**81^{1}\text{Br} and 127^{1}\text{I} NQR Studies of (CH}_3\text{NH}_3)_2\text{HgBr}_4 and (CH}_3\text{NH}_3)_2\text{Hgl}_4\right)^{*}$

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The $^{81}\text{Br}$ and $^{127}\text{I}$ NQR frequencies in (CH$_3$NH$_3$)$_2$HgBr$_4$ and (CH$_3$NH$_3$)$_2$HgI$_4$, 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 $^1\text{H} - ^2\text{D}$ isotope effects have been observed between (CH$_3$ND$_3$)$_2$HgBr$_4$ and (CH$_3$NH$_3$)$_2$HgBr$_4$. 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 • • • X, between the halogen atoms and the CH$_3$NH$_3^+$ 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 – • • • H bond.


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**Introduction**

In a previous paper [1] we have investigated the temperature dependence of the $^{81}\text{Br}$ and $^{127}\text{I}$ NQR frequencies of CH$_3$NH$_3$HgBr$_4$ and CH$_3$NH$_3$HgI$_4$ 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$_3$NH$_3^+$ ions which are likely to perform considerable motions. Thus it seems that the H-bonding, X – • • • H – N, and the motions of CH$_3$NH$_3^+$ ions 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 find 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$_3$NH$_3$)$_2$HgBr$_4$ and (CH$_3$NH$_3$)$_2$HgI$_4$, has been also determined by Körfer et al. [3]. There exist isolated units of HgX$_2^+$ 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...
measured the $^{81}\text{Br}$ and $^{127}\text{I}$ NQR in these compounds and also in a partially deuterated compound (CH$_3$ND$_3$)$_2$HgBr$_4$ in order to obtain information about the H-bonding and the motions of CH$_3$NH$_3$.

**Experimental**

The crystals of (CH$_3$NH$_3$)$_2$HgBr$_4$ and (CH$_3$NH$_3$)$_2$Hgl$_4$ were prepared from a methanol solution [3] or a diluted halogenoacid solution of stoichiometric amounts of CH$_3$NH$_3$X and HgX$_2$. C, H and N analyses were consistent with their chemical formula. The deuterated compound (CH$_3$ND$_3$)$_2$HgBr$_4$ was prepared by mixing CH$_3$ND$_3$Br and HgBr$_2$ in a diluted D$_2$O solution of DBr. The partially deuterated compound CH$_3$ND$_3$Br was prepared from repeated cycles of dissolution of CH$_3$ND$_3$Br in D$_2$O and evaporation of D$_2$O. 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**

$^{81}\text{Br}$ NQR Frequencies in (CH$_3$NH$_3$)$_2$HgBr$_4$

The resonance frequencies in (CH$_3$NH$_3$)$_2$HgBr$_4$ were measured between 77 K and ca. 400 K. In accordance with the crystal structure at room temperature [3] four resonance lines due to $^{81}\text{Br}$ were observed (Figure 1). The $^{81}\text{Br}$ 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$_3$NH$_3$)$_2$HgBr$_4$ and those of CH$_3$NH$_3$HgBr$_3$ [1]. The line $\nu_1^H$ exhibits a normal negative temperature dependence having a rather large coefficient. The line $\nu_2^H$ shows also a negative temperature dependence and has a slight downward curvature. The line $\nu_3$ exhibits an anomalous positive temperature dependence. Notice that the frequency vs. temperature curve of $\nu_3^H$ changes symmetrically to that of $\nu_2^H$. With increasing temperature from 77 K, the frequency $\nu_4^H$ increases slightly at the beginning,

![Fig. 1. The temperature dependence of $^{81}\text{Br}$ NQR frequencies in (CH$_3$NH$_3$)$_2$HgBr$_4$ (filled circle) and (CH$_3$ND$_3$)$_2$HgBr$_4$ (open circle).](image)

<table>
<thead>
<tr>
<th>T/K</th>
<th>$\nu$/MHz$^a$</th>
<th>$\nu^D-\nu^H$/MHz$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>D</td>
</tr>
<tr>
<td>77</td>
<td>90.471</td>
<td>90.583</td>
</tr>
<tr>
<td></td>
<td>88.444</td>
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<tr>
<td></td>
<td>78.869</td>
<td>78.800</td>
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<tr>
<td></td>
<td>77.012</td>
<td>76.928</td>
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<tr>
<td>295</td>
<td>84.509</td>
<td>84.591</td>
</tr>
<tr>
<td></td>
<td>84.301</td>
<td>84.311</td>
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<td></td>
<td>81.718</td>
<td>81.830</td>
</tr>
<tr>
<td></td>
<td>76.031</td>
<td>76.115</td>
</tr>
</tbody>
</table>

$^a$ 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.

\[ H-^2D \text{Isotope Effects of the } ^{81}\text{Br NQR Resonance Frequencies of } (\text{CH}_3\text{NH}_3)_2\text{HgBr}_4 \]

The temperature dependence of the \(^{81}\text{Br NQR frequencies in } (\text{CH}_3\text{ND}_3)_2\text{HgBr}_4 \text{ 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 } v_1^H \text{ and } v_2^H \text{ from the respective } v_1^H \text{ and } v_2^H \text{ are positive at 77 K and decrease with increasing temperature. At room temperature, the shift of } v_2^D \text{ becomes almost negligible. The shifts of } v_3^D \text{ and } v_4^D \text{ are negative at 77 K and become almost zero around 120 K and 140 K, respectively. Above these temperatures the shifts are positive.} \]

\[ ^{127}\text{I NQR Frequencies, Nuclear Quadrupole Coupling Constants, and Asymmetry Parameters in } (\text{CH}_3\text{NH}_3)_2\text{HgI}_4 \]

Both resonances \( v^I \) and \( v^{II} \) 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 \( v^I \) (Fig. 2) and to 300 K for \( v^{II} \) (Figure 3). There are four crystallographically nonequivalent I atoms in the unit cell [3]. In accordance with this, respective four resonance lines of \( v^I \) and \( v^{II} \) were observed at 77 K. The \( v_1^I \) and \( v_3^I \) lines approach each other with increasing temperature. Above ca. 210 K the weaker line \( v_3^I \) is not resolved from \( v_1^I \). The line \( v_3^{II} \) fades with increasing temperature and becomes unobservable above ca. 260 K. The respective pairs of \( v^I \) and \( v^{II} \) were easily found by considering the relation \( 2v^I \geq v^{II} \) and the temperature dependence of resonance frequencies. The resonance frequencies (\( v \)), nuclear quadrupole coupling constants (\( e^2qQ/h \)), and asymmetry parameters (\( \eta \)) at representative temperatures are listed in Table 2.

There is some similarity between the \( v^I \) spectra of \( (\text{CH}_3\text{NH}_3)_2\text{HgL}_{4} \) and \( \text{CH}_3\text{NH}_3\text{HgL}_{3} \) [1]. The lines \( v_1^I, v_2^I, v_3^I, \text{ and } v_3^{II} \) have large negative temperature coefficients. The \( v_2^I \) line shows a smaller negative temperature dependence, but its temperature curve is rather curious. On the other hand \( v_2^{II} \) exhibits a positive temperature dependence until around ca. 270 K and then decreases gradually. \( v_2^I \) shows a broad minimum at ca. 130 K and increases above this temperature, while \( v_2^{II} \) increases with temperature throughout. The temperature dependence of the respective components of the nuclear quadrupole coupling tensor and the \( \eta \) values for the pairs of \( v_2^I-v_2^{II} \) and \( v_4^I-v_4^{II} \) are shown in Figs. 4 and 5, respectively.
Discussion

Unusual Temperature Dependence in \((\text{CH}_3\text{NH}_3)_2\text{HgBr}_4\)

The crystal of \((\text{CH}_3\text{NH}_3)_2\text{HgBr}_4\) 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 \(\text{CH}_3\text{NH}_3^+\) 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 \(\text{CH}_3\text{NH}_3^+\) ions because

\[
\nu = \frac{e^2 q_{zz} Q_{h1}}{4 \pi \hbar} \quad \text{and} \quad \eta = \frac{e^2 q_{zz} Q_{h1}}{4 \pi \hbar} n
\]

and the best fitted values \(\nu(T) = a + b T + c T^2 + d T^3\).

Table 2. \(^{127}\text{I}\) NQR frequencies (\(\nu\)), nuclear quadrupole coupling constants \(\left(\frac{e^2 q_{zz} Q_{h1}}{\hbar}\right)\), and asymmetry parameters (\(\eta\)) in \((\text{CH}_3\text{NH}_3)_2\text{Hgl}_4\).

<table>
<thead>
<tr>
<th>T/K</th>
<th>(\nu/\text{MHz})</th>
<th>(\frac{e^2 q_{zz} Q_{h1}}{\hbar}/\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>113.01 222.50</td>
<td>743.50 0.111</td>
</tr>
<tr>
<td>v_1</td>
<td>119.99 211.22</td>
<td>710.69 0.218</td>
</tr>
<tr>
<td>v_2</td>
<td>109.19 217.89</td>
<td>726.55 0.041</td>
</tr>
<tr>
<td>v_3</td>
<td>94.47 168.13</td>
<td>571.13 0.315</td>
</tr>
<tr>
<td>v_4</td>
<td>96.20 181.25</td>
<td>609.97 0.220</td>
</tr>
</tbody>
</table>

\(a\) Estimated accuracy is within \(\pm 0.01\) MHz.

\(b\) \(\pm 0.02\) MHz. \(c\) \(\pm 0.04\) MHz.
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]:

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

(1)

where $N_x$, $N_y$, and $N_z$ denote the effective numbers of corresponding p orbitals, respectively, and $e^2q_{zz}Q/h$ 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 CI atoms, $N_z$ (and/or $N_y$) is decreased through the polarization of the lone pair electrons, resulting in a decrease of the resonance frequencies of the CI 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 $N_z$ (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 $N_z$ (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 $v_3^H$ and partly for $v_4^H$ in the present case. Their frequencies are low at low temperature; for $v_3^H$ a positive temperature dependence is observed in the observed temperature range, and for $v_4^H$ 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 $v_3^H$ presumably undergo smaller tortional vibrations compared to that of the Br atom for $v_4^H$.

On the other hand, though all halogen atoms seem to be involved in H-bonding in the present crystal, $v_1^H$ and $v_2^H$ are rather high in frequency compared to $v_3^H$ and $v_4^H$ at 77 K. Further, their (negative) temperature dependence is rather large, though the HgBr$_2^-$ 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 $\sigma^*$ 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.

$^{1}H-^{2}D$ 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 sup-
pressed 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 $v^i_3$ and $v^i_4$ are consistent with the above prediction. On the contrary, the reverse shifts from the prediction are obtained in case of $v^i_1$ and $v^i_2$ at lower temperatures. However this contradiction is solved 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, the increase of $N_x$ 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]:

$$e^2q_{xx}Q/h = [(N_x + N_y)/2 - N_z] e^2q_{xy}Q/h,$$  \hspace{1cm} (2)

$$e^2q_{yy}Q/h = [(N_x + N_y)/2 - N_z] e^2q_{xy}Q/h.$$  \hspace{1cm} (3)

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

$e^2q_{xx}Q/h$ for $v_1$ ($v^i_1 - v^i_1$) and $v_3$ decrease sharply with increasing temperature, and $e^2q_{yy}Q/h$ and $e^2q_{xy}Q/h$ have the tendency of decreasing though the temperature dependence of these values is not shown. This shows that the decrease of $N_y$ by the H-bond occurs at low temperature; $e^2q_{zz}Q/h$ may decrease sharply with increasing temperature. In this case $e^2q_{xx}Q/h$ and $e^2q_{yy}Q/h$ are also decreasing with increasing temperature, see (2) and (3). Though $e^2q_{zz}Q/h$ for $v_2$ is large, its value undergoes a relatively small temperature dependence exhibiting a maximum (Figure 4). The corresponding $e^2q_{xx}Q/h$ increases monotonically with increasing temperature, while $e^2q_{yy}Q/h$ decreases monotonically. This situation may be interpreted by supposing that $N_z$ as well as $N_y$ are mainly decreased by the H-bonds (the large $\eta$ value may show the decrease of $N_z$); as both $N_x$ and $N_y$ increase with increasing temperature, the increase of the first and the second terms in (1) may result in the relatively small variation of $e^2q_{zz}Q/h$. In this case $e^2q_{xx}Q/h$ increases because the contribution of the increase of $N_z$ may be larger than that of the increase of $N_x$ in (2); $e^2q_{yy}Q/h$ may decrease because the increase of the first term is larger than the increase of the second term in (3). $v_4$ (Figure 5) may be similarly understood if we imagine that both $N_y$ and $N_x$ may be decreased by the H-bonds. As $N_x$ and $N_y$ are increased

Unusual Temperature Dependence in (CH$_3$NH$_3$)$_2$Hgl$_4$

The crystal of (CH$_3$NH$_3$)$_2$Hgl$_4$ 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 non-equivalent 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 ($\eta$) must result from the existence of H-bonds (directed to the $p_x$ lone pair). Further, the decrease of $\eta$ 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$_3$NH$_3^+$ ions in the same manner as in case of the bromide. That is, the
with increasing temperature, \( e^2 q_{zz} Q/h \) increases according to (1). In this case \( e^2 q_{zz} Q/h \) may increase because the effect of the increase of \( N_x \) overwhelms that of the increase of \( N_y \) and \( N_z \) in (2). \( e^2 q_{yy} Q/h \) 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 \( \sigma^* \) 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 \( \cdots \) H bond.

### Acknowledgement

We are grateful to Professor Akinobu Sasane, Shinshu University, for valuable comments.