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Nuclear Quadrupole Resonance Study of Charge Transfer Complexes: Chloranil Complexes

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^{35}Cl nuclear quadrupole resonance frequencies were measured in electron donor-acceptor complexes between chloranil (tetrachloro-*p*-benzoquinone) and such donors as aromatic hydrocarbons, polyaromatics and amines. Some correlations between the resonance frequencies and infrared spectra were found and discussed in a qualitative way in terms of the π-electron transfer between donors and the chloranil molecule as acceptor. A Zeeman effect experiment was carried out on a single crystal of the 1:2 chloranil-8-hydroxyquinoline complex. The direction of one of the two non-equivalent C–Cl bonds obtained slightly differs from that determined by an X-ray diffraction study. Possible effects of the charge transfer on the resonance frequency and the asymmetry parameter are discussed according to the Mulliken theory of 'weak' charge-transfer complex. No simple relations could be found between the experimental resonance frequencies and the ionization potential of the donor. This suggests that crystal field effects are rather large in comparison with the effect of charge transfer interaction.

A great number of experimental works have been carried out on various charge transfer (CT) complexes. Most of the data on the electronic and infrared spectra, dipole moments, and electron spin resonances were successfully interpreted by Mulliken's theory of the electron donor-acceptor complexes.[1]

Recently some questions have been raised about the role of the CT forces in the formation of the CT complexes.[2-4] Moreover, the extent to which the CT forces contribute to the stability of the CT complexes has not been settled.[5]

As the electric field gradient (EFG) at a nucleus is a quantity sensitive to a small intermolecular perturbation in a crystal,[6] one should be able to obtain some information about the existence and/or the degree of charge transfer from the donor (D) to the acceptor (A), by applying the nuclear quadrupole resonance (NQR) method to the CT complexes in a coordinated way. Hooper found that the shift in the NQR frequencies upon the complex formation was so slight that it could reasonably be concluded that there was virtually no CT in the ground state.[7] On the other hand, Read and others have found that the NQR frequencies both of Br_2 and of C_6H_5Br are influenced when they form a CT complex.[8]

Gilson and O'Konski pointed out that an NQR frequency at a temperature other than 0°K can not be directly correlated with the CT force because the frequency changes with temperature.[9] The controversial situation as to whether the charge transfer is in fact responsible for the formation of such complexes seems to arise from differences in the nature of interactions between a particular pair of the donor and the acceptor molecules.

The complexes studied are so called σ-π complexes and analysis of the NQR data may be complicated by a variety of donor-acceptor interactions. The π-π complexes, on the other hand, usually assume rather simple crystal structures in which D and A molecules stack alternately and can be treated as approximately rigid molecules.[10] Thus information concerning CT interaction could be obtained from the NQR data of weak CT complexes containing one specified acceptor and various donors, since the crystal field effect is not expected to change seriously.

We chose chloranil (CA) as an acceptor and measured the NQR frequencies in its CT complexes. While our work was in progress several authors reported on

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[1] a) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952). b) R. S. Mulliken, *Rec. Trav. Chim.*, **75**, 845 (1956). c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

[2] M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron Suppl.*, **7**, 97 (1966).

[3] J. L. Lippert, M. W. Hanna, and P. J. Trotter, *J. Amer. Chem. Soc.*, **91**, 4035 (1969).

[4] R. J. W. Lefevre, D. V. Radford, and P. J. Stiles, *J. Chem. Soc.*, **1968**, B 1297.

[5] R. S. Mulliken and W. B. Person, *J. Amer. Chem. Soc.*, **91** 3409 (1969).

[6] a) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press, New York (1958). b) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York (1969).

[7] H. O. Hooper, *J. Chem. Phys.*, **41**, 599 (1964).

[8] M. Read, R. Cahay, P. Cornil, and J. Duchesene, *Compt. Rend.*, **257**, 1778 (1963).

[9] D. F. R. Gilson and C. T. O'Konski, *J. Chem. Phys.*, **48**, 2767 (1968).

[10] a) S. C. Wallwork, *J. Chem. Soc.*, **1961**, 494. b) C. K. Prout and J. D. Wright, *Angew. Chem.*, **80**, 688 (1968).

NQR studies on organic CT complexes.[11–13]

Semin and others found that in picryl chloride complexes the ^{35}Cl NQR frequencies can be correlated with the ionization potential of D's.[13]

This paper presents NQR frequencies of CA complexes with aromatic hydrocarbons and amines and gives discussion on the relation of NQR parameters to other quantities pertaining to the CT interactions in the light of Mulliken's CT theory. The result of the Zeeman effect experiment on CA-8-hydroxyquinoline complexes is compared with that of X-ray analysis.[14]

Experimental

Chloranil was purified by recrystallization from a benzene solution. The *N*,*N*-dimethylaniline complex was obtained by mixing solid chloranil and *N*,*N*-dimethylaniline directly under stirring followed by washing with ether. Bis-8-hydroxyquinolinatocopper(II) complex was prepared after the method in literature.[15] Other complexes were prepared by mixing the warm benzene solutions of the D- and A-components.

The ^{35}Cl NQR was observed at liquid nitrogen temperature with a Dean-type super-regenerative detector.[16] The resonace frequencies (ν_Q) were determined on an oscilloscope by use of a VHF signal generator (Yokogawa-Hewlett-Packard Model 608C) and a frequency counter (Takeda Riken TR-5578). The error in the frequency measurement was about 1 kHz except for the case of *p*-phenylenediamine complex for which the resonance line was very weak and broad, the uncertainty being about 5 kHz. The Zeeman effect study was carried out at liquid nitrogen temperature with Helmholtz coils and a goniometer designed for low temperature studies.[17] The zero-splitting loci for the ^{35}Cl reosnance lines were determined on an oscilloscope by rotating the sample and the magnetic field about mutually orthogonal axes. A magnetic field strength between 150 and 300 gauss was used.

Unsuccessful attempts were made to find the ^{35}Cl resonance lines in the frequency range 25—42 MHz in the chloranil complexes with the following donors: phenothiazine, *p*-anisidine, benzidine, tetramethyl-*p*-phenylenediamine, *p*-aminodiphenylamine, 1,8-diaminonaphthalene, and K$^+$-(chloranil)$^-$. Absence of the resonance lines is probably

Table 1. Nuclear quadrupole resonance frequencies, infrared frequencies and the ionization potentials of chloranil complexes

No	Donor	ν_Q at 77°K (MHz)	ν(C–Cl) b_{2u} (cm^{-1})	ν(C=O) (cm^{-1})	I_p (eV)
1	Durene	27.3958	739	1685	8.3[b]
2	Hexamethylbenzene	37.5031	737	1686	7.95[b]
		37.7127			
3	Pyrene	37.735	731	1687	7.45[c]
		37.872			
4	Perylene	37.3448	731	1682	7.1[c]
		37.3595	737		
		37.4102			
		37.4775			
5	*N*,*N*-Dimethylaniline	36.9039	730	1682	7.3[b]
		37.1373	739		
		37.3612	744		
6	*P*-Phenylenediamine	36.944			
7	Tetramethylbenzidine	37.3561			
8	1,5-Diaminonaphthalene	36.875			
		37.520			
9	8-Hydroxyquinoline(1:2)	37.2808	742	1688	7.9[d]
		37.3904			
10	Bis-8-hydroxyqunolinato-Copper (II)	36.8353	741	1680	7.3[d]
		37.2196	755		
	Chloranil	37.4414	755[a]	1683[a]	
		37.4693		1695[a]	
		37.5134			
		37.5830			

a) Reference 22. b) G. Bregleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959). c) Reference 15. d) Reference 15.

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11) R. A. Bennett and H. O. Hooper, *J. Chem. Phys.*, **47**, 4855 (1967).

12) G. A. Bowmaker and S. Hacobian, *Aust. J. Chem.*, **22**, 2047 (1969).

±0.2° and $x/a=5269(14)$ for the coordinate of O(2) in Table 2 of his paper.

15) A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc.*, **1965**, 2579.

due either to some imperfections in the complex or to the effect of the occlusion of the solvent. It is also possible that delocalized unpaired electrons prevent the observation of the NQR lines in the case of the radical salts.

Results and Discussion

The ^{35}Cl NQR frequencies of chloranil in the complexes together with those in the pure chloranil crystal are listed in Table 1. The resonance frequencies in CA-hexamethylbenzene complex slightly differ from those in literature.[18] The number of resonance lines in 8-hydroxyquinoline, hexamethylbenzene, and pyrene complexes coincides with that of the non-equivalent chlorine atoms in these complexes.[14,19,20]

It is to be noted that the resonance signals have been observed in freshly prepared specimens of *N*,*N*,-*N'*,*N'*-tetramethylbenzidine, 1,5-diaminonaphthalene and *p*-phenylenediamine complexes but they faded out in about a week. This phenomenon is perhaps due to decomposition of the complexes. On the other hand, in hexamethylbenzene, pyrene and perylene complexes the resonance lines became progressively sharper during several months. This might be due to the relaxation of the lattice strain produced in the preparation process.

In Table 1, C–Cl b_{2u} and C=O stretching frequencies are also recorded. They were measured for solid complexes in nujol mull and were assigned according to Prichard[21] and Yamada and Kawamori.[22]

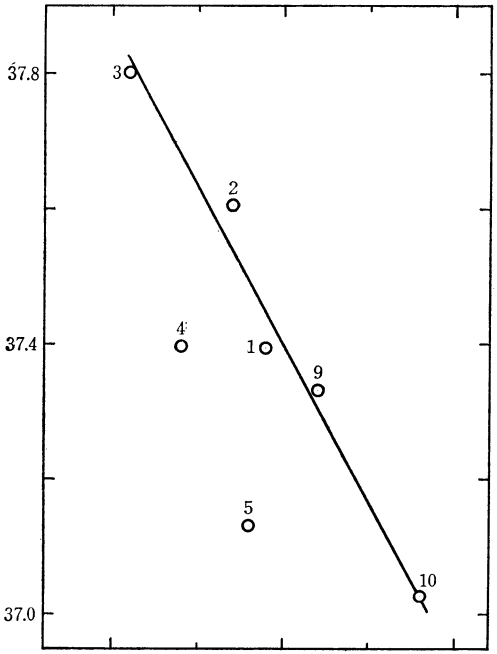

Fig. 1. The average nuclear quadrupole resonance frequency plotted against the C-Cl b_{2u} stretching frequency. For the numbers expressing the complexes cf. Table 1.

Correlation between the Quadrupole Resonance Frequencies and Infrared Spectra. In Figs. 1 and 2 the average NQR frequency ν_Q is plotted against the average C–Cl b_{2u} and C=O stretching frequencies for each complex, respectively. Although almost linear relationship between ν_Q and C–Cl b_{2u} mode holds in Fig. 1, the slope inclined in the opposite direction to that found experimentally[23] or predicted theoretically[24] for simple σ-bonded molecules. We see from Fig. 2 that ν_Q changes more rapidly than the C=O stretching frequency in the same direction.

These facts can be interpreted qualitatively as follows: The large inductive effect of an oxygen atom, making its π-electron density increase, increases the partial π-bond character between the carbon and the chlorine atoms in a free CA molecule to make the bond stronger than those in chlorobenzenes. Now, if a charge transfer complex is formed between CA and a molecule acting as an electron donor, the π-electron density on the CA molecule increases. This seems to make the two C=O bonds stronger,[25] whereas the π-bond character in the four C–Cl bonds decreases in

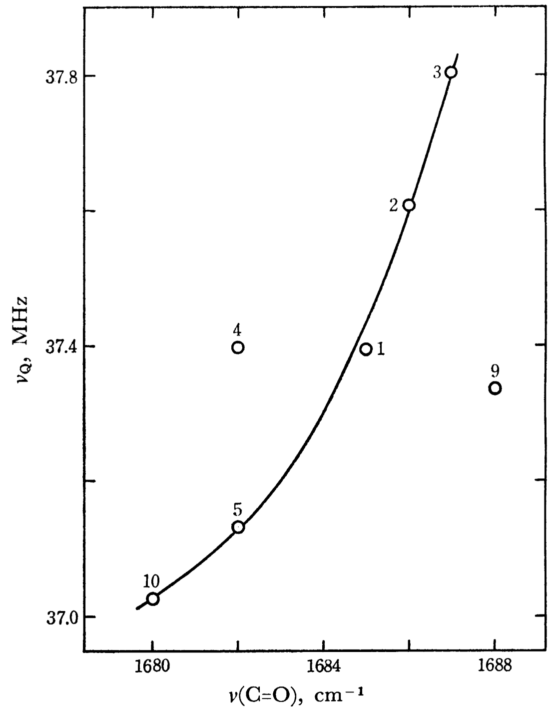

Fig. 2. The average nuclear quadrupole resonance frequency plotted against the C=O stretching frequency. For the numbers expressing the complexes, cf. Table 1.

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[18] D. C. Douglass, *J. Chem. Phys.*, **32**, 1882 (1966).

[19] T. T. Harding and S. C. Wallwork, *Acta Crystallogr.*, **8**, 787 (1955).

[20] K. Ogawa, private communication.

[21] F. E. Prichard, *Spectrochim. Acta*, **20**, 127 (1964).

[22] H. Yamada and M. Kawamori, to be published.

[23] R. Gerdil, *Nature*, **212**, 922 (1966).

[24] A. B. Anderson, N. C. Handy, and R. G. Parr, *J. Chem. Phys.*, **50**, 3634 (1969).

[25] In view of the very narrow range in which ν(C=O) changes its frequency, the trend appearing in Fig. 2 may not be significant enough for us to state that the charge transfer increases the C=O bond order (strength). In fact, ν(C=O) is displaced to a *lower* frequency by a radical ion formation (*cf.* Y. Matsunaga, *Can. J. Chem.*, **38**, 1172 (1960); Y. Iida, This Bulletin, **43**, 345 (1970); M. A. Slifkin, *Phys. Lett.*, **7**, 195 (1970)). Perhaps in the limit of weak complexes, the transfer of minute quantity of electronic charge might affect the C=O and C–Cl bonds in a different way from that in the case of strong complexes.

comparison with that in the bonds in a free CA molecule. Therefore, ν(C=O) shifts to a higher frequency and ν(C–Cl) to a lower with an increase in the effective number of π-electrons on CA due to the complex formation. ν_Q is expected to increase in such a situation as will be discussed in the next section. Then it seems reasonable to consider that the correlations between ν_Q and infrared frequencies in Figs. 1 and 2 originate from the charge transfer.

Predictions by Theory of Charge Transfer and Comparison with Experiments. The ground state wave function of a CT complex may be given after Mulliken[1b)] by

$$\Psi_N = a\phi_0 + b\phi_1 \tag{1}$$

where ϕ_0 and ϕ_1 are the wave functions for the no-bond and the CT structures, respectively, and both are assumed to have been normalized.

We are interested in the electric field gradient (EFG) q at a chlorine nucleus in the acceptor molecule, which is given by

$$q = \sum_i e_i \int \Psi_N(3\cos^2\theta_i - 1)/r_i^3)\Psi_N d\tau + q_{ex} \tag{2}$$

In this equation the resonant ^{35}Cl nucleus is assumed to be at the origin; the sum represents the contributions to q from the nuclear or the electronic charges e_i at the position r_i and θ_i in the molecule. The summation in Eq. (2) must be carried out over all the nuclei and the electrons in the molecule. The second term q_{ex} is the EFG which comes from all molecules in the crystal except for the acceptor under consideration. Substituting Eq. (1) into Eq. (2), q is written as

$$q = a^2q_0 + 2abq' + b^2q_{CT} + q_{ex} \tag{3}$$

where

$$q_0 = \sum_i e_i \int \phi_0(3\cos^2\theta_i - 1)/(r_i^3)\phi_0 d\tau$$

$$q' = \sum_i e_i \int \phi_0(3\cos^2\theta_i - 1)/(r_i^3)\phi_1 d\tau$$

and

$$q_{CT} = \sum_i e_i \int \phi_1(3\cos^2\theta_i - 1)/(r_i^3)\phi_1 d\tau$$

q_0 is the EFG in the no-bond structure and is thought to be approximately equal to that in a free acceptor molecule. q' is the EFG connecting the no-bond and the CT states. It will be roughly proportional to the overlap integral between the donor and the acceptor $S=\int\phi_0\phi_1 d\tau$. q_{CT} represents the EFG in the CT state where one π-electron has been transfered from the donor to the acceptor.

By using the normalization condition on Ψ_N,

$$a^2 + 2abS + b^2 = 1$$

Eq. (3) can be rewritten as follows.

$$q = q_0 + 2ab(q' - Sq_0) + b^2(q_{CT} - q_0) + q_{ex} \tag{4}$$

If it is assumed that the second term on the right hand side of Eq. (4) is small in comparison with the other terms, and that q_{ex} varies only slightly from one donor to another, we can expect that the EFG is linearly dependent on the amount of contribution of the CT state b^2 to the ground state of the complex. Then it follows that

$$q \doteqdot q_0' + b^2\Delta q_{CT} \tag{5}$$

where $q_0' = q_0 + q_{ex}$ and $\Delta q_{CT} = q_{CT} - q_0$ or in terms or the resonance frequencies

$$\nu_Q \doteqdot \nu_0' + b^2\Delta\nu_{CT} \tag{6}$$

The contribution of the CT structure b^2 can also be related to the ionization potential I_p of a donor through the formula

$$b/a \doteqdot cS/(I_p - A) \tag{7}$$

where c and A are constants. Since $a \approx 1$ for a weak complex, it follows that

$$\nu_Q \doteqdot \nu_0' + \Delta\nu_{CT}(cS)^2/(I_p - A)^2 \tag{8}$$

A comparison of the experimental results with theoretical predictions is a very crucial matter.

Equation (6) states that ν_Q should increase when chloranil forms a CT complex. However, Table 1 shows that the resonance frequencies for some of the complexes are lower than the frequency for chloranil itself, whereas those for other complexes are higher. This fact may be an indication of the relieved strain of chloranil molecules upon complex formation. Therefore comparison among a family of donors seems more practical. Hydrocarbon donors give higher ν_Q than do the nitrogen- or oxygen-containing donors. Reliable values of b^2 have not been obtained except for hexamethylbenzene[26)] and durene[27)] complexes which b^2 of the order of 0.04 has been assigned.

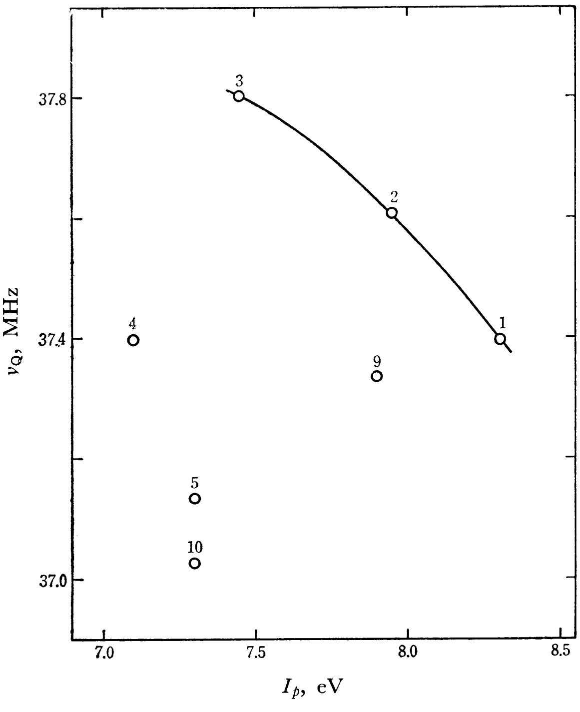

Fig. 3. The average nuclear quadrupole resonance frequency ν_Q *vs.* the ionization potential of the complex.
For the numbers expressing the complexes cf. Table 1.

[26)] G. Briegleb, J. Czekalla, and G. Reuss, *Z. Phys. Chem.*, **30**, 333 (1961).

[27)] G. Briegleb and J. Czekalla, *Angew. Chem.*, **72**, 401 (1960).

Correlation of ν_Q with I_p or the CT absorption bands is also very poor as seen in Fig. 3.

The reason for the poor correlation between the quadrupole resonance and the available CT properties is probably twofold. One is that for weak complexes the crystalline field effect (q_{ex}) is often as large as the CT effect. This is shown by the fact that *N,N*-dimethylaniline, for example, gives three resonance lines between 36.9 and 37.4 MHz. The other reason would be that the charge transfer is mainly responsible for the appearance of the so-called CT band but may not be so for the intermolecular interaction. In other words the field of force in which the acceptor molecule is placed consists not merely of the charge transfer interaction but also of other contributions. One evidence of the latter is found in the good relationship between ν_Q and vibrational frequencies as depicted in Figs. 1 and 2.

Zeeman Effect on Chloranil-8-Hydroxyquinoline Complex (1 : 2). Electrons transferred from the donor molecule will enter a π-orbital of the acceptor molecule which will then migrate to some extent to the *p*-orbital of the chlorine atom. Such an effect will cause a change in the asymmetry parameter of the EFG. We have grown a large single crystal of CA-8-hydroxy quinoline complex and carried out a Zeeman effect experiment of the ^{35}Cl resonance lines at room temperature. This crystal belongs to the triclinic space group $P\bar{1}$ and contains one formula unit in the unit cell: There are two crystallographically nonequivalent chlorine atoms and only one equivalent direction exists for each C-Cl bond.[14]

The zero-splitting loci were determined for the two ^{35}Cl lines, ν_1 and ν_2. The directions of the principal axes (X, Y, Z) of the EFG tensor in the laboratory-fixed coordinate system were determined and were transformed to X_c, Y_c, and Z_c in the crystal-fixed coordinate system. Calculation of the directions of X, Y, and Z was carried out by the least squares method programmed for the NEAC-2200 digital computer.

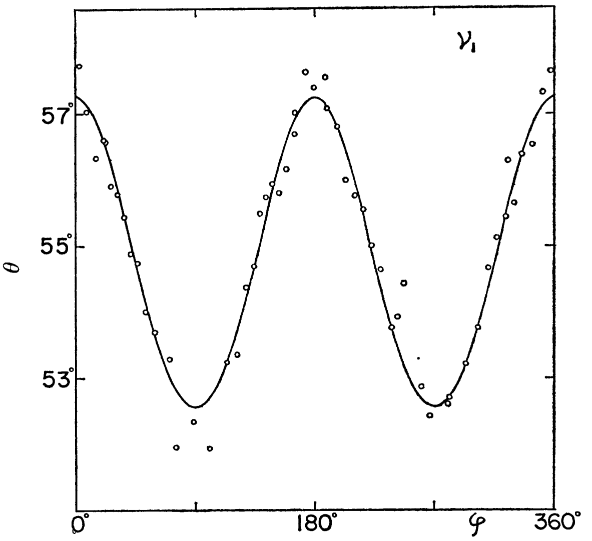

Fig. 4. The zero-splitting locus of ν_1 in 8-hydroxyquinoline complex in the principal axes system of the electric field gradient tensor.

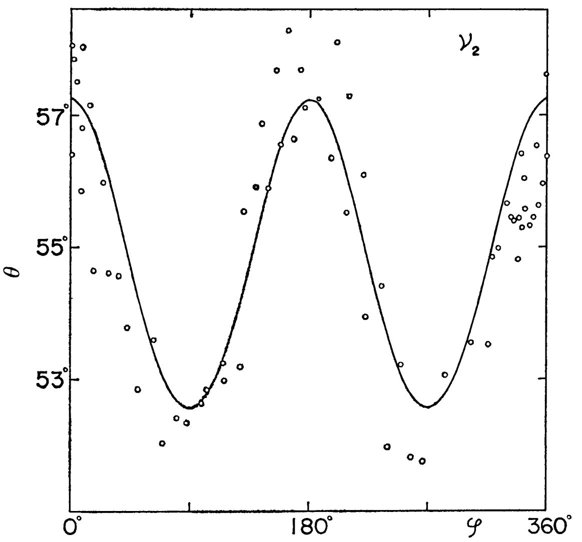

Fig. 5. The zero-splitting locus of ν_2 in 8-hydroxyquinoline complex in the principal axes system of the electric field gradient tensor.

The numbers of the data employed were 55 and 70 for ν_1 and ν_2, respectively.

The results are shown in Figs. 4 and 5. In these figures θ and φ express the direction of the zero splitting locus in the principal axes system of the EFG tensor. The solid curve in each figure corresponds to the theoretical relation[28]

$$\sin^2\theta = 2/(3-\eta\cos^2\varphi) \tag{9}$$

where η was chosen so as to obtain the best fit between experimental data and the theoretical curve.

The direction cosines in the crystal fixed coordinate system are given in Table 2, where the X-axes of the EFG are taken to be perpendicular to the quinone ring. The direction cosines of the Z-axes of the EFG's can be compared with the C-Cl bond directions determined by X-ray analysis.[14] Although the principal Z-axis of the EFG for ν_2 coincides with the direction of the C_2-Cl_{12} bond,[29] that for ν_1 differs from the direction of the C_1-Cl_{11} bond by about 17°. The reason for this discrepancy is not obvious.

η is thus given, in terms of the number of unbalanced *p*-electrons U_X, Y_Y, and U_Z, by the formula[6a]

$$\eta = (3/2)(U_X - U_Y)q_{at}/q \tag{10}$$

where q_{at} is the EFG in an atomic chlorine. If it is assumed that the charge transfer is accompanied only by an increase in the π-electron density of the acceptor molecule, U_Y can be put equal to $U_Y{}^0$ corresponding to the free acceptor molecule whereas U_X can be expressed as $U_X = U_X + \delta$, where δ expresses the increase in the excess electrons in the p_X- or the π-orbital of the chlorine. Then, Eq. (10) can be written as

$$\begin{aligned}\eta &= (3/2)(U_X{}^0 - U_Y{}^0)q_{at}/q + (3/2)\delta q_{at}/q \qquad (11)\\ &\doteqdot \eta_0 + (3/2)\delta q_{at}/q\end{aligned}$$

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28) C. Dean, *Phys. Rev.*, **96**, 1053 (1954).

29) See Ref. 14 for the numbers affixed to the atoms.

30) a) S. S. C. Chu, G. A. Jeffrey, and T. Sakurai, *Acta Crystallogr.*, **15**, 661 (1962). b) C. B. Richardson, *J. Chem. Phys.*, **38**, 510 (1963).

TABLE 2. NUCLEAR QUADRUPOLE COUPLING CONSTANTS, ASYMMETRY PARAMETERS, AND THE DIRECTION COSINES OF THE PRINCIPAL Z-AXES OF THE ELECTRIC FIELD GRADIENT TENSORS

The direction cosines are compared with the direction of the C–Cl bond determined by X-ray analysis (Ref. 14).

Bond	Method	R (A)	e^2Qq/h (MHz)	η %	X_c (a^*)	Y_c (b)	Z_c (c')
C_{11}-Cl_1	NQR	—	74.191	17.3	−0.5182	−0.5251	0.6752
	X-ray	1.77	—	—	−0.5680	−0.5448	0.5556
C_{12}-Cl_2	NQR	—	74.416	17.2	0.5420	−0.5591	−0.6274
	X-ray	1.70	—	—	0.5504	−0.5062	−0.6639

	NQR	X-ray
Angle between Cl_1 σ bond and Cl_2 σ bond	65°43′	66°04′
Cl_1 π bond and Cl_2 π bond	2°25′	—

where η_0 is the asymmetry parameter in the free acceptor.

On the other hand, the EFG q is expressed by using the unbalanced electron numbers as

$$q = \left(U_Z - \frac{(U_X + U_Y)}{2}\right)q_{\mathrm{at}} + q_{\mathrm{ex}}$$

$$= q_0'\ (\delta/2)q_{\mathrm{at}}$$

By comparing this equation with Eq. (5), we get

$$(\delta/2)q_{\mathrm{at}} \doteqdot -b^2\Delta q_{\mathrm{CT}}$$

and therefore

$$\eta \doteqdot \eta_0 - 3b^2\Delta q_{\mathrm{CT}}/q$$

Since $\Delta q_{\mathrm{CT}}>0$, η should decrease with an increase in CT. As shown in Table 3, η's in CA-8-hydroxy quinoline complex are significantly small in comparison with those in pure chloranil crystal for which η is about 0.21:[30] and this is consistent qualitatively with Eq. (12). However a quantitative comparison does not seem of any value for reason given in the preceding Section.

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