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Nuclear Quadrupole Resonance of the 1:1 Molecular Complex between Antimony Trichloride and Ethylbenzene

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We have already reported on the antimony-halogen bond character and the molecular shape of antimony trihalide in its 2:1 molecular complex with an aromatic compound, as determined by means of the nuclear quadrupole resonance (NQR).[1-3] As for the 1:1 molecular complex, NQR studies have been performed by several authors.[4] All of them, however, used polycrystalline samples, and their crystal structures are still unknown except for $SbCl_3 \cdot C_6H_5NH_2$,[5] in which the NQR has not yet been observed.

In the present experiment, we observed the Zeeman effect of NQR in $SbCl_3 \cdot C_6H_5C_2H_5$ in order to obtain information on the Sb–Cl bond character and the molecular structure of antimony trichloride in its molecular complex.

The molecular complex was prepared by the method of Shinomiya and Asahina,[6] and the single crystal was obtained by the Bridgman-Stockbarger method. A Weber-Todd type[7] super-regenerative oscillator was used for the detection of the resonance line. The magnetic field used for the Zeeman study was provided by a Helmholtz coil[8] with a field strength of about 200 gauss.

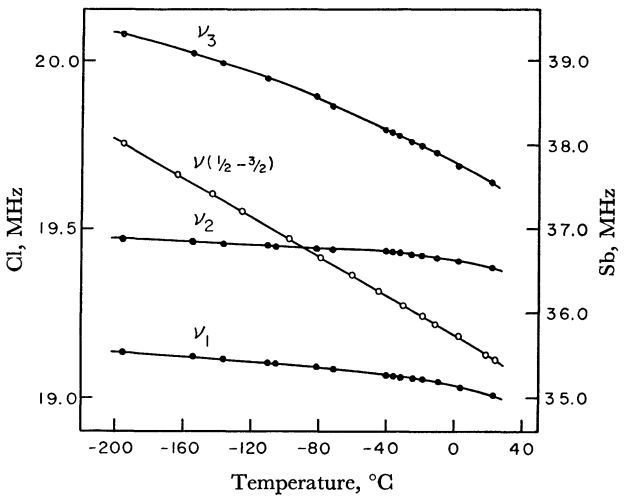

Fig. 1. Temperature dependence of ^{35}Cl and ^{123}Sb NQR frequencies in $SbCl_3 \cdot C_6H_5C_2H_5$.

1) T. Okuda, A. Nakao, M. Shiroyama, and H. Negita, This Bulletin, **41**, 61 (1968).
2) T. Okuda, H. Terao, O. Ege, and H. Negita, *ibid.*, **43**, 2398 (1970).
3) T. Okuda, *J. Sci. Hiroshima Univ., Ser. A*, **35**, 213 (1971).
4) I. P. Biryukov, M. G. Voronkov, and I. A. Safin, "Frequency Tables of Nuclear Quadrupole Resonance," Israel Program for Scientific Translations, Jerusalem (1969).
5) R. Hulme and J. C. Scruton, *J. Chem. Soc., A*, **1968**, 2448.
6) S. Shinomiya and T. Asahina, *Nippon Kwagaku Kwaishi*, **59**, 1165 (1938).
7) K. E. Weber and J. E. Todd, *Rev. Sci. Instr.*, **33**, 390 (1962).
8) K. Shimomura, *J. Phys. Soc. Jap.*, **12**, 657 (1957).

Table 1. Nuclear quadrupole resonance frequencies, ν, asymmetry parameters, η, and quadrupole coupling constants, eQq_{zz}, in antimony trichloride and its complex with ethylbenzene at room temperature (20°C)

Compound	Resonance line	ν, MHz	η, %	eQq_{zz}, MHz
$SbCl_3 \cdot C_6H_5C_2H_5$	$^{35}Cl\ \nu_1$	19.010	5.5±1.4	38.001
	$^{35}Cl\ \nu_2$	19.388	13.5±1.7	38.426
	$^{35}Cl\ \nu_3$	19.641	9.0±1.5	39.126
	$^{123}Sb\ \nu$ (1/2—3/2)	35.478	13.3±0.3	467.698
$SbCl_3$	$^{35}Cl\ \nu'_1$	19.180	15.3	38.211
	$^{35}Cl\ \nu'_2$	20.422	5.7	40.822
	$^{123}Sb\ \nu'$ (1/2—3/2)	37.431	15.9	481.560

The NQR frequencies of ^{35}Cl and ^{123}Sb were observed between the temperature of liquid nitrogen and room temperature, as is shown in Fig. 1. The present molecular complex gave three ^{35}Cl resonance lines (designated as ν_1, ν_2, and ν_3) and one ^{123}Sb (1/2↔3/2) resonance line (designated as ν(1/2—3/2)), as Table 1 shows.

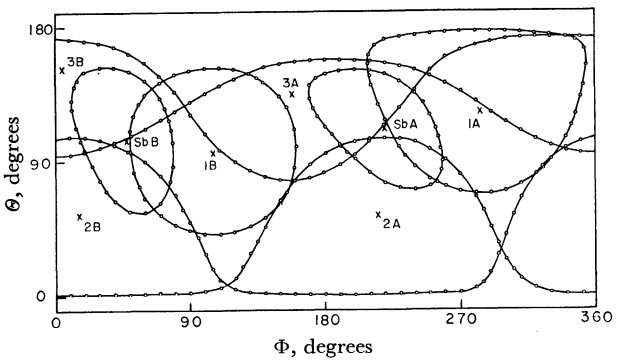

Fig. 2. Zero-splitting patterns of ^{35}Cl and ^{123}Sb Zeeman lines in $SbCl_3 \cdot C_6H_5C_2H_5$. Θ and Φ are polar and azimuthal angles, respectively, in the coordinate fixed to the sample.

The patterns of the zero-splitting were obtained by measuring the Zeeman effect on the resonance line as is shown in Fig. 2. Two patterns were obtained for each resonance line, indicating that the molecular complex is monoclinic. The angles between any two Sb–Cl bonds can be calculated by assuming that the z axis of the field gradient of chlorine is parallel to the Sb–Cl bond. The bond angles, ∠Cl–Sb–Cl, thus obtained are 90°26′, 93°8′, and 96°1′. These angles are almost the same as those of pure antimony trichloride[9] and $2SbCl_3 \cdot C_{10}H_8$,[10] indicating that the molecular shape of antimony trichloride hardly changes upon complex-formation with ethylbenzene. On the other hand, it is considerably different from that of $SbCl_3 \cdot C_6H_5NH_2$, though both crystals are 1:1 molecular complexes. This discrepancy may be attributed to the difference in the strength of the intermolecular bond, which may deform the molecular shape to various degrees.

The values of the asymmetry parameter were determined from the distortion of the zero-splitting loci. Once the asymmetry parameter was obtained, the quadrupole coupling constant could be calculated from the observed resonance frequency. The results are listed in Table 1, along with those for pure antimony trichloride. In pure antimony trichloride, the quadrupole coupling constant and the temperature gradient of the lower ^{35}Cl resonance line (ν'_1) is considerably smaller than those of the higher (ν'_2), so the former is assigned to the chlorine atom, which forms the stronger Sb···Cl intermolecular bond.[9,11] In the present complex, since the quadrupole coupling constants and the temperature gradients of ν_1 and ν_2 are smaller than those of ν_3 and all comparable to those of ν'_1 in pure antimony trichloride, ν_1 and ν_2 may be assigned to the chlorine atoms (Cl_1 and Cl_2) in the stronger Sb···Cl intermolecular bonds, and ν_3, to that (Cl_3) in the weaker bonds. However, the asymmetry parameter of ν_1 is too small to be attributed to that in the stronger Sb···Cl intermolecular bond. This suggests the presence of another effect such as the *trans* effect, which is considered to exist in $2SbCl_3 \cdot C_{10}H_8$.[10] That is, if the configuration of the antimony atom in the present complex is a distorted sp^3d or sp^3d^2 environment and if the Cl_1 atom occupies the position opposite to the intermolecular bond between ethylbenzene and antimony trichloride, a part of the charge from ethylbenzene may transfer to the Cl_1 atom through the antimony atom. Such an effect will cause the quadrupole coupling constant to decrease without any increase in the asymmetry parameter because the electron populations of the p_z orbital increase. As the temperature increases, the degree of the charge transfer to the Cl_1 atom decreases since the intermolecular bond becomes weaker, resulting in the smaller change of ν_1 in comparison with that of ν_3.

9) G. E. Peterson, Thesis, Pittsburgh, 1962.

10) R. Hulme and J. T. Szymanski, *Acta Crystallogr.*, **B 25**, 753 (1969).

11) H. Chihara, N. Nakamura, and H. Okuma, *J. Phys. Soc. Jap.*, **24**, 306 (1968).