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Charge Transfer in Acetonitrile-Halogen Complexes

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The charge transfer in acetonitrile-halogen complexes was examined by means of the nuclear quadrupole resonances resulting from the relevant nuclei. ^{14}N NQR parameters ($|e^2Qq|=3.6000$ MHz and $\eta=0.0183$) and ^{35}Cl NQR parameters ($|e^2Qq|=107.44$ and 108.50 MHz) were obtained for the acetonitrile-chlorine complex, whereas ^{14}N NQR parameters ($|e^2Qq|=3.5439$ MHz and $\eta=0.0043$) and a ^{81}Br NQR parameter ($|e^2Qq|=640.52$ MHz) were obtained for the acetonitrile-bromine complex. From these parameters, the charged states of the nitrogen, chlorine, and bromine atoms in these charge-transfer complexes were calculated by means of the Townes and Dailey theory. In the case of the acetonitrile-bromine complex, the charge loss at the nitrogen atom was not equal to the gain at the bromine atom, as long as the charge was assumed to be transferred only to the p-orbital of the latter. This discrepancy was explained by assuming some d-hybridization at the bromine atom. The charged states of the nitrogen atoms in these complexes were qualitatively in good agreement with the electron affinities of the chlorine and bromine molecules. Moreover, the temperature dependences of the ^{14}N and ^{81}Br nuclear quadrupole coupling constants in the acetonitrile-bromine complex were investigated in the range from -196 to -60 °C.

The charge-transfer (CT) complexes of nitriles or amines with halogens have been investigated by various spectroscopic methods. The NQR method is particularly useful for investigating the charge distribution in the CT complexes. However, NQR data have been reported only on the halogen atoms in electron acceptors. Therefore, we planned to examine ^{14}N NQR in some weak CT complexes, including the CT complexes of acetonitrile with the chlorine and bromine molecules. The crystal structure of the acetonitrile-bromine complex was recently determined to be as is shown in Fig. 1.[1] The open and shaded circles represent atoms at $y=0$ and $y=\pm 1/2$ respectively. The intramolecular bonds are represented by the solid lines, while the intermolecular bonds are represented by the broken lines. The distance between the nitrogen and bromine atoms in the acetonitrile-bromine complex is shorter by 0.61 Å than the sum of their van der Waals radii. Therefore, it may be considered that there is a weak interaction between the acetonitrile and bromine molecules. A similar intermolecular interaction may be expected to exist between the acetonitrile and chlorine molecules.

1) K. M. Marstokk and K. O. Strømme, *Acta Crystallogr.*, **B24**, 713 (1968).

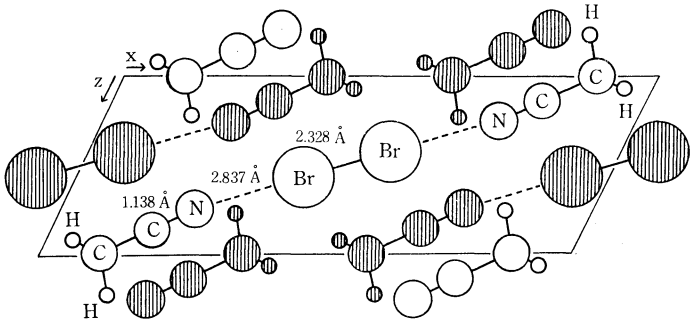

Fig. 1. The crystal structure of the acetonitrile-bromine complex.

Experimental

The ^{14}N NQR spectra of these CT complexes were obtained by the use of a frequency-modulated spectrometer described previously,[2] whereas the ^{35}Cl and ^{81}Br NQR spectra of these CT complexes were obtained by the use of a superregenerative spectrometer. The resonance frequencies were measured by means of two heterodyne-type frequency meters, BC-221 and TS-175C/U, whose frequencies were checked by means of a frequency counter, TR-5578, of the Takeda Riken Co. The measurements were carried out at the temperature of liquid nitrogen, but the studies of the temperature dependences were performed by blowing the vapour of the liquid nitrogen from a Dewar bottle. The temperatures were measured by the use of a thermocouple.

Preparation of the Acetonitrile-chlorine Complex. Gaseous chlorine was generated by the reaction of hydrogen chloride with manganese dioxide, and was liquefied by the use of a mixture of acetone and dry ice as the coolant. Then acetonitrile obtained from commercial sources was mixed with liquid chlorine in the mol ratio of 2: 1 at about −70 °C.

Preparation of the Acetonitrile-bromine Complex. Commercial acetonitrile was mixed with commercial bromine in the mol ratio of 2: 1 at about −40 °C.

Results and Discussion

Generally a pair of ^{14}N NQR frequencies, ν_I and ν_{II}, are observed as follows:

$$\nu_I = |e^2Qq|(3-\eta)/4, \quad (1)$$

$$\nu_{II} = |e^2Qq|(3+\eta)/4. \quad (2)$$

On the other hand, the ^{35}Cl or ^{81}Br NQR frequency, ν_0, is obtained according to the following equation:

$$\nu_0 = |e^2Qq|(1+\eta^2/3)^{1/2}/2, \quad (3)$$

where $|e^2Qq|$ and η are the quadrupole coupling constant and the asymmetry parameter respectively. Our sample of the acetonitrile-chlorine complex revealed a pair of ^{14}N resonance lines and two ^{35}Cl resonance lines, with an intensity ratio of about 5: 3, as is shown in Fig. 2. We attributed the resonance line of 53.72 MHz to the ^{35}Cl nuclei in the CT complex, and that of 54.25 MHz, to the ^{35}Cl nuclei in the non-reacted chlorine molecules. The acetonitrile-bromine complex showed a pair of ^{14}N resonance lines and a ^{81}Br resonance line, as is shown in Fig. 2. The ^{14}N nuclear quadrupole coupling constant in the acetonitrile-bromine complex is lower than that in the acetonitrile-chlorine complex. This seems to suggest that the interaction between the nitrogen and bromine atoms is stronger than that between the nitrogen and chlorine atoms in the CT complexes. The quadrupole coupling constants and asymmetry parameters derived by substituting these resonance frequencies into Eqs. (1), (2), and (3) are listed in Table 1.

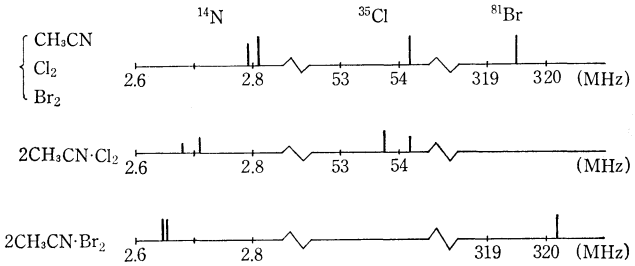

Fig. 2. NQR absorption lines in acetonitrile-halogen complexes.

The orbitals at the nitrogen atom or halogen atoms have the general form listed in Table 2, where the value of s is 0.5 in the case of the nitrogen atom[3] and 0 in the cases of the halogen atoms. The occupation numbers of these orbitals at the nitrogen atom in acetonitrile are denoted by a, a, b, and 2, whereas those in the CT complexes denoted by a, a, b', and x. The quadrupole coupling constant has been related to

Table 1. NQR parameters in acetonitrile-halogen complexes

Complex		ν (MHz)	$\lvert e^2Qq\rvert$ (MHz)	η (%)
$2CH_3CN\cdot Cl_2$	^{14}N	2.6835;2.7165	3.6000	1.83
	^{35}Cl	53.72	107.44	—
		54.25	108.50	
$2CH_3CN\cdot Br_2$	^{14}N	2.6541;2.6618	3.5439	0.43
	^{81}Br	320.26	640.52	—

2) H. Negita, M. Hayashi, and T. Okada, *J. Sci. Hiroshima Univ., Ser. A*, **35**, 85 (1971).

3) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London and New York (1969), p. 227.

Table 2. Orbitals and their occupation numbers at the nitrogen atom

Orbital	Occupation number[a]	
$\varphi_1=\chi_{P_x}$	a	(a)
$\varphi_2=\chi_{P_y}$	a	(a)
$\varphi_3=\sqrt{s}\,\chi_s+\sqrt{1-s}\,\chi_{P_z}$	b	(b')
$\varphi_4=\sqrt{1-s}\,\chi_s-\sqrt{s}\,\chi_{P_z}$	2	(x)

a) The numbers in the parentheses are those in the complex.

the occupation numbers of p-orbitals (N_x, N_y, and N_z) by Townes and Dailey:[4]

$$|e^2Qq/e^2Qq_p| = N_z - (N_x+N_y)/2, \quad (4)$$

where $|e^2Qq_p|$ is the quadrupole coupling constant produced by one p-electron in the outmost occupied shell. From Table 2, the N_x, N_y, and N_z values of the nitrogen atom in an acetonitrile molecule are found to be a, a, and $(b+2)/2$ respectively, while those in the CT complexes are found to be a, a, and $(b'+x)/2$ respectively. Therefore, the electron number transferred from the nitrogen atom, δ, is shown by the following equation:

$$\delta = (b+2) - (b'+x)$$
$$= 2(|e^2Qq_{compound}| - |e^2Qq_{complex}|)/|e^2Qq_p|. \quad (5)$$

The electron numbers transferred to the halogen atoms are calculated from their coupling constants. The $|e^2Qq_p|$ values of the nitrogen, chlorine, and bromine atoms are 10, 109.74,[5] and 643.03 MHz[6] respectively.

Table 3. The values of δ in acetonitrile-halogen complexes

Complex	Value of δ	
	Nitrogen	Halogen
$2CH_3CN\cdot Cl_2$	+0.028	−0.021
$2CH_3CN\cdot Br_2$	+0.029	−0.004

Table 3 lists these values of δ in the CT complexes. In spite of the rough approximations, the values of δ at the nitrogen and chlorine atoms in the acetonitrile-chlorine complex are complementary. However, the value of δ at the bromine atom in the acetonitrile-bromine complex is about one-seventh of that at the nitrogen atom. This discrepancy can be interpreted by theorizing that a part of the charge transferred from the nitrogen atom enters the d_z-orbital of the bromine atom, which has less effect on the coupling constant than the p_z-orbital. This interpretation is along the same lines as that for the bromine molecular crystal, where the d-orbital of the atom has been taken by Kojima *et al.*,[7] to be used for the intramolecular bond. The recently-reported values of the electron affinities of the chlorine and bromine molecules are 2.52±0.17 and 2.87±0.14 eV respectively,[8] these values are parallel with the values of δ at the nitrogen atoms. According to the crystal structure of the acetonitrile-bromine complex, the bromine-bromine length, 2.328 Å, is longer than that observed in the free molecule, 2.284 Å.[1] This indicates that the negatively-charged bromine atoms repel each other.

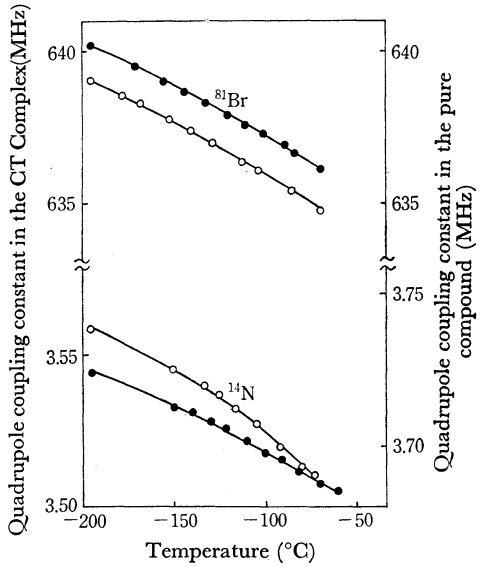

Fig. 3. The temperature dependences of ^{14}N and ^{81}Br quadrupole coupling constants in acetonitrile (○), bromine (○), and acetonitrile-bromine complex (●).

The temperature dependences of the ^{14}N and ^{81}Br quadrupole coupling constants in acetonitrile, bromine, and the acetonitrile-bromine complex are shown in Fig. 3. No phase transition is observed in the range from −196 to −60 °C. The temperature dependence of the ^{14}N quadrupole coupling constant in the CT complex is smaller than that in acetonitrile. Therefore, we see that the vibration of an acetonitrile molecule in the CT complex is suppressed by the interaction with the bromine atom. On the other hand, the temperature dependence of the ^{81}Br quadrupole coupling constant in the CT complex is nearly the same as that in solid bromine. This suggests that the bromine molecule interacts with its neighboring molecules to some extent, even in the molecular crystal, as is to be expected from its crystal structure.[9]

4) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).
5) V. Jaccarino and J. G. King, *Phys. Rev.*, **83**, 471 (1951).
6) J. G. King and V. Jaccarino, *ibid.*, **94**, 1610 (1954).
7) S. Kojima, K. Tsukada, A. Shimauchi, and Y. Hinaga, *J. Phys. Soc. Jap.*, **9**, 795 (1954).
8) J. J. DeCorpo and J. L. Franklin, *J. Chem. Phys.*, **54**, 1885 (1971).
9) J. Donohue and S. H. Goodman, *Acta Crystallogr.*, **18**, 568 (1965).