^{81}Br and ^{127}I NQR Studies of $(CH_3NH_3)_2HgBr_4$ and $(CH_3NH_3)_2HgI_4$*

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The ^{81}Br and ^{127}I NQR frequencies in $(CH_3NH_3)_2HgBr_4$ and $(CH_3NH_3)_2HgI_4$, respectively, have been recorded from above 77 K to around room temperature. The resonance lines exist in a wide range of frequencies. An unusual temperature dependence of the resonance frequencies has been observed. Small $^1H-^2D$ isotope effects have been observed between $(CH_3ND_3)_2HgBr_4$ and $(CH_3NH_3)_2HgBr_4$. Both negative and positive frequency differences between the deuterated and the nondeuterated compound have been observed at 77 K. The relatively large asymmetry parameters in the iodine compound decrease with increasing temperature, indicating the existence of H-bonds. The present results are interpreted qualitatively by considering the effects of H-bonding, $N-H \cdots X$, between the halogen atoms and the $CH_3NH_3^+$ ions which may undergo large molecular motions. It is suggested that not only frequency-lowering but also frequency-rising effects may be produced, depending on the direction of the H-bond, i.e., the angle between the Hg–X bond and the $X \cdots H$ bond.

Key words: ^{81}Br NQR, ^{127}I NQR, Anomalous temperature dependence, $^1H-^2D$ isotope effect, H-bonding, Motions of $CH_3NH_3^+$.

Introduction

In a previous paper [1] we have investigated the temperature dependence of the ^{81}Br and ^{127}I NQR frequencies of $CH_3NH_3HgBr_3$ and $CH_3NH_3HgI_3$ and the phase transitions in these crystals. Apart from the phase transitions, it was noticed that the frequency vs. temperature curves of these compounds show interesting features: (i) Not only the resonance line of the bridging I atom in the iodine compound but also the resonance lines of the terminal Br atom in the bromine compound exhibit a positive temperature dependence in a certain temperature range. (ii) The resonance lines of the terminal halogen atoms cover a wide range of frequencies at low temperature (very large in the iodine compound). (iii) The temperature coefficients of the resonance frequencies of the terminal halogen atoms are large (especially so in the iodine compound). On the other hand, the crystal structure investigation at room temperature by Körfer et al. [2] has shown that the terminal halogen atoms in both crystals may participate in H-bonding with $CH_3NH_3^+$ ions which are likely to perform considerable motions. Thus it seems that the H-bonding, $X \cdots H-N$, and the motions of $CH_3NH_3^+$ ion play an important role in the interesting behavior of these resonance lines. The anomaly may also have some connection with the phase transitions of the compounds. It is therefore interesting to investigate if a similar anomaly of the resonance lines occurs in other alkylammonium halogenomercurates which do not undergo phase transitions.

The crystal structure of the 2:1 stoichiometric compounds consisting of the same chemical species, $(CH_3NH_3)_4HgBr_4$ and $(CH_3NH_3)_4HgI_4$, has been also determined by Körfer et al. [3]. There exist isolated units of HgX_4^{2-} with slight deformation from a regular tetrahedron in both structures which are connected with each other by the H-bonds. These crystals seem not to undergo any phase transitions [3]. Accordingly, these compounds may be good examples to check the origin of the above anomaly. We have

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measured the ^{81}Br and ^{127}I NQR in these compounds and also in a partially deuterated compound $(CH_3ND_3)_4HgBr_4$ in order to obtain information about the H-bonding and the motions of $CH_3NH_3^+$.

Experimental

The crystals of $(CH_3NH_3)_2HgBr_4$ and $(CH_3NH_3)_2HgI_4$ were prepared from a methanol solution [3] or a diluted halogenoacid solution of stoichiometric amounts of CH_3NH_3X and HgX_2. C, H and N analyses were consistent with their chemical formula. The deuterated compound $(CH_3ND_3)_2HgBr_4$ was prepared by mixing CH_3ND_3Br and $HgBr_2$ in a diluted D_2O solution of DBr. The partially deuterated compound CH_3ND_3Br was prepared from repeated cycles of dissolution of CH_3ND_3Br in D_2O and evaporation of D_2O. The preparation of the deuterated compounds was done under N_2 gas in glove bags.

The NQR measurements were carried out with a superregenerative type oscillator. The signals were directly observed on an oscilloscope with frequency modulation or recorded on a recorder with Zeeman modulation. The temperature of the samples was measured with an estimated accuracy of ±1 K.

Results

^{81}*Br NQR Frequencies in* $(CH_3NH_3)_2HgBr_4$

The resonance frequencies in $(CH_3NH_3)_2HgBr_4$ were measured between 77 K and ca. 400 K. In accordance with the crystal structure at room temperature [3] four resonance lines due to ^{81}Br were observed (Figure 1). The ^{81}Br NQR frequencies at representative temperatures are listed in Table 1. The observed frequencies range widely and their temperature dependences differ much. There is some similarity between the spectra of $(CH_3NH_3)_2HgBr_4$ and those of $CH_3NH_3HgBr_3$ [1]. The line ν_1^H exhibits a normal negative temperature dependence having a rather large coefficient. The line ν_2^H shows also a negative temperature dependence and has a slight downward curvature. The line ν_3 exhibits an anomalous positive temperature dependence. Notice that the frequency vs. temperature curve of ν_3^H changes symmetrically to that of ν_2^H. With increasing temperature from 77 K, the frequency ν_4^H increases slightly at the beginning,

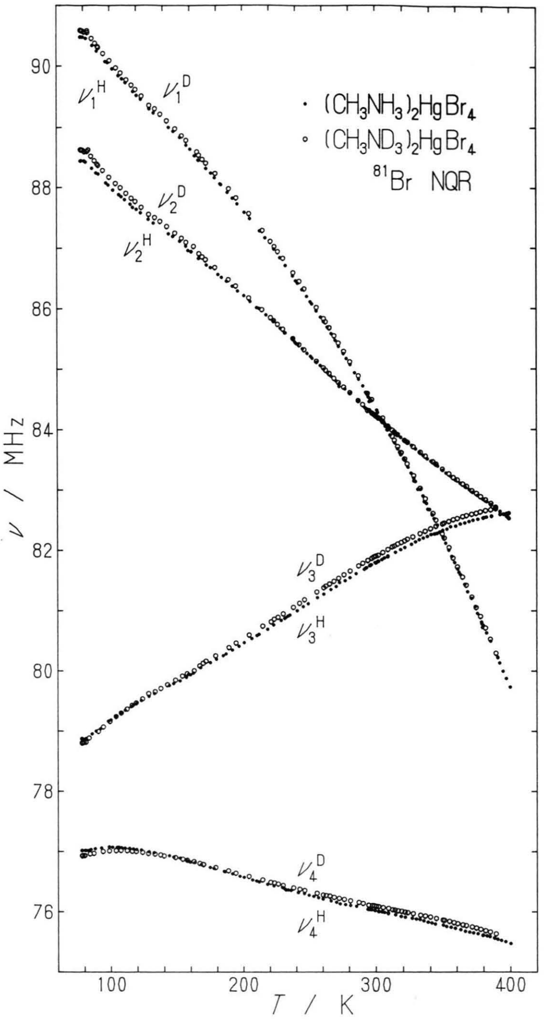

Fig. 1. The temperature dependence of ^{81}Br NQR frequencies in $(CH_3NH_3)_2HgBr_4$ (filled circle) and $(CH_3ND_3)_2HgBr_4$ (open circle).

Table 1. ^{81}Br NQR frequencies in $(CH_3NH_3)_2HgBr_4$ (H) and $(CH_3ND_3)_2HgBr_4$ (D).

T/K		ν/MHz [a]		$\nu^D-\nu^H$/MHz [b]
		H	D	
77	ν_1	90.471	90.583	0.112
	ν_2	88.444	88.628	0.184
	ν_3	78.869	78.800	−0.069
	ν_4	77.012	76.928	−0.084
295	ν_1	84.509	84.591	0.082
	ν_2	84.301	84.311	0.010
	ν_3	81.718	81.830	0.112
	ν_4	76.031	76.115	0.084

[a] Estimated accuracy is within ±0.01 MHz.
[b] Deuterated shifts.

reaches a maximum at around 104 K and then decreases with a small temperature coefficient.

^1H–^2D *Isotope Effects of the* ^{81}Br *NQR Resonance Frequencies of* $(CH_3NH_3)_2HgBr_4$

The temperature dependence of the ^{81}Br NQR frequencies in $(CH_3ND_3)_2HgBr_4$ are also shown in Figure 1. The figure shows that small but definite frequency shifts are observed on deuteration. The resonance frequencies of the deuterated compound, and also the frequency differences between deuterated and nondeuterated compounds are listed in Table 1. Both positive and negative frequency shifts are observed. The shifts of ν_1^D and ν_2^D from the respective ν_1^H and ν_2^H are positive at 77 K and decrease with increasing temperature. At room temperature, the shift of ν_2^D becomes almost negligible. The shifts of ν_3^D and ν_4^D are negative at 77 K and become almost zero around 120 K and 140 K, respectively. Above these temperatures the shifts are positive.

^{127}I *NQR Frequencies, Nuclear Quadrupole Coupling Constants, and Asymmetry Parameters in* $(CH_3NH_3)_2HgI_4$

Both resonances ν^{I} and ν^{II} due to the respective $\Delta m = \pm 1/2 - \pm 3/2$ and $\Delta m = \pm 3/2 - \pm 5/2$ transitions were observed. The temperature dependence was measured above 77 K to ca. 370 K for ν^{I} (Fig. 2) and to 300 K for ν^{II} (Figure 3). There are four crystallographically nonequivalent I atoms in the unit cell [3]. In accordance with this, respective four resonance lines of ν^{I} and ν^{II} were observed at 77 K. The ν_1^{I} and ν_3^{I} lines approach each other with increasing temperature. Above ca. 210 K the weaker line ν_3^{I} is not resolved from ν_1^{I}. The line ν_3^{II} fades with increasing temperature and becomes unobservable above ca. 260 K. The respective pairs of ν^{I} and ν^{II} were easily found by considering the relation $2\nu^{\mathrm{I}} \geqq \nu^{\mathrm{II}}$ and the temperature dependence of resonance frequencies. The resonance frequencies (ν), nuclear quadrupole coupling constants ($e^2 q_{zz} Q/h$), and asymmetry parameters (η) at representative temperatures are listed in Table 2.

There is some similarity between the ν^{I} spectra of $(CH_3NH_3)_2HgI_4$ and $CH_3NH_3HgI_3$ [1]. The lines ν_1^{I}, ν_1^{II}, ν_3^{I}, and ν_3^{II} have large negative temperature coefficients. The ν_2^{I} line shows a smaller negative temperature dependence, but its temperature curve is rather curious. On the other hand ν_2^{II} exhibits a positive temperature dependence until around ca. 270 K and then decreases gradually. ν_4^{I} shows a broad minimum at ca. 130 K and increases above this temperature, while ν_4^{II} increases with temperature throughout. The temperature dependence of the respective components of the nuclear quadrupole coupling tensor and the η values for the pairs of $\nu_2^{\mathrm{I}} - \nu_2^{\mathrm{II}}$ and $\nu_4^{\mathrm{I}} - \nu_4^{\mathrm{II}}$ are shown in Figs. 4 and 5, respectively.

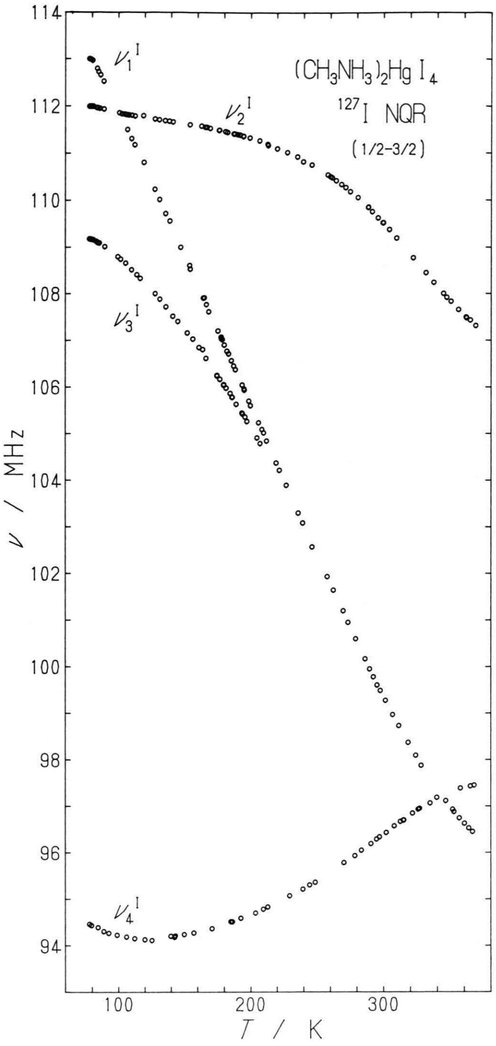

Fig. 2. The temperature dependence of ^{127}I NQR frequencies ascribed to the $\Delta m = \pm 1/2 - \pm 3/2$ transitions in $(CH_3NH_3)_2HgI_4$. Above ca. 210 K the ν_3^{I} line is not detected because of the proximity to the more intense ν_1^{I} line.

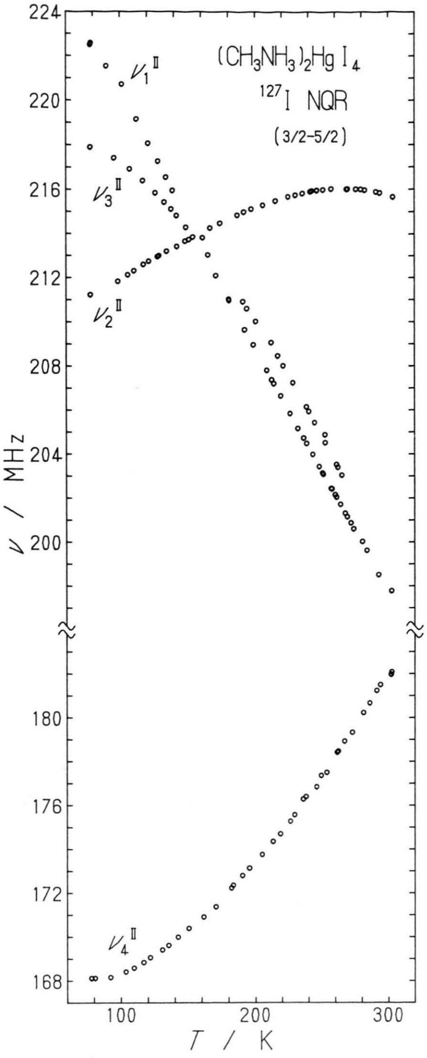

Fig. 3. The temperature dependence of ^{127}I NQR frequencies ascribed to the $\Delta m = \pm 3/2 - \pm 5/2$ transitions in $(CH_3NH_3)_2HgI_4$.

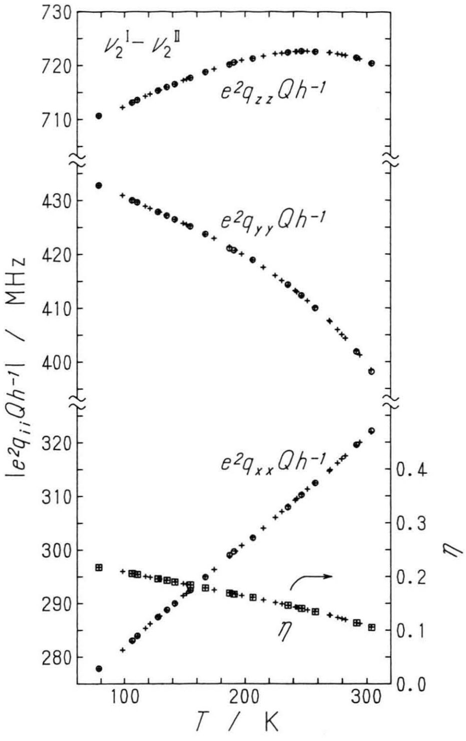

Fig. 4. The temperature dependence of $e^2q_{ii}Qh^{-1}$ and η for $\nu_2^{\mathrm{I}} - \nu_2^{\mathrm{II}}$ of $(CH_3NH_3)_2HgI_4$. The + marks are the values obtained from the measured values $\nu_2^{\mathrm{II}}(T)$ and the best fitted values $\nu_2^{\mathrm{I}}(T) = a + bT + cT^2 + dT^3$.

Table 2. ^{127}I NQR frequencies (ν), nuclear quadrupole coupling constants ($e^2q_{zz}Qh^{-1}$), and asymmetry parameters (η) in $(CH_3NH_3)_2HgI_4$.

T/K		ν/MHz		$e^2q_{zz}Qh^{-1}$/ MHz	η
		I (1/2−3/2)[a]	II (3/2−5/2)[b]		
77	ν_1	113.01	222.50	743.50	0.111
	ν_2	111.99	211.22	710.69	0.218
	ν_3	109.19	217.89	726.55	0.041
	ν_4	94.47	168.13	571.13	0.315
270	ν_1	101.20	201.15 [c]	671.15	0.069
291	ν_2	109.75	215.88	721.49	0.114
194	ν_3	105.42	210.58 [c]	702.06	0.030
291	ν_4	96.20	181.25	609.97	0.220

[a] Estimated accuracy is within ±0.01 MHz.
[b] ±0.02 MHz. [c] ±0.04 MHz.

Discussion

Unusual Temperature Dependence in $(CH_3NH_3)_2HgBr_4$

The crystal of $(CH_3NH_3)_2HgBr_4$ belongs to the monoclinic space group $P2_1/c$ with $Z = 4$ [3]. The Hg−Br distances range from 2.591 to 2.602 Å, and the Br−Hg−Br angles from 105.36 to 112.03°. All crystallographically nonequivalent Br atoms seem to be involved in H-bonds having short N ⋯ Br distances in the range 3.38 to 3.55 Å. In addition, it is known that the motions of $CH_3NH_3^+$ ions are quite large in the present type of crystals [4]. Then we may ascribe the unusual behavior of the resonance lines (a widely-ranged frequency, a positive temperature dependence, and a large negative temperature dependence) to the H-bonding and the motions of $CH_3NH_3^+$ ions because

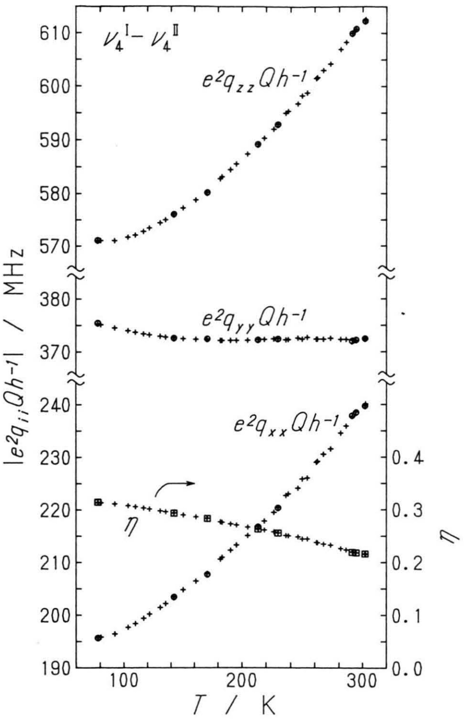

Fig. 5. The temperature dependence of $e^2q_{ii}Qh^{-1}$ and η for $\nu_4^{I}-\nu_4^{II}$ of $(CH_3NH_3)_2HgI_4$. The + marks are the values obtained from the measured values $\nu_4^{II}(T)$ and the best fitted values $\nu_4^{I}(T)=a+bT+cT^2+dT^3$.

other special inter- and intramolecular bond schemes and phase transitions do not seem to exist.

The strength of the H-bonds in the present crystals may be compatible with that of the H-bonds, O–H ··· X, in the hexachlorometalate salts with the waters of crystallization. The effect of H-bonds on ^{35}Cl NQR frequencies of these compounds has been extensively investigated by Nakamura et al. [5]. They suggested that the H-bonding affects the resonance frequencies of the H-bonded Cl atoms according to the following mechanism. The quadrupole coupling constant, to which the resonance frequency is proportional, is related to the populations of p electron orbitals as follows [6]:

$$e^2q_{zz}Q/h=\{(N_x+N_y)/2-N_z\}\,e^2q_{\mathrm{at}}Q/h\,, \quad (1)$$

where N_x, N_y, and N_z denote the effective numbers of corresponding p orbitals, respectively, and $e^2q_{\mathrm{at}}Q/h$ denotes the atomic quadrupole coupling constant. When the H atoms of water molecules are connected to the lone-pair p_x and/or p_y electrons of the Cl atoms, N_x (and/or N_y) is decreased through the polarization of the lone pair electrons, resulting in a decrease of the resonance frequencies of the Cl atoms from (1). With increasing temperature the lattice vibrations and molecular motions increase, which may weaken the H-bonds. This results in an increase of N_x (and N_y). On the other hand, such excitations may create a decrease of N_z through increasing amplitudes of tortional vibrations in the main bonds of the Cl atoms [6]. Thus, when the increase in the frequency due to the increase of N_x (and N_y) overwhelms the decrease in the frequency due to the increase of N_z, the observed frequency may increase with increasing temperature. This explanation may be applicable for ν_3^{H} and partly for ν_4^{H} in the present case. Their frequencies are low at low temperature; for ν_3^{H} a positive temperature dependence is observed in the observed temperature range, and for ν_4 a positive dependence is observed initially, and then the frequency decreases with a small temperature coefficient. The Hg–Br bonds of the Br atoms for ν_3^{H} presumably undergo smaller tortional vibrations compared to that of the Br atom for ν_4^{H}.

On the other hand, though all halogen atoms seem to be involved in H-bonding in the present crystal, ν_1^{H} and ν_2^{H} are rather high in frequency compared to ν_3^{H} and ν_4^{H} at 77 K. Further, their (negative) temperature dependence is rather large, though the $HgBr_4^{2-}$ tetrahedra are linked by H-bonds. Thus we have to consider another effect in H-bonding which results in an increase of the frequency. If we suppose that the H atom is situated toward the antibonding σ^* orbital of the Br atom on the prolonged line of Hg–Br bond, the Br atom (the Hg–Br bond) may be polarized in such a way that N_z decreases, resulting in an increase of the resonance frequency according to (1). In this instance the resonant atom may show a larger negative temperature dependence because N_z is increased not only by the usual librations but also by the weakening of the H-bond with increasing temperature.

^1H–^2D Isotope Effects between $(CH_3NH_3)_2HgBr_4$ and $(CH_3ND_3)_2HgBr_4$

The observed frequency shifts are small and also comparable to the deuteration isotope effects in the case of the hexachlorometalate salts with the waters of crystallization [5]. The ^{1}H–^{2}D isotope effects in the latter compounds have been well explained on the assumption that the H-bonds are directed to the p_x and/or p_y lone pairs of electrons: (i) At the low temperature limit, the molecular motions are well suppressed and only the low frequency lattice vibrations exist; the frequency of the resonant atoms is lowered by the deuteration because the D atom is able to approach in a shorter distance to the resonant atom due to its heavier mass than the H atom [7]. (ii) At the high temperature limit, several types of motions are well activated, and the stretch vibrations in the main bond of the resonant atom become influential for the isotope effect; the H atom is able to approach closer to the resonant atom than the D atom owing to the anharmonicity of the interatomic potential, which results in higher-frequency values in the deuterated compounds compared to the nondeuterated ones [8].

It is evident that the effects on deuteration for ν_3^H and ν_4^H are consistent with the above prediction. On the contrary, the reverse shifts from the prediction are obtained in case of ν_1^H and ν_2^H at lower temperatures. However this contradiction is solved if we imagine that the H-atoms exist on the prolonged line of the Hg–Br bonds as described above. In this case the D atom, which can approach more to the resonant atom, decreases N_z more effectively compared to the H atom. A high frequency shift is consequently observed at lower temperature. Furthermore, such H-bonds may be more feasible to the temperature effects compared to the H-bonds directed to the p_x (and p_y) lone pair. Thus, when the temperature is raised, the H-bond may be more easily broken in the former case; the frequency shifts on deuteration will remain positive and become gradually zero as the temperature is raised.

Unusual Temperature Dependence in $(CH_3NH_3)_2HgI_4$

The crystal of $(CH_3NH_3)_2HgI_4$ has an orthorhombic lattice (Pbca) with $Z=8$ [3]. The Hg–I distances range from 2.751 to 2.789 Å, and the I–Hg–I angles from 106.06 to 115.68°. All crystallographically nonequivalent I atoms seem to be concerned with the H-bonding having short N ··· I distances ranging from 3.63 to 3.85 Å. The observed large asymmetry parameters (η) must result from the existence of H-bonds (directed to the p_x lone pair). Further, the decrease of η with increasing temperature may indicate the weakening of H-bonds. The wide frequency range of the resonance frequencies and their unusual temperature dependence are also observed here. This may be understood by taking into consideration the H-bonding and the large motions of $CH_3NH_3^+$ ions in the same manner as in case of the bromide. That is, the decrease of N_z by the H-bond (Hg–I ··· H ≈ 180°) may cause the increase of the frequency (at low temperature), see (1); the activation of molecular motions with increasing temperature results in steep negative temperature coefficients. On the contrary, the polarization of the p_x (and p_y) lone pair by the H-bond (Hg–I ··· H ≈ 90°) may result in a decrease of the resonance frequency; the frequency increases with increasing temperature. The effects of H-bonding for the resonance frequencies may be larger in the iodine compounds than in the bromine compounds because the polarizability of the I atom is larger than that of the Br atom.

For the I atom more precise information on N_x, N_y, and N_z is obtained from the remaining components of the EFG. Similar equations as (1) are written as follows [6]:

$$e^2 q_{xx} Q/h = \{(N_y + N_z)/2 - N_x\}\, e^2 q_{\text{at}} Q/h, \quad (2)$$

$$e^2 q_{yy} Q/h = \{(N_z + N_x)/2 - N_y\}\, e^2 q_{\text{at}} Q/h. \quad (3)$$

$e^2 q_{xx} Q/h$ and $e^2 q_{yy} Q/h$ must have an opposite sign of $e^2 q_{zz} Q/h$ because $q_{xx} + q_{yy} + q_{zz} = 0$.

$e^2 q_{zz} Q/h$ for ν_1 ($\nu_1^I - \nu_1^{II}$) and ν_3 decrease sharply with increasing temperature, and $e^2 q_{xx} Q/h$ and $e^2 q_{yy} Q/h$ have the tendency of decreasing though the temperature dependence of these values is not shown. This shows that the decrease of N_z by the H-bond occurs at low temperature; $e^2 q_{zz} Q/h$ may decrease sharply with increasing temperature. In this case $e^2 q_{xx} Q/h$ and $e^2 q_{yy} Q/h$ are also decreasing with increasing temperature, see (2) and (3). Though $e^2 q_{zz} Q/h$ for ν_2 is large, its value undergoes a relatively small temperature dependence exhibiting a maximum (Figure 4). The corresponding $e^2 q_{xx} Q/h$ increases monotonically with increasing temperature, while $e^2 q_{yy} Q/h$ decreases monotonically. This situation may be interpreted by supposing that N_z as well as N_x are mainly decreased by the H-bonds (the large η value may show the decrease of N_x); as both N_z and N_x increase with increasing temperature, the increase of the first and the second terms in (1) may result in the relatively small variation of $e^2 q_{zz} Q/h$. In this case $e^2 q_{xx} Q/h$ increases because the contribution of the increase of N_x may be larger than that of the increase of N_z in (2); $e^2 q_{yy} Q/h$ may decrease because the increase of the first term is larger than the increase of the second term in (3). ν_4 (Figure 5) may be similarly understood if we imagine that both N_x and N_y may be decreased by the H-bonds. As N_x and N_y are increased with increasing temperature, $e^2q_{zz}Q/h$ increases according to (1). In this case $e^2q_{xx}Q/h$ may increase because the effect of the increase of N_x overwhelms that of the increase of N_y and N_z in (2). $e^2q_{yy}Q/h$ may remain at almost constant because the increase of N_y is more effective compared to the increase of N_x and N_z, and then the former effect is comparable to the latter one in (3).

Concluding Remark

It is suggested that not only frequency-lowering but also frequency-rising effects result, depending on the direction of the H-bonds for the main bonds of halogen atoms. In the above discussion only two extreme directions of the H-bonds, i.e., directed toward the p_x (and p_y) lone pair and directed toward the antibonding σ^* orbital were considered, but the frequency shifts created by H-bonds may, in general, be a function of the angle between the Hg–X bond and the X ··· H bond.

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