Single-Crystal Raman Spectra of Mercurous Bromide, Mercurous Iodide, and Mercuric Iodide

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The Raman active factor-group fundamentals of Hg₂Br₃, Hg₂I₃, and HgI₄ are unambiguously assigned from the single-crystal observations.

The mercurous halides have been extensively investigated by means of both Raman and infrared spectroscopy,¹⁻⁵ and several complete vibrational assignments of the fundamentals have been proposed during the last 10 years. In their study on Hg₂Cl₂ Mathieu et al.¹,² reported a vibrational assignment of the internal modes. Goldstein,³ however, observed a previously unreported absorption at ca. 260 cm⁻¹ in a re-investigation of the far infrared spectrum and a new assignment of the fundamentals was proposed. In more recent works by Durig et al.⁴ and by Conney et al.⁵ the vibrational spectra of mercurous bromide and iodide were analysed. The above-mentioned studies were based on a molecular model and insufficient attention was given to the external crystal modes. A single-crystal Raman study on Hg₂Cl₂ by Beattie and Gilson⁶ resulted in a revised assignment of the external and internal Raman active modes, and recently Osaka ⁷ measured the infrared absorption spectra of Hg₂X₂ (X = Cl, Br, I) in detail and made an analysis in terms of crystalline solids. In the present work we have obtained single-crystal Raman polarisation data for Hg₂Br₂ and Hg₂I₂ and have attributed the Raman active fundamentals to their respective symmetry classes.

The two mercuric halides HgCl₂ and HgBr₂ have a linear configuration in all phases, and the crystal lattice is distinctly molecular.¹⁸,¹⁴ Mercuric iodide, however, has two modifications.¹⁵,¹⁶ The red form that is stable at room temperature undergoes a reversible phase transition to a yellow form at 126°C. The bonding in yellow HgI₄ is apparently molecular, while the red form consists of layers of HgI₄ tetrahedra in the crystal.

A number of vibrational spectroscopic studies have been carried out already on these compounds. The ν₁ and ν₃ stretching frequencies are well

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established from gas and melt spectra.\textsuperscript{14,17–21} By comparing the \( v_1 \) frequency in passing from vapour \textsuperscript{17,18} to melt \textsuperscript{19,20} it appears that the frequency shift decreases along the series HgCl\(_2\), HgBr\(_2\), HgI\(_2\). The bonding forces within HgI\(_2\) are considered as being much less sensitive to environmental effects. The doubly degenerate bending frequency \( v_2 \) is determined from infrared gas \textsuperscript{22} and matrix isolation studies.\textsuperscript{21} A considerable discrepancy from electronic spectral data \textsuperscript{23} was found.

The solid state spectra of HgCl\(_2\),\textsuperscript{2,24} HgBr\(_2\),\textsuperscript{24} and HgI\(_2\)\textsuperscript{2,25,26} are interpreted on the basis of the symmetry properties of the crystals. Poulet and Mathieu \textsuperscript{2} applied vibrational spectroscopy on an HgCl\(_2\) single-crystal. While the present work was in progress Adams \textit{et al.}\textsuperscript{25} reported the single-crystal Raman spectrum of red mercuric iodide. However, the two translatory modes were unobserved. A crystal of good optical quality was grown and all the Raman active modes appeared. Raman spectra of HgBr\(_2\) single-crystal were also obtained. However, the crystals were very imperfect and no meaningful interpretation in terms of crystal structure was possible.

**EXPERIMENTAL**

The single-crystals of Hg\(_3\)Br\(_4\) and Hg\(_2\)I\(_3\) were prepared by slow sublimation in a nitrogen atmosphere. The HgI\(_2\) crystal was grown from the vapour phase in an evacuated glass-tube. The spectra were recorded with a Spex 1401 monochromator with a Spectra Physics He/Ne 6328 Å laser excitation of about 50 mW power. Since the mercurous iodide crystal quickly decomposed in the 50 mW laser beam, this crystal was excited with a He/Ne laser of about 0.5 mW power. No decomposition was observed under these conditions.

**RESULTS AND DISCUSSION**

Previous infrared and Raman data\textsuperscript{4,7} of the halides are consistent with the assumption that Hg\(_2\)X\(_2\) (X = Cl, Br, I)\textsuperscript{11} belong to the same space group as mercurous fluoride,\textsuperscript{12} \( D_{4h} \). The Hg\(_2\)X\(_2\) molecules have a fourfold axis in common with the lattice and have consequently \( D_{4h} \) site symmetry. Factor group analysis gives four Raman active modes of symmetry type \( 2a_{1g} + 2e_g \), which should arise only in \( (xx) \), \( (yy) \), \( (zz) \), and \( (xz) \), \( (yz) \) observations, respectively.

The single-crystal observations are summarized in Tables 1 and 2 for Hg\(_3\)Br\(_4\) and Hg\(_2\)I\(_3\), respectively. The data enable an unambiguous assignment of the Raman active bands. Our results confirm the interpretation reported by Ōsaka.\textsuperscript{7} The weak Raman bands observed at 92 and 65 cm\(^{-1}\) for the bromide and iodide, respectively, by Durig \textit{et al.}\textsuperscript{4} should clearly be associated with the non-totally symmetric Hg – Hg – X bending mode \( v_4 \), whereas the strong band located at the lowest frequency in the spectra is attributed to the external mode of rotatory origin. Apparent from the \( (zz) \), \( (xz) \), \( (yz) \), and \( (yz) \) measurements of the iodide the broad band at ca. 68 cm\(^{-1}\) consists of two partly overlapping bands, one associated with the \( v_4 \) vibration, while the other might arise from a second-order process.

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Table 1. Oriented single-crystal Raman polarisation data \(^a\) for Hg\(_3\)Br\(_2\).

<table>
<thead>
<tr>
<th>(v) (cm(^{-1}))</th>
<th>(I_x(zz)y)</th>
<th>(I_x(xx)y)</th>
<th>(I_x(yz)y)</th>
<th>(I_x(yz)y)</th>
<th>(I_x(xy+zx)y) (^b)</th>
<th>(I_x(yy+yz)z) (^b)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>221</td>
<td>1.17</td>
<td>0.33</td>
<td>0.06</td>
<td>0.08</td>
<td>0.18</td>
<td>0.07</td>
<td>(v_1(\alpha_{1g}))</td>
</tr>
<tr>
<td>135</td>
<td>17.04</td>
<td>4.72</td>
<td>0.70</td>
<td>1.25</td>
<td>2.78</td>
<td>0.45</td>
<td>(v_2(\alpha_{1g}))</td>
</tr>
<tr>
<td>92</td>
<td>0.13</td>
<td>0.42</td>
<td>0.08</td>
<td>0.19</td>
<td>0.18</td>
<td>0.08</td>
<td>(v_4(\epsilon_g))</td>
</tr>
<tr>
<td>(\sim 72)</td>
<td>36</td>
<td>2.63</td>
<td>6.95</td>
<td>1.30</td>
<td>3.39</td>
<td>0.85</td>
<td>(2v_L = 72)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(v_L(\epsilon_g))</td>
</tr>
</tbody>
</table>

\(^a\) Peak areas measured in arbitrary units.
\(^b\) Recorded in a different intensity scale.

Table 2. Oriented single-crystal Raman polarisation data \(^a\) for Hg\(_3\)I\(_2\).

<table>
<thead>
<tr>
<th>(v) (cm(^{-1}))</th>
<th>(I_x(zz)y)</th>
<th>(I_x(xx)y)</th>
<th>(I_x(yz)y)</th>
<th>(I_x(yz)y)</th>
<th>(I_x(xy+zx)y) (^b)</th>
<th>(I_x(yy+yz)xy) (^b)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sim 223)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>193</td>
<td>0.86</td>
<td>0.29</td>
<td>0.04</td>
<td>0.07</td>
<td>0.01</td>
<td>0.03</td>
<td>(2v_3 = 226)</td>
</tr>
<tr>
<td>113</td>
<td>46.2</td>
<td>14.6</td>
<td>1.40</td>
<td>3.44</td>
<td>0.86</td>
<td>0.80</td>
<td>(v_3(\alpha_{1g}))</td>
</tr>
<tr>
<td>(\sim 73)</td>
<td>0.06</td>
<td>0.14</td>
<td>0.12</td>
<td>0.29</td>
<td>0.09</td>
<td>0.05</td>
<td>(v_4(\epsilon_g))</td>
</tr>
<tr>
<td>(\sim 64)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(2v_L = 62)</td>
</tr>
<tr>
<td>31</td>
<td>3.94</td>
<td>5.14</td>
<td>2.12</td>
<td>6.70</td>
<td>5.20</td>
<td>1.10</td>
<td>(v_L(\epsilon_g))</td>
</tr>
</tbody>
</table>

\(^a\) Peak areas measured in arbitrary units.
\(^b\) Recorded in a different intensity scale.
Table 3. Oriented single-crystal Raman polarisation data\textsuperscript{a} for red HgI\textsubscript{2}.

<table>
<thead>
<tr>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$I_{x'(y'z')y'}$</th>
<th>$I_{z'(y'z')y'}$</th>
<th>$I_{x'(z'z')y'}$</th>
<th>$I_{x'(y'z')y'}$\textsuperscript{b}</th>
<th>$I_{x'(y'z')y'}$\textsuperscript{b}</th>
<th>$I_{x'(x'z')y'}$\textsuperscript{b}</th>
<th>$I_{x'(x'z')y'}$\textsuperscript{b}</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>143.5</td>
<td>10.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>$b_{1g}$</td>
</tr>
<tr>
<td>114.0</td>
<td>24</td>
<td>20</td>
<td>336</td>
<td>68</td>
<td>68</td>
<td>68</td>
<td>219</td>
<td>70</td>
</tr>
<tr>
<td>54.5</td>
<td>2.0</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>4.8</td>
<td>1.5</td>
<td>0.5</td>
<td>$b_{1g}$</td>
</tr>
<tr>
<td>49.0</td>
<td>2.5</td>
<td>0.8</td>
<td>3.0</td>
<td>4.5</td>
<td>0.5</td>
<td>1.5</td>
<td>5.5</td>
<td>$e_{g}$</td>
</tr>
<tr>
<td>28.5</td>
<td>204</td>
<td>730</td>
<td>114</td>
<td>584</td>
<td>402</td>
<td>201</td>
<td>228</td>
<td>476</td>
</tr>
<tr>
<td>17.5</td>
<td>200</td>
<td>1788</td>
<td>212</td>
<td>1112</td>
<td>745</td>
<td>276</td>
<td>430</td>
<td>88.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Peak heights measured in arbitrary units.
\textsuperscript{b} Recorded in a different intensity scale.
The crystal structure of red HgI$_2$ is built up from layers of HgI$_4$ tetrahedra. It has space symmetry $P4_g/mnc$ ($D_{4h}^{15}$) ($Z = 2$) with I-atoms on sites of symmetry $C_{2v}$, and Hg-atoms on sites of $D_{4h}$ symmetry. The factor group analysis leads to the irreducible representation.

$I_{\text{cryst}} = a_{1g} + a_{2u} + 2b_{1g} + b_{2u} + 3e_g + 2e_u$

The Raman tensor components are as follows: $a_{1g}$, $R_{xx} + R_{yy}$, $R_{zz}$; $b_{1g}$, $R_{xx} - R_{yy}$; $e_g$, $R_{xy}$. To distinguish between $a_{1g}$ and $b_{1g}$ modes we recorded the polarisation measurements at 45° to $x$- and $y$-axis. By use of the experimental set of axes ($x'$, $y'$, $z$) the $a_{1g}$, $b_{1g}$, and $e_g$ modes should arise only in ($x'x'$), ($y'y'$), (zz); ($x'y'$); ($x'z$) and ($y'z$) measurements, respectively. The results of the oriented single-crystal measurements are shown in Table 3. The data led to unambiguous assignments of the 6 Raman active modes. Weak bands were previously observed in the region 30–70 cm$^{-1}$ and attributed to combinations because of lack of single crystal observations. Two of these bands showed apparent orientation effects and are assigned to the two translational modes, ($b_{1g} + e_g$), unobserved by Adams $et$ $al$. In addition two weak bands were observed at 38 and 64 cm$^{-1}$, which may be due to second-order effects.

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REFERENCES


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