid, Cl_3CCOOH. For the numbers cf. [130].

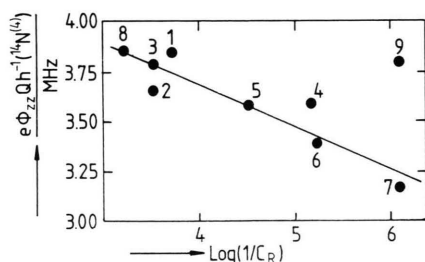| Nr.	R_1	R_2
1	H	H
2	H	CH_3
3	CH_3	CH_3
4	H	$COCH_3$
5	H	C_6H_5
6	H	CNCHCHCHCH *
7	H	CNCHCHS **
8	H	$SO_2C_6H_4NH_2$
9	H	CNCHCHCHN ***

    * – pyridine

  ** – thiazole

 *** – pyrimidine

Fig. 15. Biological activity (in vitro) of sulfanilamides versus $e\Phi_{zz}Qh^{-1}(^{14}N^{(4)})$. C_R is the biological activity of the compounds.

(bleaching out effect) in compounds $Cl_3CCOOH \cdot X$ have been correlated with $\nu(^{35}Cl)$, too [130]. We think that a more sensitive way to study correlations between hydrogen bond strength and electric field gradients would be ^2H QFS-NMR.

Lucken et al. [103a] have correlated the pK-values of carboxylic acids with the ^{35}Cl-NQR frequencies of carboxylates RCO_2SbCl_4.

NQR and Activity of Pharmaceuticals

A most interesting connection between NQR frequencies (quadrupole coupling constants and EFGT's, respectively, and chemical bond was shown by Bray et al. [131–133] who investigated the correlation between the biological activity of nitrogen containing compounds and $e\Phi_{zz}Qh^{-1}(^{14}N)$. As an example, in Fig. 15 $e\Phi_{zz}Qh^{-1}(^{14}N)$ is plotted versus the logarithm of the reciprocal bacteriostatic activity of sulfanilamides in vitro. It was possible to decide from the correlation the site of activity, which is $N^{(4)}$.

Several groups of biologically active compounds, such as substituted anilines, nitrogen mustards and so on, have been the subject of the studies of Bray et al. (for a review of the work, see [131]). The correlations they found are convincing. The correlations of $e\Phi_{zz}Qh^{-1}(^{14}N)$ with the biological activity was also crosscorrelated by these authors with Hammett σ [131]. There is hope that this rather new field of NQR will be a fruitful one in biochemistry.

Conclusions

The correlations of NQR parameters, the NQR frequencies, the nuclear quadrupole coupling constants $e\Phi_{zz}Qh^{-1}$, and the asymmetry parameters η with direct (bond lengths, bond angles, coordinations) and indirect (ionicity, ionic character i, s-character, π-character, Hammett σ, kappa, etc.) bond parameters have given a lot of information and will do so in future. Cross correlations will help to establish quantitative relations. Single crystal NQR work will strengthen the quantitative character of them. We think that the correlations of NQR with biochemical properties of molecules will find increasing interest. Particularly ^{14}N- and ^2H NQR may be of growing importance in this respect.

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