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The Nuclear Quadrupole Resonance of Dibromoiodate Ions

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The NQR sepctra due to ^{81}Br and ^{127}I in potassium dibromoiodate and its monohydrate were observed, and the Zeeman effect of ^{81}Br NQR in the monohydrate was examined. The resonance lines indicate that both compounds have two kinds of dibromoiodate ions and that these ions in the anhydride are slightly asymmetric, while those in the monohydrate are symmetric. The difference in frequency between the two resonance lines due to each resonant nucleus in the monohydrate is explained in terms of the I···Br intermolecular interaction. The charge distributions in both compounds were evaluated to be about $-0.6e$ and $0.2e$ on the terminal and central atoms respectively.

In general, trihalide ions are almost linear and the iodine atom occupies the center of the ion.[1)] The reported halogen-halogen length is considerably larger than the sum of the covalent bond radii. The bonding in these ions is considered to result from the overlap of the valence np$_\sigma$ orbitals of the constituting atoms. Trihalide compounds have been studied so far by means of the nuclear quadrupole resonance,[2—9)] since they can give more useful information about the bond character and the charge distribution.

According to the crystal structure of $KIBr_2 \cdot H_2O$ as determined by X-ray analysis,[10)] the space group is Pnnm and all atoms lie on the mirror planes at $z=0$ $z=1/2$. The structure consists of nearly linear chains of halogen atoms extending infinitely along the b axis, as is shown in Fig. 1. The two independent IBr_2^- anions are linear and symmetric. The closest O···Br and I···Br distances are 3.60 Å and 3.87 Å respectively, indicative of weak hydrogen bonding and intermolecular interaction. Therefore, it is interesting to examine not only the charge distribution on halogen atoms but also the influence of the intermolecular interaction on the electric field gradient of the halogen atom.

Experimental

The potassium dibromoiodate monohydrate was prepared by heating an aqueous solution of potassium bromide, bromine, and iodine. Its anhydride was obtained by dehydrating the monohydrate. The single crystal of the monohydrate was obtained by slowly lowering an ampoul filled with a saturated aqueous solution of potassium dibromoiodate through an electric furnace. The single crystal of the anhydride could not be obtained.

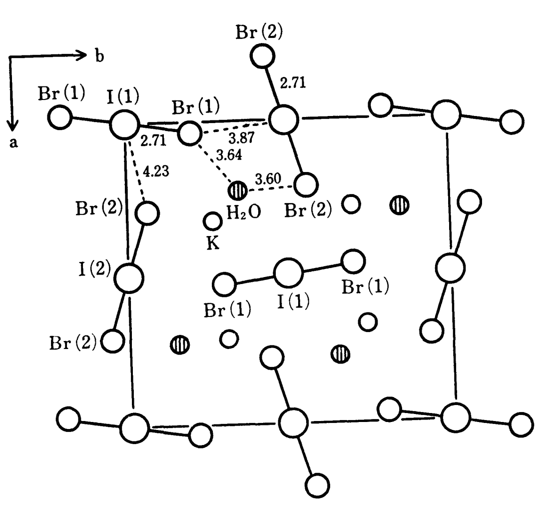

Fig. 1. The crystal structure of $KIBr_2 \cdot H_2O$ projected onto the ab plane.

A super-regenerative oscillator was used for the detection of the NQR line. The absorption lines were displayed on an oscilloscope. The resonance frequencies were determined by the use of a universal counter, TR-5578, of the Takeda Riken Industry Co. Ltd. The Zeeman effect was measured by means of the zero-splitting cone method. The magnetic field was provided by a Helmholtz coil with a field strength of about 200 G.

Results and Discussion

Table 1 shows ^{81}Br and ^{127}I NQR frequencies of $KIBr_2 \cdot H_2O$ and $KIBr_2$. Since ^{127}I has a nuclear spin equal to 5/2, it shows two NQR lines. However, we could not observe the resonance line due to the transition between the ±3/2 and ±5/2 levels, because the resonance frequency was too high to be detected with a conventional NQR spectrometer. Two resonance lines each were observed for ^{81}Br and ^{127}I nuclei in the monohydrate. On the other hand, four and two resonance lines were observed for ^{81}Br and ^{127}I respectively in the anhydride. These findings indicate that both compounds have two kinds of IBr_2^- ions in the crystals, and that the IBr_2^- ions are symmetric in the monohydrate, while those in the anhydride are slightly asymmetric. In general, it is accepted that the trihalide ions are symmetric only when the cation in a trihalide compound is as large as a tetralkylammonium ion.[8)] In the present case, the IBr_2^- ions seem to become symmetric in spite of having a small cation because the crystal includes a water of crystallization. The two resonance frequencies of ^{81}Br in the mono-

TABLE 1. ^{81}Br AND ^{127}I NQR FREQUENCIES IN $KIBr_2 \cdot H_2O$ AND $KIBr_2$ AT 300 K

Compound	Resonance frequency (MHz)	
	$\nu(^{81}Br)$	$\nu_{(1/2 \leftrightarrow 3/2)}(^{127}I)$
$KIBr_2 \cdot H_2O$	124.17	421.51
	128.41	438.77
$KIBr_2$	123.54	425.83
	129.33	433.24
	129.63	
	130.22	

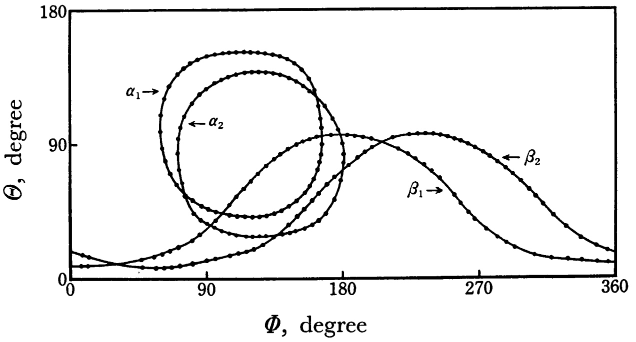

Fig. 2. Zero-splitting patterns of ^{81}Br Zeeman lines in $KIBr_2 \cdot H_2O$.

Table 2. Angles between dibromoiodate ions in $KIBr_2 \cdot H_2O$

	$IBr_2^-(\alpha_1)$	$IBr_2^-(\alpha_2)$	$IBr_2^-(\beta_1)$
$IBr_2^-(\alpha_2)$	17.21°		
$IBr_2^-(\beta_1)$	80.87°	63.66°	
$IBr_2^-(\beta_2)$	116.77°	99.56°	35.90°

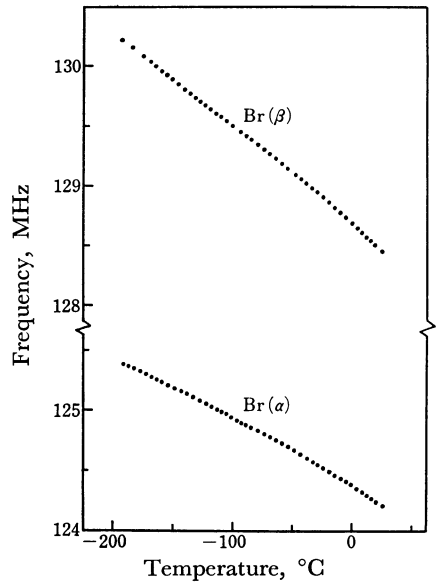

Fig. 3. Temperature dependences of ^{81}Br NQR frequencies in $KIBr_2 \cdot H_2O$.

Table 3. ^{81}Br NQR parameters of $KIBr_2 \cdot H_2O$ at 300 K

Resonance line	ν(MHz)	η(%)	e^2Qq/h(MHz)
^{81}Br(α)	124.17	0.5±0.3	248.34
^{81}Br(β)	128.41	3.4±1.1	256.77

hydrate are so different that the interactions between the resonant nucleus and the surrounding atoms are quite different. This must be clarified by the assignment of the Br atoms. Therefore, we observed the Zeeman effect on ^{81}Br NQR. The results are shown in Fig. 2. Each resonance line gives two zero-splitting patterns, indicating that the monohydrate crystal belongs to a monoclinic or a higher symmetric system. The Br atom was assigned on the basis of the angles between the IBr_2^- ions, assuming that the principal z axis of the Br atom is parallel to the linear ion. The angles thus obtained are listed in Table 2. The X-ray analysis indicates that the angles between the chemically equivalent ions are 17.66° for the ions with Br(1) and 35.92° for those with Br(2). Therefore, the Br atoms contributing to the lower and higher resonance lines were assigned to Br(1) and Br(2) respectively.

Fortunately, the I atoms could be assigned from the intensities of the resonance lines on the single crystal. The principal z axis of the I atom is considered to be parallel to the linear IBr_2^- ion, that is, parallel to that of the Br atom. The Zeeman analysis indicates that the angles between the principal z axis of the Br atoms and the rf coil axis are about 90° for Br(1) and about 45° for Br(2). Therefore, the strong resonance line is assigned to the I atoms bonded to Br(1), and the weak line, to those bonded to Br(2). The observed intensity ratio of the higher resonance line to the lower was nearly 2 : 1, indicating that the former line is due to I(1) and the latter to I(2).

The resonance frequency of Br(1) is considerably lower than that of Br(2). Therefore, Br(1) seems to be strongly affected by the intermolecular interaction. This is obvious from the temperature dependence of the resonance frequency shown in Fig. 3. The intermolecular interactions which affect the Br atoms include the OH···Br hydrogen bonding and the Br···I interaction. The hydrogen bondings at both Br atoms are considered to affect the nuclei to almost the same extent, because the X-ray analysis[10] indicates that the O···Br(1) and O···Br(2) distances are 3.60 Å and 3.64 Å respectively. On the other hand, the I(1)···Br(2) distance is 4.23 Å and the I(2)···Br(1) distance is 3.87 Å, which is about 0.2 Å less than the sum of the van der Waals radii. Therefore, the difference in the resonance frequencies between Br(1) and Br(2) is mainly to be ascribed to the I···Br interaction. In this case, the I(2)···Br(1) interaction is considered to be formed by the charge transfer from I to Br. The charge from the lone-pair orbital of I(2) enters the bonding orbital of Br(1), and the quadrupole coupling constant of Br(1) decreases and that of I(2) increases.

The asymmetry parameters of the electric field gradient are obtained from the zero-splitting loci; they are listed in Table 3. The asymmetry parameters of both Br atoms are so small that the electric field gradients are almost axially symmetric. This may be seen from the fact that the IBr_2^- ions are symmetric and the Br–I bond has little double-bond character.

The charge on the Br atom can be obtained from the quadrupole coupling constant. All the asymmetry parameters of Br in $KIBr_2 \cdot H_2O$ and those of I in the trihalide ions are so small (up to 4%)[5] that they can be neglected. Furthermore, s hybridization does not seem to participate in the halogen-halogen bond. Using the Townes-Dailey method,[11] the following equations are obtained for the terminal and the central halogen atoms.

For a terminal atom:

$$\frac{(e^2Qq)_{\text{obsd}}}{(e^2Qq)_{\text{atom}}} = 1 - i = 2 - N_z \qquad (1)$$

Table 4. Electron populations and charge distributions in linear trihalide ions

Compound	N_z		$Q_x(e)$		Total charge (e)
	Terminal	Central	Terminal	Central	
$KIBr_2\cdot H_2O$	1.61	0.78	−0.61	0.22	−1.00
	1.60	0.82	−0.60	0.18	−1.02
$KIBr_2$	1.60	0.80	−0.60	0.20	−1.00
$KICl_2\cdot H_2O$	1.66	0.70	−0.66	0.30	−1.02
$KICl_2$	1.65	0.71	−0.65	0.29	−1.01

For a central atom:

$$\frac{(e^2Qq)_{\mathrm{obsd}}}{(e^2Qq)_{\mathrm{atom}}} = (1-i) + 2i(1+\varepsilon) = 1 + (1-N_z)(1+2\varepsilon), \tag{2}$$

where $(e^2Qq)_{\mathrm{obsd}}$ is the observed quadrupole coupling constant and $(e^2Qq)_{\mathrm{atom}}$ is that due to one p_z electron, *i.e.*, 643.03 MHz for ^{81}Br and 2292.71 MHz for ^{127}I.[12,13] ε is a correction factor for a positively charged resonant atom and 0.12 for ^{127}I.[11] N_z is the electron number of the p_z orbital. Using the N_z values obtained from Eqs. 1 and 2, the charges, Q_x, on the halogen atoms are readily calculated by means of the following relation: $Q_x = 1 - N_z$. The values thus obtained are listed in Table 4, in which the values for the ICl_2^- ions are given for purposes of comparison. Since no resonance lines except those in $KIBr_2\cdot H_2O$ are assigned, the charges on the halogen atoms were calculated for the averaged resonance frequency. The charges of the terminal and central halogen atoms in the ICl_2^- ions are larger than those in the IBr_2^- ions. This can be explained by the difference in electronegativity between Br and Cl. In any case, the calculated total charges are equal to the theoretical value, $-e$. Therefore, the approximation used in the present work is reasonable.

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