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The Bromine Nuclear Quadrupole Resonance of the Molecular Complex of Aluminum Tribromide with Benzene

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The bromine nuclear quadrupole resonance (NQR) and its Zeeman effect have been observed in the molecular complex of aluminum tribromide with benzene at room temperature. The resonance frequencies are 79.99, 90.10, and 91.18 MHz for ^{81}Br at 301°K. The asymmetry parameters of the field gradient are 28.9 ± 1.1, 8.6 ± 1.0, and $6.0\pm0.9\%$ for the bromine atoms in the order of increasing resonance frequency. Aluminum tribromide forms the dimer in the complex crystal as well as in the pure state. The bond angle between a pair of terminal bromine atoms and the interbond angle at the bridging bromine atom are found to be $117.3\pm0.5°$ and $95.5\pm0.2°$ respectively; these values correspond to those of $122\pm2°$ and $87\pm2°$ obtained from the X-ray analysis. Furthermore, the charge-transfer from the benzene ring to the bromine atom is discussed on the basis of the NQR parameters.

It has been established that aluminum tribromide forms molecular complexes with many organic compounds, and they have been studied extensively by various methods. These complexes with organic compounds belong mostly to the type of $AlBr_3 \cdot D$,[1] where the aluminum atom coordinates the oxygen or nitrogen atom of the donor, D. There is also another type of complex, such as $Al_2Br_6 \cdot D$,[2] where the bromine atom may combine with the aromatic ring of a donor, D, such as benzene or toluene.

The NQR frequency depends on the electric-field gradient at the site of the resonant nucleus. As the bromine atom seems to be involved in the binding between the component molecules in the complex of $Al_2Br_6 \cdot D$, the Br NQR will clarify the extent and direction of the charge-transfer as well as the molecular structure of Al_2Br_6. In this respect, it will be interesting to examine the Br NQR of the $Al_2Br_6 \cdot C_6H_6$ complex and to observe the Zeeman effect on the NQR, using the single crystal of the complex.

Concerning aluminum tribromide itself, both the Al[3] and Br NQR frequencies[4] as well as the Br Zeeman effect[5] have been measured. The ^{81}Br NQR spectrum is composed of the singlet of 81.82 MHz and the doublet of 95.01 and 96.43 MHz at 77°K. The singlet was attributed to the bridging bromine atom, and the doublet, to the two different sites of the terminal bromine atoms in the dimer. NQR studies of the bromine atoms in some complexes of $AlBr_3 \cdot D$ have been reported,[6] but none on the complex of $Al_2Br_6 \cdot D$ are known to us.

According to the crystal structure of $Al_2Br_6 \cdot C_6H_6$ established by X-ray analysis,[7] the space group is C_i, with one species, $Al_2Br_6 \cdot C_6H_6$, in a unit cell of the dimensions of $a=6.85$ Å, $b=6.91$ Å, $c=9.00$ Å, $\alpha=104.6°$, $\beta=103.1°$, and $\gamma=90.0°$. The aluminum tribromide molecule in the complex was confirmed to form the dimer as in its pure crystal, and the centers of both the Al_2Br_6 and C_6H_6 components are centrosymmetric. Figure 1 shows the crystal structure projected along the *b* axis. The shortest distance between the layer of the bromine atoms and the plane of the benzene ring is 3.2 Å.

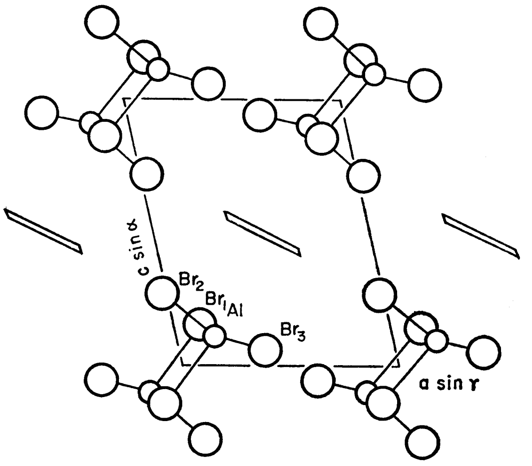

Fig. 1. Crystal structure of $Al_2Br_6 \cdot C_6H_6$ projected along *b* axis.

Experimental

Aluminum tribromide was prepared by dropping liquid bromine into aluminum metal and was purified by distillation several times. The purification of benzene and the synthesis of the complex were performed with reference to the literature.[7] The single crystal of the complex was obtained by lowering an ampoule of the saturated benzene solution of aluminum tribromide slowly through an electric furnace at about 40°C.

The NQR spectrometer employed was a superregenerative oscillator with frequency modulation, and the absorption lines were displayed on an oscilloscope. The resonance frequencies, ν, were measured with a standard frequency generator whose frequency was determined by means of a universal counter, TR-5578, of the Takeda Riken Industry

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[1] M. J. Sienko, R. A. Plane, and R. E. Hester, "Inorganic Chemistry," Benjamin, Inc. New York (1965), Part 2, p. 91.

[2] H. C. Brown and W. J. Wallace, *J. Amer. Chem. Soc.*, **75**, 6265 (1953).

[3] P. A. Cassabella, P. J. Bray, and R. G. Barnes, *J. Chem. Phys.*, **30**, 1393 (1959).

[4] R. G. Barnes and S. L. Segel, *ibid.*, **25**, 180 (1956).

[5] T. Okuda, H. Terao, O. Ege, and H. Negita, *ibid.*, **52**, 5489 (1970).

[6] Yu. K. Maksyutin, E. V. Bryukhova, G. K. Semin, and E. N. Cur'yanova, *Izv. Akad. Nauk SSSR. Ser. Khim.*, **1968**, 2658.

[7] D. D. Eley, J. H. Taylor, and S. C. Wallwork, *J. Chem. Soc.*, **1961**, 3869.

Co., Ltd. The Zeeman effect was measured by means of the zero-splitting cone method in the low-magnetic field. The magnetic field of about 300 gauss was supplied by a Helmholtz coil, and the patterns of the zero-splitting loci were observed at room temperature.

Results and Discussion

The observed NQR frequencies for the bromine atoms in the complex at 301°K are listed in Table 1.

TABLE 1. ^{81}Br NQR PARAMETERS OF $Al_2Br_6 \cdot C_6H_6$ AND Al_2Br_6 AT 301°K

Compound	ν (MHz)	e^2Qq (MHz)	η (%)	ρ
$Al_2Br_6 \cdot C_6H_6$	79.99	157.8	28.9±1.1	0.45
	90.10	180.0	8.6±1.0	0.67
	91.18	182.3	6.0±0.9	0.67
Al_2Br_6	79.85	158.1	24.8[a]	0.45
	92.36	184.6	7.3[a]	0.66
	93.47	186.6	10.6[a]	0.66

a) Ref. 5

The spectrum of each bromine isotope consists of three resonance lines; in the case of ^{81}Br, the singlet is about 10 MHz below the doublet in the 90 MHz region, and three lines have almost the same intensity. This feature of the spectrum and the asymmetry parameters calculated from the Zeeman effect are quite similar to those in pure aluminum tribromide and other trihalides of the IIIb group.[4,8] Therefore, the two resonance lines in the 90 MHz region may be ascribed to two kinds of terminal bromine atoms, and the remaining one, to the bridging bromine atom.

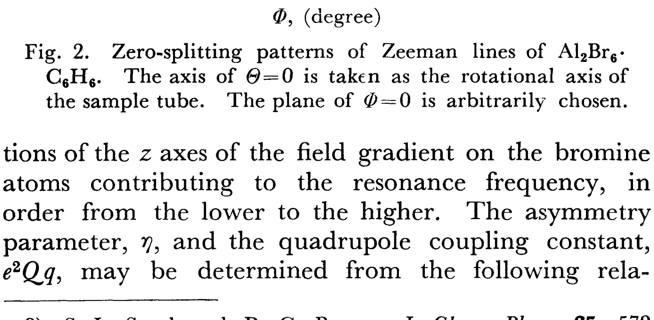

Fig. 2. Zero-splitting patterns of Zeeman lines of $Al_2Br_6 \cdot C_6H_6$. The axis of $\Theta=0$ is taken as the rotational axis of the sample tube. The plane of $\Phi=0$ is arbitrarily chosen.

Bond Angle. The zero-splitting patterns observed are shown in Fig. 2, where Br_1, Br_2, and Br_3 are the directions of the z axes of the field gradient on the bromine atoms contributing to the resonance frequency, in order from the lower to the higher. The asymmetry parameter, η, and the quadrupole coupling constant, e^2Qq, may be determined from the following relation:[9]

$$\eta = 3(\sin^2\theta_{max} - \sin^2\theta_{min})/(\sin^2\theta_{max} + \sin^2\theta_{min}) \qquad (1)$$

$$\nu = \tfrac{1}{2} e^2Qq(1+\eta^2/3)^{1/2} \qquad (2)$$

where θ_{max} and θ_{min} are the maximum and minimum zero-splitting angles corresponding to the directions of the x and y axes of the field gradient respectively. The values of η and e^2Qq are listed in Table 1, along with those of pure aluminum tribromide. The z axes on the monovalent bromine atoms, Br_2 and Br_3, are usually parallel to the relevant bond directions. The bond angle, α, and the asymmetry parameter, η, at Br_1 are related by the following equation[3] under the coordinate system of the field gradients, as is shown in Fig. 3:

$$\eta = -3\cos\alpha. \qquad (3)$$

The molecular shape of aluminum tribromide in the complex thus obtained is shown in Fig. 3; it is similar to that in the pure state.[5] The agreement of the results of the NQR with those of the X-ray analysis is fairly good for the $\angle Br_2\text{–}Al\text{–}Br_3$ angle, but not good for the $\angle Al\text{–}Br_1\text{–}Al$ angle. This discrepancy is probably caused by the bent bond, as is the case in pure Al_2Br_6[5] and Ga_2Cl_6.[10]

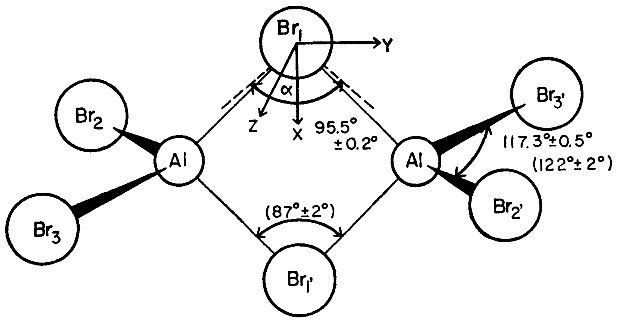

Fig. 3. The coordinate system of the principal field gradient on the bridging bromine atom and the molecular shape of Al_2Br_6 in $Al_2Br_6 \cdot C_6H_6$. Values in parenthsis are cited from the X-ray analysis.

The z axis of Br_1 is parallel to the plane including the z axes of Br_2 and Br_3, as may be seen in Fig. 2. The angles which the z axis of Br_1 makes with those of Br_2 and Br_3 are 30.5° and 32.2° respectively.

Intramolecular and Intermolecular Bonds. The asymmetry parameter depends on the unbalance of the π-electrons of the atom and on the intermolecular interaction, as is seen in the case of solid iodine.[11] Fairly large values of η for the terminal bromine atoms are observed, so the intermolecular interaction can not be ignored in the solid state. In this complex, two kinds of intermolecular interaction are possible. One would be that between a given terminal bromine atom and the nearest bromine of the neighboring Al_2Br_6 molecule. There are short interatomic distances, 3.7Å and 3.9Å for $Br_3 \cdots Br''_3$ and $Br_2 \cdots Br'_1$ whereas the sum of the van der Waals radii of the

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[8] S. L. Segel and R. G. Barnes, *J. Chem. Phys.*, **25**, 578 (1956); R. G. Barnes, S. L. Segel, P. J. Bray, and P. A. Cassabella, *ibid.*, **26**, 1345 (1957).

[9] T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Solid State Physics, Suppl. 1, Academic Press, New York (1958).

[10] G. E. Peterson and P. M. Bridenbaugh, *J. Chem. Phys.*, **51**, 238 (1969).

[11] Ref. 9, p. 173.

bromine atoms is 3.90Å. The shorter distance for $Br_3 \cdots Br''_3$ is evidently ascribable to the intermolecular bonding. The $\angle Al–Br_3 \cdots Br''_3$ angle is about 140°, whereas the $\angle Al–Br_2 \cdots Br'_1$ angle is 90°. Accordingly the η of Br_2 can be expected to be larger than that of Br_3. This is really the case.

The other intermolecular interaction may be seen between the bridging bromine atom and benzene. The interatomic distance for $Br_1 \cdots C$ is 3.7Å, which is comparable to the sum of the van der Waals radii, 3.65Å. The interaction seems to be smaller than the $Br_3 \cdots Br''_3$ bonding. All the other distances between bromine and carbon atoms are not less than 4Å.

The quadrupole coupling constant of the bromine atom depends primarily on its own bonding electron population. If the charge transfers from the benzene to the bromine atom, the e^2Qq value of the atom may be expected to decrease due to an increase in its electronic charge. As can be seen from Table 1, the e^2Qq values of the terminal bromine atoms are lower by about 4 MHz than those of pure aluminum tribromide. On the other hand, the shift of the e^2Qq of the bridging bromine atom is only 0.3 MHz. According to Townes and Dailey, the field gradient can be ascribed to $4p$ electrons of the bromine atom, and one may calculate the number of the electrons, ρ, which the bromine atom gains from its own molecule and neighboring ones. The equations used here are

$$\rho = 1 - Up/0.85 \tag{4}$$

for the terminal bromine atom, and

$$\rho = (1+2\,Up)/(1-2\,\varepsilon\,Up) \tag{5}$$

for the bridging bromine atom,[3] where Up is the number of unbalanced p electrons and where ε, which is estimated to be 0.25, is a known factor. These values of ρ are listed in Table 1. Those at the terminal Br_2 and Br_3 of the complex are increased by only 0.01, and that of the bridging Br_1 remains almost unchanged in comparison with those of pure aluminum tribromide. Therefore, taking account of the asymmetry parameters and the quadrupole coupling constants at the bromine atoms in the complex, it may be suggested that the charge transfer if any, takes place from the benzene to the terminal bromine atoms.