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Nuclear Quadrupole Resonances of Phosphorus Iodides and Some Phosphorus Trihalide–Boron Trihalide Complexes

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Nuclear quadrupole resonance (NQR) frequencies due to ^{79}Br and ^{127}I are examined in phosphorus iodides, PI_3 and P_2I_4, and the complexes $PBr_3 \cdot BBr_3$, $PBr_3 \cdot BI_3$, and $PI_3 \cdot BBr_3$. The quadrupole coupling constants and asymmetry parameters are also derived for ^{127}I in PI_3, P_2I_4, and $PBr_3 \cdot BI_3$. The resonance lines of PI_3 fade out above 257 K, at which temperature a structural phase transition is suggested. The number of resonance lines in P_2I_4 shows that the molecular symmetry of P_2I_4 is $\bar{1}$ instead of 2/m in its crystal. The similarity of the resonance patterns of the three complexes indicates that they are isomorphous with one another. The electronic structures of the halogens in the compounds mentioned above have been discussed by using the Townes-Dailey theory. On complexing, the electric charge of the halogen atoms in the donor PX_3 decreases due to the polarization of pσ bonds, whereas that of the halogen atoms in the acceptor BY_3 increases owing to the backdonation through pπ bonds.

Two kinds of phosphorus iodides, PI_3 and P_2I_4, are known,[1] but no NQR investigation of these compounds has yet been reported. Phosphorus halides can form complexes with boron halides, in which the former act as electron donors and the latter as acceptors.[2] Only the complexes involving the heavier halogen atoms are stable at room temperature. In the case of these complexes, somewhat large shifts of the quadrupole coupling constants are expected on complexing. We have therefore observed NQR spectra due to ^{79}Br and ^{127}I in two kinds of phosphorus iodides and three complexes: $PBr_3 \cdot BBr_3$, $PBr_3 \cdot BI_3$, and $PI_3 \cdot BBr_3$, and have examined the bond character of these compounds. In the related complexes, $PI_3 \cdot BI_3$ and $P_2I_4 \cdot 2BBr_3$, NQR could not be observed. This failure may be caused by the imperfection of the samples.

Experimental

PI_3 and P_2I_4 were obtained by the reaction of the relevant elements in carbon disulfide, followed by recrystallization.[3] PBr_3 and BBr_3 were obtained from commercial sources. BI_3 was synthesized by the method of Renner[4] and was purified by sublimation. The complexes were prepared according to the methods in the literature.[2] All the procedures were performed under a nitrogen or helium atmosphere.

The NQR spectra were obtained with an externally quenched super-regenerative Lecher-line oscillator; the absorption lines were observed on an oscilloscope. The resonance frequencies were measured by the use of a signal generator and a frequency counter with an estimated accuracy of ±0.01 MHz.

Results and Discussions

Phosphorus Iodides, PI_3 and P_2I_4. In Table 1 are listed the observed frequencies for ^{127}I at liquid nitrogen temperature with the approximate signal to noise ratios observed on an oscilloscope. These frequencies were assigned to the pairs of ν_1 and ν_2, which correspond to the transitions $m=\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$, respectively. However, there is an ambiguity in pairing the resonance frequencies of PI_3, so that the pairing was done in the order of frequency. This pairing is very likely, because the middle line of each group is slightly weaker than those of both sides. Using ν_1 and ν_2, the quadrupole coupling constants e^2Qq/h and the asymmetry parameters η were derived from the table of eigenvalues for the spin 5/2,[5] and are listed also in Table 1.

The crystal structure of PI_3 was reinvestigated recently by Lance *et al.*[6] at room temperature. The structure is hexagonal, and belongs to the space group $P6_3$ with $Z=2$. A pyramidal molecular geometry is maintained in solid PI_3. In this symmetry all the iodine atoms are equivalent and only one NQR line is expected. However, three lines of almost the same intensity were observed on each transition at low temperatures, showing the existence of three crystallographically non-equivalent iodine atoms, and no resonance was observed at room temperature. The temperature dependence of each ν_1 line of PI_3 was investigated. As the temperature rose from 77 K, the resonance frequencies decreased monotonously with the average temperature coefficients $\langle\alpha\rangle = 2(\nu_{77}-\nu_{202})/(77-202)(\nu_{77}+\nu_{202}) = -3.7 \times 10^{-5}$, -3.1×10^{-5}, and -2.8×10^{-5} deg^{-1} for the lowest, the middle, and the highest lines respectively. All the resonance lines faded out abruptly at about 257 K, which is far below the melting point of 334 K. This indicates that a structural phase transition may occur at about 257 K, because the existence of the three non-equivalent iodine atoms at the lower temperature is inconsistent with the crystal structure analysed at room temperature.

The X-ray analysis by Leung and Waser shows that P_2I_4 is triclinic, space group $P\bar{1}$, and $Z=1$.[7] The two P atoms are linked together, and each P atom is linked to two I atoms at the same distance within the experimental accuracy. The molecular symmetry is 2/m within the experimental accuracy, while only the inversion center is required crystallographically. However, two pairs of NQR lines corresponding to the two non-equivalent iodine atoms are observed instead of the single pair of NQR lines which is expected for the symmetry 2/m. In view of this fact the molecular symmetry should be reduced from 2/m to $\bar{1}$ in the crystalline state.

The temperature dependencies of the ν_1 lines of P_2I_4 were also investigated from 77 K to room temperature. When the temperature is above room temperature, P_2I_4(mp, 397 K) decomposes gradually and the signals

TABLE 1. NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES, QUADRUPOLE COUPLING CONSTANTS, AND ASYMMETRY PARAMETERS IN PHOSPHORUS IODIDES AT 77 K

Compound	ν_1/MHz	S/N	ν_2/MHz	S/N	e^2Qqh^{-1}/MHz	η
PI_3	230.46	(7)	457.90	(2.5)	1527.9	0.071
	231.63	(5)	460.00	(2)	1535.1	0.074
	233.80	(7)	463.87	(2.5)	1548.2	0.079
P_2I_4	239.14	(4)	478.20	(2)	1594.1	0.011
	243.09	(4.5)	486.07	(2)	1620.3	0.013

are rapidly broadened and weakened. Within the observed temperature range the temperature dependencies of the resonance lines are normal, with the average temperature coefficients $\langle\alpha\rangle = -5.4\times10^{-5}$ and -6.3×10^{-5} deg^{-1} for the lower and the upper lines, respectively. These coefficients are larger than those of PI_3.

The observed quadrupole coupling constants of the halogen atoms were qualitatively estimated by the following equations:[8]

$$e^2Qq/h = |e^2Qq/h|_{\rm atom}\left\{(1-s)(1-i)-\frac{f}{2}\right\}, \tag{1}$$

and

$$f = \frac{2}{3}\eta\frac{e^2Qq/h}{|e^2Qq/h|_{\rm atom}}. \tag{2}$$

Here $|e^2Qq/h|_{\rm atom}$ is the atomic quadrupole coupling constant, which is 2292.71 MHz for ^{127}I,[9] s is the degree of the s-hybridization, and f is the degree of the decrease of pπ electrons. s is assumed to be equal to 0.15 in accordance with Townes and Dailey.[10] Then, using the average values of e^2Qq/h and η at 77 K, i and f are calculated to be 0.19 and 0.03 for PI_3 and 0.17 and 0.01 for P_2I_4, respectively. If the π-bonding of the P–I bonds is not different in both iodides, the slightly larger value of f (or η) of PI_3 than that of P_2I_4 may be ascribed to the intermolecular bonding involving I atoms. According to the crystal structure of PI_3,[6] the shortest P···I intermolecular distance (3.670 Å) is smaller than the sum of the relevant van der Waals radii (4.0 Å). Possibly such P···I intermolecular interactions may exist in the low temperature phase as well, where NQR spectra were observed. On the other hand the shortest intermolecular P···I distance is 3.9 Å in P_2I_4.[7] The ionic character of the P–I bonds in PI_3 is somewhat larger than in P_2I_4. This may be attributed to the larger electron withdrawing ability of PI_2 groups than that of I atoms.

Complexes: $PBr_3\cdot BBr_3$, $PBr_3\cdot BI_3$, and $PI_3\cdot BBr_3$. Table 2 shows the observed frequencies of ^{79}Br and ^{127}I of the complexes at liquid nitrogen temperature with the approximate signal to noise ratios. For bromine the resonances of ^{81}Br were also detected; these satisfy the quadrupole moment ratio $Q(^{79}\text{Br})/Q(^{81}\text{Br}) = 1.1974$ within the experimental accuracy. The ν_2 lines of the I atoms of the $PI_3\cdot BBr_3$ may probably exist in the region of about 570 MHz, at which our spectrometer did not operate.

The resonance lines of each complex are divided into two or three groups, in which two closely spaced lines exist with the intensity ratio of about 1 : 2. Referring to the fact that the resonance lines of a component in the complex are shifted to a small extent, the bromine and iodine lines can be identified easily, as shown in Table 2. This identification can be confirmed by the doublet structure,[11,12] which arises from the isotope effect of ^{10}B and ^{11}B.[12] The frequency measurements of the doublet were done at the maximum intensity position of the signals.

TABLE 2. NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES OF ^{79}Br AND ^{127}I IN THE COMPLEXES $PBr_3\cdot BBr_3$, $PBr_3\cdot BI_3$, AND $PI_3\cdot BBr_3$ AT 77 K

Compound	Species		ν/MHz	S/N
$PBr_3\cdot BBr_3$	PBr_3		258.93	(8)
			259.40	(4)
	BBr_3		181.89	(6)
			184.30	(12)
$PBr_3\cdot BI_3$	PBr_3		258.78	(3)
			259.60	(1.5)
	BI_3	ν_1	203.41	(3)
			207.58	(1.5)
		ν_2	399.80	(7)
			401.22	(15)
$PI_3\cdot BBr_3$	PI_3	ν_1	289.61	(12)
			289.91	(7)
	BBr_3		176.39	(1.5)
			180.32	(3)

The similarity of the resonance patterns of the complexes shows that these complexes are presumably isomorphous with one another, though the crystal structures of the complexes have not yet been clarified. Possibly one halogen atom is non-equivalent to the remaining two halogen atoms in each species of the complexes.

In the case of $PBr_3\cdot BI_3$, both ν_1 and ν_2 due to ^{127}I were measured. Where the pairings were done easily due to the intensity difference of the two resonances, and the e^2Qq/h and η were obtained as 1340.3 MHz and 0.104 for the stronger line and 1340.7 MHz and 0.173 for the weaker line. The values of η are greatly decreased compared to the parent BI_3, in which η is 0.455.[12]

In Table 3 the mean values of the coupling constants $\langle e^2Qq/h\rangle_{\rm AV}$ and asymmetry parameters $\langle\eta\rangle_{\rm AV}$ at 77 K are listed for the complexes and the parent molecules;[11–13] here $\langle e^2Qq/h\rangle_{\rm AV}$ were calculated by neglecting the assumed small $\langle\eta\rangle_{\rm AV}$ for the atoms in which the asymmetry parameters could not be obtained. In the last two columns of Table 3, i and f are listed; these are calculated from Eqs. 1 and 2 with $|e^2Qq/h|_{\rm atom}$

TABLE 3. MEAN COUPLING CONSTANTS, MEAN ASYMMETRY PARAMETERS, IONIC CHARACTERS, AND THE DEGREE OF THE DECREASE OF $p\pi$ ELECTRONS IN THE COMPLEXES AND THE PARENT MOLECULES AT 77 K

Compound	Species	$\langle e^2Qq/h\rangle_{AV}$/MHz	$\langle\eta\rangle_{AV}$	i	f
$PBr_3 \cdot BBr_3$	PBr_3	518	assumed to be 0	0.21	—
$PBr_3 \cdot BI_3$	PBr_3	518	assumed to be 0	0.21	—
PBr_3 a)	—	439	assumed to be 0	0.33	—
$PI_3 \cdot BBr_3$	PI_3	1931	assumed to be 0	0.01	—
PI_3	—	1537	0.075	0.19	0.03
$PBr_3 \cdot BBr_3$	BBr_3	367	assumed to be 0	0.44	—
$PI_3 \cdot BBr_3$	BBr_3	358	assumed to be 0	0.45	—
BBr_3 b)	—	340	0.45	0.41	0.12
$PBr_3 \cdot BI_3$	BI_3	1340	0.127	0.29	0.05
BI_3 c)	—	1185	0.455	0.30	0.16

a) Calculated from Ref. 13 (at 83 K). b) Ref. 11. c) Ref. 12 (at 78 K).

=769.756 MHz for ^{79}Br.[14)]

On complexing, the phosphorus halide molecule will transfer a charge to the boron halide without a significant change in its pyramidal form. This charge transfer will decrease the ionicity of the P–X bonds, and therefore the coupling constants of phosphorus halide in the complex will increase compared to the parent phosphorus halide, as seen in Eq. 1. It is apparent from Table 3 that the $\langle e^2Qq/h\rangle_{AV}$ values increased significantly, that is, the i values decreased, in the complex as compared to the parent molecule.

On the other hand, in going from the parent molecule to the complex, the boron halide changes its structure from planar triangle to pyramid, so that the forming of a π bond between boron and halogen atoms becomes difficult. The two asymmetry parameters in $PBr_3 \cdot BI_3$ are somewhat different, as stated above. This may be attributed to the intermolecular bonding containing I atoms and/or the crystal field effects. However, since these effects can not be estimated due to the lack of information about the crystal structure, average values of η were used tentatively in order to see the extent of π bondings. From Table 3, the π bond character obviously decreases on complexing, whereas the ionic character remains almost the same. Therefore, the π electrons which participated in the π bond between I and B atoms are mostly given back to the I atom. The same situation may also be expected for BBr_3 of the complexes in which η have not been obtained. The decrease of f is accompanied by the increase in the coupling constants, as is seen from Eq. 1. This is the case for the boron halides of the complexes.

On forming the complexes of $PBr_3 \cdot BBr_3$ and $PI_3 \cdot BBr_3$, the ionic character of the P–X bond, i, decreases in PI_3 much more than in PBr_3, and i of the B–Br bond increases in the latter a little more than in the former complex. Accordingly, it is evident that electrons are transferred from PI_3 to BBr_3 much more than from PBr_3 to BBr_3. This is consistent with the order of the Lewis base strengths, $PI_3 > PBr_3$, which was determined by other methods.[15)]

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