

Nuclear Quadrupole Resonance Spectra of Charge Transfer Complexes

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Nuclear quadrupole resonance spectral shifts have been measured for charge transfer complexes of *p*-dichlorobenzene, *p*-chlorophenol and *p*-chloroaniline with chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachlorophthalic anhydride, chloranilic acid and *p*-chloronitrobenzene. $\Delta\nu$ values for all these complexes show a linear relationship with $h\nu_{op}$ establishing the charge transfer nature of these complexes. However, for a quantitative interpretation the dipole-dipole, dipole-multipole interactions and crystal field effect cannot be neglected.

Weiss's¹ suggestion that NQR frequency should shift owing to molecular complex formation through charge transfer interaction has been well demonstrated with molecules having quadrupolar nucleus (³⁵Cl) either in acceptors or in donors²⁻⁹. In all these cases a linear relation was obtained between NQR shift and the charge transfer interaction energy $h\nu_{op}$ which is related to the ionization energy (*I*) of the donor, electron affinity (*E*) of the acceptor and the ion pair stabilization energy (Δ) by the Mulliken relation: $h\nu_{op} = I - E - \Delta$, where ν_{op} is the frequency of optical charge transfer transition. In order to see the effect on the NQR spectrum shift when both the donor and acceptor have quadrupolar nucleus, we have presently measured the NQR frequencies of a series of molecular compounds wherein both the donors and acceptors have ³⁵Cl quadrupolar nucleus.

Materials and Methods

The donors, viz. *p*-dichlorobenzene, *p*-chlorophenol and *p*-chloroaniline and the acceptors such as chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachlorophthalic anhydride, chloroanilic acid and *p*-chloronitrobenzene were of AR grade.

The charge transfer complexes were prepared by slow evaporation of solutions of equimolar mixtures of donors and acceptors. For low melting donors or acceptors the complexes were prepared by adding the acceptor or the donor to the molten donor or the acceptor as the case may be and then finally cooling the mass to 15°C.

The NQR frequencies of these complexes were measured on a modified super regenerative spectrometer NQR 40 fitted with a recorder manufactured by Electronic Corporation of India. All measurements were made at 295K. Although at 77K quite a number of resonance signals were obtained from systems containing chemically equivalent chlorine atoms, at

295K, only two lines were obtained for each compound. At this temperature the lines were less intense and 0.0006 MHz wide.

Results and Discussion

The NQR frequencies of the complexes and of respective donors and acceptors are presented in Table 1. The plots $\Delta\nu$ (³⁵Cl) versus $h\nu_{CT}$ are linear as demanded by the theory (see Fig. 1). When the quadrupolar nucleus is on the acceptor the theory predicts³ a positive value of $\Delta\nu$, and a negative $\Delta\nu$ is predicted when the quadrupolar nucleus is on the donor. It is evident from Table 1 that $\Delta\nu$ is negative with respect to the donor NQR frequency for the complex when the quadrupolar nucleus is on the donor whereas it is positive when the quadrupolar nucleus is on the acceptor such as in the complexes of DDQ and chloranil. However, for molecular complexes of tetrachlorophthalic anhydride, chloranilic acid and *p*-chloronitrobenzene the experimental results are not quite in accord with the theoretical prediction.

The wavefunction of the ground state of the charge transfer complex according to Mulliken is of the form $\psi = a\psi_0(DA) + b\psi_1(D^+A^-)$... (1)

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

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

Considering that the field gradient 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

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

Table 1—Nuclear Quadrupolar Resonance Shifts of Complexes having ^{35}Cl in both Donors and Acceptors

Acceptor	NQR signal of the acceptor (MHz)	NQR signal of the complexes (MHz)		$\Delta\nu_{\text{Donor}}$	$\Delta\nu_{\text{Acceptor}}$	$h\nu_{\text{CT}}$ (eV)
Donor: <i>p</i> -Dichlorobenzene; NQR signal at 34.91 MHz						
DDQ	37.00	34.66	38.25	(-)0.25	(+)1.25	3.22
Chloranil	37.50	34.33	37.66	(-)0.58	(+)0.16	2.90
Tetrachlorophthalic anhydride	37.82	33.91	37.08	(-)1.00	(-)0.74	2.20
Chloranilic acid	37.84	33.82	37.00	(-)1.09	(-)0.84	1.81
<i>p</i> -Chloronitrobenzene	36.87	33.96	35.66	(-)0.95	(-)1.21	1.73
Donor: <i>p</i> -Chloroaniline; NQR signal at 34.06 MHz						
DDQ	37.00	34.00	37.42	(-)0.06	(+)0.42	4.23
Chloranil	37.50	33.82	37.67	(-)0.24	(+)0.17	4.06
Tetrachlorophthalic anhydride	37.82	33.24	37.92	(-)0.82	(+)0.10	3.28
Chloranilic acid	37.84	33.18	37.40	(-)0.88	(-)0.44	3.38
<i>p</i> -Chloronitrobenzene	36.87	33.01	36.16	(-)1.05	(-)0.71	3.12
Donor: <i>p</i> -Chlorophenol; NQR signal at 34.96 MHz						
DDQ	37.00	34.74	38.08	(-)0.22	(+)1.08	3.80
Chloranil	37.50	34.53	37.92	(-)0.43	(+)0.42	3.48
Tetrachlorophthalic anhydride	37.82	34.16	37.67	(-)0.80	(-)0.15	3.09
Chloranilic acid	37.84	34.03	37.46	(-)0.93	(-)0.38	2.70
<i>p</i> -Chloronitrobenzene	36.87	33.95	36.04	(-)1.01	(-)0.83	2.30

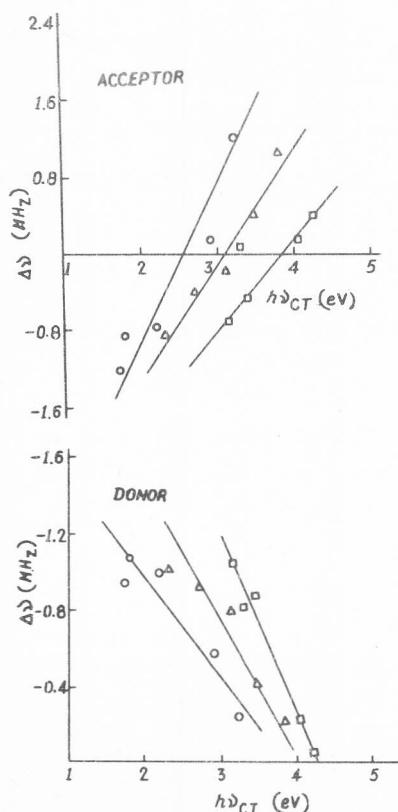


Fig. 1—Plots of $\Delta\nu$ (donor/acceptor) against $h\nu_{\text{CT}}$ of complexes [○—○, *p*-dichlorobenzene complexes; △—△, *p*-chlorophenol complexes; and □—□, *p*-chloroaniline complexes]

and

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

Thus the change in gradient is determined² 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.

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

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

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

Since the charge transfer takes place between π -MOs of the donor and the acceptor, an increase in the π -electron density on the molecule of the latter should lead to a high frequency shift in the NQR spectrum of ^{35}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 the relations (3) and (4). The degree of charge transfer is related directly to the ionisation potential of

the donor. Therefore, the presence of a linear correlation between the NQR frequency shift of ^{35}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. The transferred charge will more or less change the electric field on the atoms of the interacting molecules. This is the electronic factor. But at the same time as 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 field gradient. The magnitude of this contribution will be determined by the geometric structure of the complex as well. Moreover crystallographic effects must not be ignored as it is well known that crystalline field effects frequently shift quadrupole frequency by ± 200 kHz. So it may safely be concluded that in all these

molecular complexes although charge transfer interaction plays a dominant role, the contributions of other effects are not negligible.

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