

# Nuclear Quadrupole Resonance Studies on Molecular Complexes\*

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NQR studies of a number of molecular complexes with p-chloronitrobenzene and o-chloronitrobenzene as acceptors and different hydrocarbons as donors were carried out. A linear relationship between the NQR shift and the ionization potentials of the donors is obtained. Maksyutin's idea of a positive shift with respect to acceptors having a quadrupolar nucleus is shown to hold in those systems. Townes and Dailey's method was applied to calculate the change in the ionicity of the C–Cl bond on complexation to account for the  $\sigma$ -electronic contributions in the systems.

## Introduction

Nuclear quadrupole resonance (NQR) spectroscopy is a useful technique to gain information about the charge distribution at different positions and hence about the electronic arrangement in crystalline complexes.

Townes and Dailey's [1] method has been applied to relate NQR frequencies to the ionicity of  $\sigma$ -bonds. Maksyutin et al. [2] studied about 20 molecular compounds of picryl chloride with substituted aromatic molecules. Weiss's [3] suggestion that the NQR frequency should shift due to molecular complex formation through charge-transfer interaction has been well demonstrated with molecules having quadrupolar nucleus either in the acceptor or in the donor or in both at the same time [4–10]. In all these cases a linear relation was obtained between the NQR shift and the charge transfer interaction energy  $h\nu_{\text{op}}$ , where  $\nu_{\text{op}}$  is the frequency of optical charge transfer.

From theoretical consideration Maksyutin et al. [2] have shown that, if  $^{35}\text{Cl}$  is on the donor molecule the NQR shift  $\Delta\nu$  should be negative, and vice versa, they have not given any experimental result in support of this prediction. With picryl chloride complexes a linear relationship between  $\Delta\nu$  and the donor ionization potential was obtained, but with

polynuclear catacondensed hydrocarbons no such correlation was found. In previous communications [4, 5, 6] it has been shown that although a linear relation between  $\Delta\nu$  and the donor ionization potential or  $h\nu_{\text{op}}$  was obtained in many cases, Maksyutin's idea of a negative shift with respect to the donor or a positive shift with respect to the acceptor was not always corroborated with. However according to Maksyutin, geometrical factors would also be of importance for  $\Delta\nu$  in case of disubstituted benzenes. According to Douglass [11] the crystal field effects frequently shift NQR frequencies by  $\pm 200$  kHz. In order to determine any shift arising from charge transfer, these crystal field effects as well as geometrical factors would have to be eliminated. Unfortunately these extraneous effects are not obtainable at present either from experiments or calculations. Although the electronic factor possesses a systematic character, the geometrical factors and crystal field effects are more or less accidental and hence the superposition of all these factors becomes irregular. A way out would be to collect more data on such molecular complexes.

With this in mind we have performed experiments on molecular complexes of p-chloronitrobenzene and o-chloronitrobenzene as acceptors with different hydrocarbons as donors, the results of which are communicated herewith.

## Materials and Methods

The donors, viz. naphthalene, anthracene, pyrene, chrysene, and biphenyl, and the acceptors such as

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p-chloronitrobenzene and o-chloronitrobenzene were of AR grade. They were used without further purification.

The charge-transfer complexes of p-chloronitrobenzene with different hydrocarbons were prepared by slow evaporation of solutions of equimolar mixtures of donors and acceptors. o-Chloronitrobenzene being a low melting solid, the complexes of o-chloronitrobenzene were prepared by adding the donors to the molten acceptor and then cooling the mass to 15 °C.

The NQR frequencies were measured on a modified super-regenerative spectrometer NQR 40 fitted with a recorder manufactured by the Electronic Corporation of India. All measurements were made at 295 K. Although at 77 K quite a number of resonance signals were obtained from systems containing chemically equivalent chlorine atoms in crystals, at 295 K only one line was obtained for each compound. At this temperature the lines were less intense and 6 kHz wide.

## Results and Discussion

The NQR frequencies of the complexes and of the respective acceptors are presented in Table I. The  $\Delta\nu(^{35}\text{Cl})$  vs.  $I$  plots (ionization potentials in eV) of the donors are shown in Figure 1. The plots are linear as suggested earlier, and  $\Delta\nu$  is positive for the

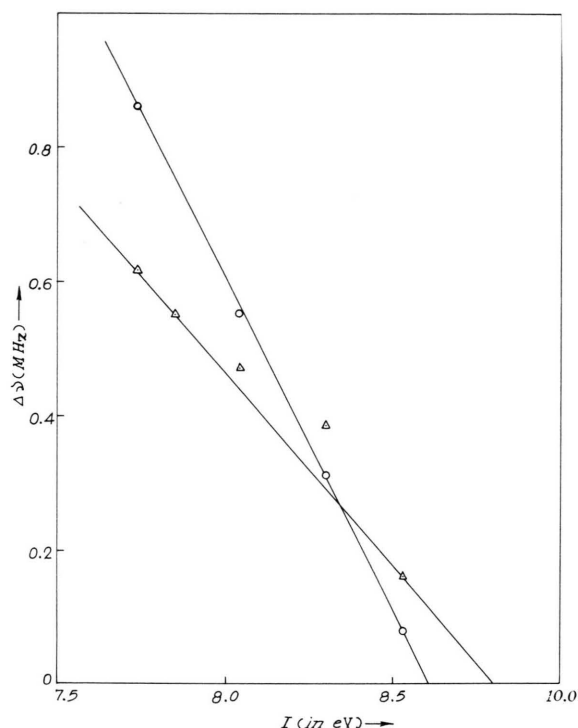


Fig. 1. Frequency shift  $\Delta\nu$  versus the ionization potential of the donor molecule. —○— o-Cl(NO<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>; —△— p-Cl(NO<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> (see also Table I).

complexes studied with respect to the acceptor  $^{35}\text{Cl}$  NQR frequency.

Following Mulliken and considering that the electric field gradient (EFG) at the atom in question is determined mainly by its p-electron density, the change in the gradient as a result of charge-transfer consists of

$$q_A = \frac{b^2}{1+s^2} \sum_i C_{A,i}^2 q_i \quad (\text{for the acceptor}) \quad (3)$$

and

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

Thus the change in gradient [11] is determined by the degree of charge transfer ( $b$ ), its density ( $C^2$ ) at the atom in question and the type of atomic orbital participating in the charge transfer. The overlap integral  $S$  of the interacting MOs can be neglected for the majority of cases.

Table I. Nuclear quadrupolar resonance shifts of complexes having  $^{35}\text{Cl}$  as quadrupolar nucleus ( $T = 295$  K).

Donor	NQR signal of the complex (MHz)	$\Delta\nu$ (MHz)	$I$ (eV)	Ionicity of the C-Cl bond in the complex
Acceptor: p-Chloronitrobenzene NQR signal at 36.87 MHz; ionicity: 0.6639				
Naphthalene	37.23	0.36	8.30	0.6606
Anthracene	37.50	0.63	7.74	0.6582
Pyrene	37.42	0.55	7.85	0.6589
Chrysene	37.34	0.47	8.04	0.6596
Biphenyl	37.03	0.16	8.53	0.6624
Acceptor: o-Chloronitrobenzene NQR signal at 36.56 MHz; ionicity: 0.6667				
Naphthalene	36.87	0.31	8.30	0.6639
Anthracene	37.42	0.86	7.74	0.6589
Chrysene	37.11	0.55	8.04	0.6617
Biphenyl	36.64	0.08	8.53	0.6660

Under these conditions the relative change in the EFG (or the relative frequency shift) will be

$$\frac{\Delta q_{zz}}{q_{zz}} = \frac{\Delta v}{v} = -\frac{b^2}{2(1+s^2)}.$$

Thus, in general, the relationship obtained leads to the conclusion that  $\Delta v$ , as a result of complex formation, is directly proportional to the degree of charge transfer.

Since the charge transfer takes place between  $\pi$ -MOs of the donor and the acceptor, an increase in the  $\pi$ -electron density on the molecule of the latter should lead to a high  $\Delta v$  of  $^{35}\text{Cl}$  in acceptors. 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 (3) and (4). The degree of charge transfer is directly related to the ionization potential of the donor. Therefore, the presence of a linear correlation between  $\Delta v$  of  $^{35}\text{Cl}$  in these compounds would suffice to confirm the charge transfer character of these compounds. No doubt, 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, which will change the EFG on the atoms of the interacting molecules. This is the electronic factor. But when the donor and acceptor molecules approach one another, various types of spatial interactions begin to play a significant part, thereby contributing to the change in the EFG. The magnitude of this contribution will be determined by geometric factors.

Frequency changes in these molecules may be due primarily to changes in electron density in the  $\pi$ - and  $\sigma$ -orbitals of the Cl atom. The EFG change considered up to now takes into account only  $\pi$ -orbital changes.

The covalency of the C–Cl bond may be calculated following Townes and Dailey's (T-D) theory by the relation

$$\left(\frac{eqQ}{h}\right)_{\text{exp}} = (1-i)\left(\frac{eqQ}{h}\right)_{\text{atom}},$$

where  $i$  is the ionic character of the bond and  $(eqQ/h)_{\text{atom}}$  the NQR frequency for atomic chlorine (109.7 MHz). In resonance terms, Townes and Dailey's method describes the bond as

$$Q = (1-i)(\text{R}-\text{Cl}) + i(\text{R}^+-\text{Cl}^-),$$

that is by ionicity is meant the magnitude of the dipole moment of the bond. In the calculation of  $i$  the fractional ionic character therefore amounts to estimating the extent of  $\sigma$ -electron density change on the Cl atom in an R–Cl bond.

From the Table I it may be observed that the ionicity, i.e., the dipole moment of the bond decreases as p-chloronitrobenzene and o-chloronitrobenzene (acceptors) enter the complex formation. The T-D analysis suggests that the dipole moment of the C–Cl bond will increase in the donor and decrease in the acceptor on charge-transfer complex formation. This contention appears to hold fairly well for these complexes. No generality can however be claimed because of the presence of dipolar and multipolar interaction in the crystals of charge-transfer complexes, which will considerably affect the bond character of the C–Cl bond.

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