Theoret. chim. Acta (Berl.) 14, 48—54 (1969)

Frequency Shift in the NQR Spectra of Charge Transfer Complexes

YU. K. MAKSYUTIN, T. A. BABUSHKINA, YE. N. GURYANOVA, and G. K. SEMIN
Institute of Heteroorganic Compounds, The Karpov Physical Chemistry Institute

Received October 21, 1968/February 27, 1969

In the framework of Mulliken's theory a frequency shift in NQR spectra has been considered. It has been shown that in MO LCAO approximation the frequency shift is proportional to the degree of the charge transfer. For the picrylchloride complexes the linearity of this dependence has been confirmed. It has been shown experimentally that the shift is appreciably affected by steric interactions.

Im Rahmen der Mullikenschen Theorie wird eine Frequenzverschiebung im NQR-Spektrum untersucht. Es wird gezeigt, daß in der MO-LCAO-Näherung die Frequenzverschiebung proportional dem Grad des "charge transfer" ist. Für Pikrylchlorid-Komplexe wird die Linearität dieser Abhängigkeit bestätigt. Experimentell wurde gezeigt, daß die Verschiebung stark durch sterische Effekte beeinflußt wird.

Dans le cadre de la théorie de Mulliken on a étudié le déplacement de fréquence dans le spectre NQR. Il a été montré que dans l'approximation MO LCAO le déplacement de fréquence est proportionnel à l'importance du transfert de charge. Pour les complexes du chlorure de picryle cette proportionalité a été confirmée par l'expérience. Le déplacement est affecté par ailleurs par les interactions stériques.

Experimentally it has been shown that a significant frequency shift in comparison with the initial components is observed in the NQR spectra of complexes of the donor-acceptor type. The interpretation of these shifts in the literature bears a controversial character.

The present work is dedicated to a theoretical and experimental investigation of the basic factors responsible for the above mentioned shift.

The formation of the complex is conditioned by a transfer of charge from the higher occupied MO of the donor to the lower free MO of the acceptor. The transferred charge will more or less change the electric field on the atoms of the interacting molecules. This is the electronic factor. As the donor and acceptor molecules approach one another various types of spatial interactions begin to play a significant part. This also contributes to the change in the field gradient. The magnitude of this contribution will be determined by the geometric structure of the complex itself and of its constituent parts. Moreover crystallographic effects must not be ignored.

The wave function of the ground state of the complex can be represented to a first approximation in the form [1]

$$\Psi_N = a\psi_0(\mathrm{DA}) + b\psi_1(\mathrm{D}^+\mathrm{A}^-) . \tag{1}$$

The contribution to the field gradient from the valence electrons of the complex is determined by the expression

$$q_{ZZ} = e \int \Psi_N^2 \frac{3\cos^2\theta - 1}{r^3} \, dv \,. \tag{2}$$

A more detailed form of the wave function Ψ_N is given in Ref. [2]. Considering, that the field gradient at the atom in question is determined in the main part by its p-electron density, the change in the gradient as a result of charge transfer consists of

$$\Delta q_A = \frac{b^2}{1+S^2} \sum_t c_{A,t}^2 q_t \qquad \text{for the acceptor,} \tag{3}$$

$$\Delta q_D = -\left(1 - a^2 + \frac{b^2 S^2}{1+S^2}\right) \sum_r c_{D,r}^2 q_r \qquad \text{for the donor.} \tag{4}$$

Thus the change in the gradient is determined by the degree of charge transfer b^2, its density at the atom in question c^2, and the type of atomic orbitals participating in the charge transfer. The overlap integral S of the interacting MO's can be neglected for the majority of cases.

In the simplest case of a σ-acceptor, for example JCl, the accepting MO is

$$\psi_a = \frac{\psi_{Cl} + i^* \psi_J}{(1 + i^{*2} + 2i^* S')^{1/2}}, \qquad S' = \int \psi_{Cl} \psi_J \, dv \,, \qquad i^* = -\frac{1}{i} \,. \tag{5}$$

$I = \frac{1-i^2}{1+i^2}$ is the ionicity of the bond J–Cl.

Under these conditions the relative change in the field gradient (or the relative frequency shift) will consist of

$$\frac{\Delta q_{ZZ}}{q_{ZZ}} = \frac{\Delta \nu}{\nu} = -\frac{b^2}{2(1+S^2)} \,. \tag{6}$$

Thus, in the general case, the relationships obtained lead to the conclusion that the quadrupolar frequency shift, as a result of complex formation, is directly proportional to the degree of charge transfer.

In order to check the obtained relationships we investigated the complexes of picrylchloride with a range of aromatic donors. The results of the measurements are shown in the Table. The measurements were made with a pulse NQR spectrometer IS-2.

From the stereochemical points of view picrylchloride as acceptor is a very convenient object studied by the NQR method. The two nitro-groups in the ortho position to the chlorine atom are forced out of the plane of the ring and make an angle of 80—90° with it [3]. In addition, the chlorine atom is shielded from the direct spatial influence of the donor molecule.

In order to study the electronic factor it would be most interesting to check to what extent the relations (3) and (4) are fulfilled. Since the charge transfer takes place between a π-MO of the donor and of the acceptor, an increase of the π-electron density on the molecule of the latter should lead to a high frequency

Table. *NQR spectra of* Cl^{35} *in picrylchloride of the complexes with aromatic donors* ($T = 77°$ K)

	Donor	ν (MHz)	$\Delta\nu$ (MHz)	I (eV)	Remarks
1	—	39.385[a]			
2	Benzene	39.578	+0.193	9.24	
3	Fluorobenzene	39.683	0.298	9.19	
4	Chlorobenzene	39.956	0.571	9.07	
		34.380			Cl^{35} chlorobenzene
5	Bromobenzene	39.998	0.613	8.98	
6	Toluene	40.075	0.690	8.82	anti-
		39.622	0.277		syn-
7	Iodobenzene	40.250	0.865	8.73	
8	Phenol	40.544	1.159	8.50	
9	Nitrobenzene	39.466	0.081		
10	p-Xylene	39.425	0.040	8.44	
11	p-Iodotoluene	39.431	0.046	8.50	
12	p-Cresol	39.501	0.116		
13	p-Bromotoluene	39.606	0.221	8.67	
14	p-Chlorotoluene	40.152	0.767	8.69	anti-
		39.907	0.522		syn-
		34.836			Cl^{35} p-chloro-
		34.703			toluene
15	p-Fluorotoluene	40.040	0.655	8.78	
16	Mesitylene	40.387	1.002	8.39	
17	Durene	39.970	0.585	8.02	
18	Pentamethylbenzene	40.264	0.879	7.92	
19	Naphthalene	39.935[b]	0.550	8.12	
20	Anthracene	39.802	0.417	7.40	
21	Phenanthrene	39.914	0.529	8.02	

[a] Bray, P., and R. Barnes: J. chem. Physics **27**, 551 (1957).

[b] Kitaigorodskii, A. I., and E. I. Fedin: Zhur. Strukturnoi Khim. **2**, 216 (1961).

shift in the NQR spectrum of Cl^{35} in picrylchloride. A direct check of these relations is not possible since the parameters b^2, c^2 and S are unknown. However it is possible to check the linearity of relation (3). The degree of charge transfer is related directly to the ionisation potential of the donor [4]. Therefore the presence of a linear correlation between the NQR frequency shift of Cl^{35} in picrylchloride would suffice to confirm the correctness of the above relations. In addition however, it is necessary to consider donors with only a single geometric structure.

As can be seen from the Table, a high frequency shift in the NQR spectrum of Cl^{35} in picrylchloride is observed for all cases. The magnitude of these shifts is in the limits of 0.1—3 %. The absence of low frequency shifts indicates the essential role of the electronic factors, independent of the existence of geometric factors. For certain complexes a doublet character of the NQR spectra of Cl^{35} in picrylchloride is observed. This is explained by the presence of two types of conformations of the complexes: syn- and anti- in accordance with the syn- or anti-position of the most bulky substituent in the ring of the donor relative to the bulk of the picrylchloride group. In all other cases it is assumed that the complexes have the anti-conformation. From structural considerations the donors investigated can be divided into four groups: 1) benzene and its monosubstituents, 2) paradisubstituted toluenes, 3) polymethylsubstituted benzenes, 4) polycyclic aromatic systems. Introducing this specification we examine the NQR spectra of each group of complexes separately.

Complexes of Picrylchloride with Monosubstituted Benzenes

The presence of one substituent in the donor molecule cannot lead to an essential change in the conditions of complex formation of monosubstituents as compared to benzene itself, since both bulky groups of the donor and acceptor can occupy anti-positions relative to one another, and so do not afford serious steric hindrance. Consequently, the quadrupolar frequency shift for complexes with monosubstituted benzene should in the main be determined by the donor properties of the molecules C_6H_5X. In Fig. 1 the dependence of the quadrupolar frequency shift of Cl^{35} ($\Delta\nu$) in picrylchloride in the complex on the ionisation potential of the donor (I) is shown. The presence of linear correlation serves as an extremely good confirmation of the existance of a linear dependence between the quadrupolar frequency shift and the degree of charge transfer. The dependence $\Delta\nu(I)$ can be used to determine the ionisation potential of the donors. After processing the data with the method of least squares

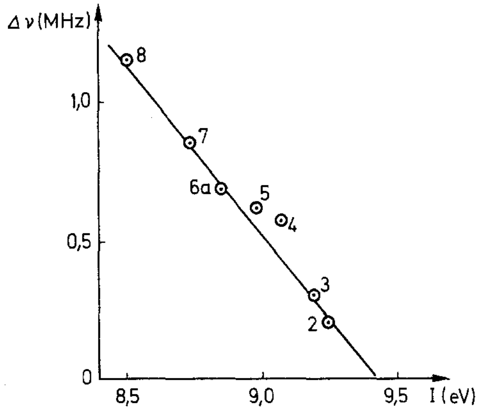

Fig. 1. Cl^{35} NQR frequency shift dependence of the picrylchloride in its complexes with monosubstituted benzenes on the donor ionization potential (point notations correspond to the Table)

$$\Delta\nu = (11.410 - 1.211\, I) \pm 0.035\ \text{MHz}, \qquad r = 0.987$$

an ionisation potential of 9.4 eV was obtained for nitrobenzene with a standard deviation of 0.05 eV. However so far it is not possible to estimate the general error in determining the ionisation potential by this method.

Complexes of Picrylchloride with Parasubstituted Toluenes

The introduction of a second substitutent into the ring of the donor in para-position to the methyl group greatly increases the distance between the molecules of the donor and the acceptor on account to the mutual Van-der-Waals repulsion of the bulky substituents. An increase in the distance between the donor and acceptor molecules causes a decrease of the overlap integral of the interacting MO's and consequently a decrease of the degree of charge transfer. Since the difference in the ionisation potentials within this series is insignificant, the NQR frequency shift in this case will in the main depend not on the ionisation potential of the donor but on the distance between the components of the complex, which is determined by the volume of the substituents. The dependence between the quadrupolar frequency shift and the Van-der-Waals radius of the para-substituents in the donor molecule is shown in Fig. 2.

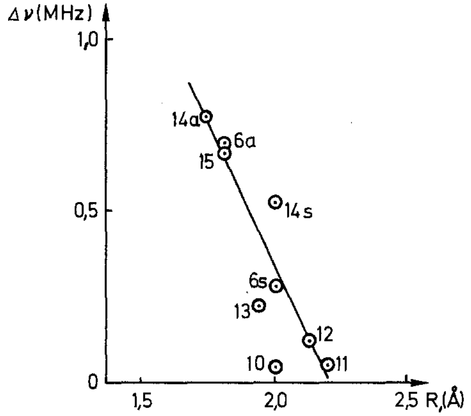

Fig. 2. Cl^{35} NQR frequency shift dependence of the picrylchloride in its complexes with p-substituted toluenes on Van-der-Waals radii of p-substituents (point notations correspond to the Table)

$$\Delta\nu = (4.60 - 2.13\,R) \pm 0.05\ \text{MHz}\,, \qquad r = 0.85\,.$$

As seen from the figure, this dependence can well enough be approximated by a straight line. The presence of syn- and anti-conformations requires taking into account in one case the Van-der-Waals radius of the methyl group ($R = 2.0$ Å), in the other, the half thickness of the benzene ring ($R = 1.85$ Å), for toluene and para-fluorotoluene because of the small volume of the atoms of hydrogen and fluorine. The radius of the methyl group and the chlorine atom is correspondingly considered for parachlorotoluene.

Thus for the NQR spectra of complexes of picrylchloride with para-substituted toluenes the following tendency is observed: the greater the volume of the substituent, the smaller the quadrupolar frquency shift.

Complexes of Picrylchloride with Polysubstituted Benzenes and Condensed Aromatic Systems

In the previous cases we examined complexes with donors having similar structures. We now attempt to reveal what effect on the NQR spectrum shift a change in the structure of the donor will have. For this purpose we take as donors, polymethyl-substituted benzenes. We also attempt to elucidate the influence of size and structure of several other aromatic systems on the NQR frequency shift. A change in the symmetry of the donor molecules will strongly affect the symmetry of the mutual arrangment of the donor and acceptor molecules. Since the electronic factor possesses a systematic character, while the geometric factor to a certain degree possesses an accidental character, the superposition of both factors leads to the absence of any definite regularity in the NQR frequency shifts. Fig. 3 shows the dependence of quadrupolar frequency shifts on the ionisation potential of the donor of the complexes of picrylchloride with polymethylsubstituted benzenes (I) and condensed aromatic systems (II). Although in both cases a general tendency is observed, that the NQR frequency shift of Cl^{35} in picrylchloride increases while the ionisation potential of the donor decreases, the differences in the geometric structure of the donor have a large influence on the quadrupolar frequency; therefore the sequence of points on the graph has no systematic character.

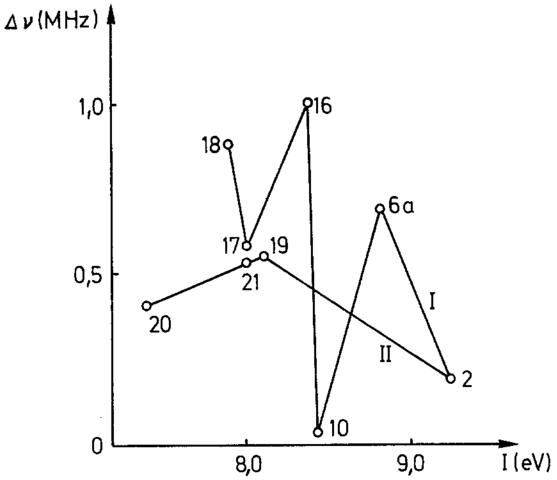

Fig. 3. Cl^{35} NQR frequency shift dependence of the picrylchloride in its complexes with polysubstituted benzenes and condensed systems on the ionization potential (point notations according to the Table)

Conclusions

1. The influence of charge transfer on the NQR frequency shift in complexes of the donor-acceptor type is theoretically examined. It is shown that the frequency shift is directly proportional to the degree of charge transfer.

2. A check of the relations obtained was carried out for 20 complexes of picrylchloride with aromatic donors. The linear relationship between the frequency shift and the degree of charge transfer is confirmed.

3. The influence of geometric factors on the quadrupolar frequency shift is shown.

References

1. Mulliken, R. S.: J. Chim. physique **61**, 20 (1964).
2. — J. Amer. chem. Soc. **74**, 811 (1952).
3. Golder, G. A., G. S. Zhdanov, and M. M. Umanskii: Doklady Akad. Nauk SSSR **92**, 311 (1953).
4. Arzamanova, I. G., and Ye. N. Guryanova: Zhur. Obshchei Khim. **36**, 1157 (1966).

Professor Dr. G. K. Semin
Institute of Heteroorganic Compounds
Academy of Sciences of the USSR
ul. Vavilova 28, Moscow, USSR