Effect of Impurities on the ^{81}Br Quadrupole Resonance in p-Dibromobenzene

By Juro MARUHA, Jun KOIZUMI, Masahiko SUHARA and Tokuzo TONOMURA

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Some investigations have been done concerning the effect of impurities on the nuclear quadrupole resonance absorption of ^{35}Cl in molecular crystals[1,2]. In particular Monfils

1) See for instance: J. Duchesne, "Advances in Chemical Physics", Vol. II, Ed. by I. Prigogine, Interscience Publishers, Inc., New York (1959), p. 190.
2) S. Kojima, S. Ogawa, M. Minematsu and M. Tanaka, *J. Phys. Soc. Japan*, 13, 446 (1958).

and Grosjean derived an equation for the line height (I) of the absorption curve as follows[3]:

$$I=I_0\exp(-NC) \qquad (1)$$

where C is the concentration of impurity, and N, a "characteristic number", represents the number of resonant nuclei per impurity molecule whose resonance have been perturbed so they can no longer contribute to the central portion of the line. The main effect of impurity was considered the lattice defect due to the volume difference between the resonant atom and the substituted one[1,2]. For bromine compound, however, only one investigation has been reported. Dreyfus and Dautreppe studied the intensity of the resonance line of ^{79}Br in p-dibromobenzene[4]. The present paper contains the study of the effect of impurities on the resonance line of ^{81}Br in p-dibromobenzene.

The spectrometer used was similar one reported by Kojima[5]. The intensity of resonance line war observed with a video amplifier and an oscilloscope. The frequency of the resonace was about 224 Mc/sec. Samples are carefully purified and mixed, then sealed into glass tubes. The mixed sample in each tube was melted and crystallized slowly by standing overnight. The tube containing the mixed crystal was placed in a r-f coil of the spectrometer. All the measurements were carried out at 4±1°C, hence p-dibromobenzene exists in the α-phase.

The results are shown in Fig. 1, graphically. In each case plots of log (I/I_0) vs. C is not a single straight line but is nearly hyperbolic. If a linear relation is assumed in the small impurity region, the characteristic number is calculated according to Eq. 1, from the slope. These values are listed in Table I. The values

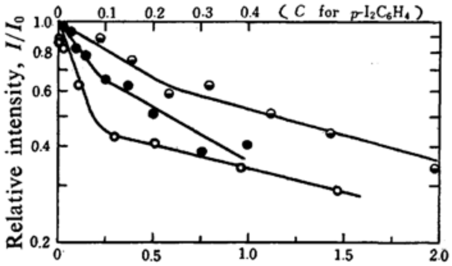

Fig. 1. Variation of relative intensities with concentration of impurities.
◒ p-BrC_6H_4Cl ● p-$I_2C_6H_4$ ○ p-$Cl_2C_6H_4$

3) A. Monfils and D. Grosjean, *Physica*, **22**, 541 (1956).
4) B. Dreyfus and D. Dautreppe, *Compt. rend.*, **243**, 1517 (1956).
5) S. Kojima, K. Tsukada, K. Shimauchi and A. Hinaga, *J. Phys. Soc. Japan*, **9**, 795 (1954).

obtained for p-dichlorobenzene and p-diiodobenzene are not consistent with the Dreyfus and Dautreppe's values. In their experiment log (I/I_0) decreases linearly with C over wide concentration range for the above two cases, whereas it is hyperbolic for the case of p-bromochlorobenzene, and they considered the latter is an exceptional case. On the contrary Kojima et al. showed in their experiment concerning the ^{35}Cl resonance[2] that the results are always hyperbolic, as we obtained. Thus the results of Dreyfus and Dautreppe are considered to be dubious.

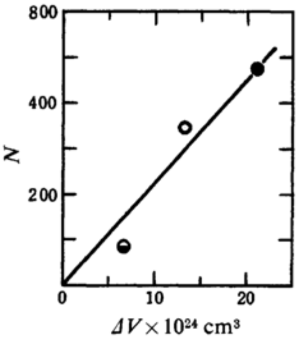

Fig. 2. Relation between characteristic number and volume difference.
● p-$I_2C_6H_4$ ○ p-$Cl_2C_6H_4$ ◒ p-BrC_6H_4Cl

TABLE I. CHARACTERISTIC NUMBER AND VOLUME DIFFERENCE

Impurity molecule	N	ΔV (10^{-24} cm^3)	$N'^{a)}$
p-BrC_6H_4Cl	82	− 6.63	—
p-$Cl_2C_6H_4$	348	−13.26	32
p-$I_2C_6H_4$	475	+21.14	80

a) Dreyfus and Dautreppe's value.

The relation between the characteristic number (N) and the volume difference (ΔV) is shown in Fig. 2, and can be expressed by

$$N=k\Delta V \qquad (2)$$

where k is 22.5×10^{24} cm^{-3}. Compared with the corresponding results for chlorine compounds[6], it may also be true for the bromine compound that the main effect of impurity is attributed to the volume difference between the Br atom and the substituted one.

Department of Chemistry
Faculty of Science
Kanazawa University
Sengoku-cho, Kanazawa

6) R. E. Michel and R. D. Spence, *J. Chem. Phys.*, **26**, 954 (1957).