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LIBRATIONAL MODES OF WATER IN CRYSTAL HYDRATES AND PHASE-TRANSITIONS

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Abstract: Temperature dependence of infrared active librational modes of water in polycrystalline \( \text{M(CIO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \) (\( \text{M} = \text{Mg} \) and \( \text{Zn} \), respectively) shows phase transitions at 225.5, 193 and 110 K in the former and at 284, 256.5 and 233 K in the latter.

1. Introduction. In the isomorphous metal perchlorate hexahydrates of general formula \( \text{M(CIO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \), where \( \text{M} = \text{Mg}, \text{Fe}, \text{Co}, \text{Ni} \) and \( \text{Zn} \); the M"ossbauer\(^2\)+\(^3\), magnetic susceptibility and anisotropy\(^4\), and EPR\(^5\)+\(^6\) studies have revealed that these systems undergo one (or more) phase transition(s) between 80-373 K. There are two different views regarding the change in the perchlorate crystal structure at the phase transition (PT) below room temperature (RT). According to M"ossbauer studies\(^2\)+\(^3\), the water octahedron surrounding the metal ion in the crystal is trigonally stretched at higher temperature (HT) and it becomes trigonally compressed at lower temperatures (LT) after the PT. According to Choudhuri\(^4\), the water octahedron trigonally stretched at HT becomes tetragonally compressed after the PT, thus involving a structural change. However, EPR studies\(^5\) show supporting evidence to one or another view point in the same series below and above RT\(^6\).

Ross has reported the fundamental modes of \( \text{CIO}_4^- \) ion in various anhydrous and hydrated perchlorates.\(^7\) No data are available for librational modes of water in hydrated perchlorates, except \( \text{LiCIO}_4 \cdot 3\text{H}_2\text{O} \)\(^8\) and \( \text{Zn(CIO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \). We have undertaken the study of water modes in perchlorates with a view to understand the dynamics of PT and the relative significance of polyatomic anions, water dipoles and cations for affecting the PT.

2. Experimental. \( \text{Mg(CIO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \) (MPHH) is prepared dissolving magnesium carbonate in dilute perchloric acid and purified by reported procedure\(^9\). Infrared spectra at RT and LT were taken by the KBr pellet technique using a Perkin Elmer 580 spectrophotometer and Specac variable temperature cell fitted with its automatic temperature control unit. The relevant bands are reported in Table 1.

3. Results and Discussion. The librational assignments are based on: (I) comparison of hydrated (RT & LT) spectra and anhydrous MPHH (Table 1A) showing that the bands at 602, 485, 423, 380 & 360 cm\(^{-1}\) are the bands due to water molecules and at 640, 630 (\( \nu_1 \)) and 457 cm\(^{-1}\) (\( \nu_2 \)) that of \( \text{CIO}_4^- \) ion; (II) the bands at 602, 485, 423 and 360 cm\(^{-1}\) are assigned as rocking (R), wagging (W), twisting
TABLE 1. Observed bands in the IR spectrum of (A) hydrated and anhydrous and 
(B) partially deuterated magnesium perchlorate.

(A) Hydrated Anhydrous Assignment (B) Partially Deuterated Assignment

<table>
<thead>
<tr>
<th>LT</th>
<th>Hydrated</th>
<th>Anhydrous</th>
<th>Assignment</th>
<th>LT</th>
<th>Partially Deuterated</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v (\text{cm}^{-1}))</td>
<td>(I)</td>
<td>(v (\text{cm}^{-1}))</td>
<td>(I)</td>
<td>(v (\text{cm}^{-1}))</td>
<td>(H_2O)</td>
<td>(HOD)</td>
</tr>
<tr>
<td>360</td>
<td>40</td>
<td>356</td>
<td>23</td>
<td>--</td>
<td>(M-O_w)</td>
<td>360</td>
</tr>
<tr>
<td>380</td>
<td>21</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>(M-O_w)</td>
<td>380</td>
</tr>
</tbody>
</table>
| 423 | 31 | -- | -- | -- | \(T\) | 423 | 382 | 290 | -- | -- | \(T\)
| 457 | 13 | -- | -- | 461 | \(v_P\) | 485 | 450 | 335 | 470 | 445 | 330 \(W\) |
| 485 | 100 | 470 | 100 | -- | \(W^2\) | 602 | 523 | 420 | 605 | 505 | 423 \(R_w\) |
| 602 | 85 | 605 | 73 | -- | \(R\) | 1633 | 1441 | 1208 | 1634 | 1442 | 1209 \(v_2\) |
| 630 | 26 | 630 | 18 | 630 | \(v_4\) | 2242 | 1945 | -- | 2242 | 1950 | -- | \(v_2+R\) |
| 640 | 25 | 640 | 16 | 639 \(T\) | -- | -- | -- | -- | -- | -- |

(T) and \(M-O_w\), respectively, on the basis of intensity (I),\(^8\) sequence of frequency (\(v\)),\(^8\) frequency shift on partial deuteration\(^8\) (Table 1B), expected \(M-O_w\) vibration of transition metal-aquo complexes, and (III) a new criterion using a combination band (of the bending & rocking modes of bound water) at 2235 cm\(^{-1}\) corroborating that the 602 cm\(^{-1}\) band is due to the \(R\) modes of water. Similar studies were made in ZPHH and have been discussed earlier.\(^9\)

For structural studies of MPHH isotopic dilution technique\(^11\) was used. Figure 1 shows the bands due to OD stretching fundamentals of isotopically dilute HDO in MPHH in the temperature range 303-100K. Between 303-100K the six water molecules are equivalent, confirmed by the single bending mode. The shoulder appearing at 225.5 ± 1.5K in the OD stretching modes that the water molecules are distorted due to non-equivalent hydrogen bonding,\(^12\) as a result of which the space group of MPHH including hydrogen is no more \(C_{2v}\) but one of the lower symmetry. At 193 ± 1K the water molecules are distorted further, due to the weakening of one hydrogen bond. The peak intensity enhancement at 110 ± 5K and width considerations suggest a positional ordering of hydrogen atoms in the system. The T mode shows similar behaviour as the OD stretch. The PT at 225.5K is being reported here for the first time.\(^2,5\) Present study shows that all the PT are 2nd or higher order.

Figure 2 shows the bands in (A) stretching and (B) bending regions of water in ZPHH in the temperature range.
305-123K. Detailed study of the variation of intensity, and full width at half maximum intensity (FWHMI) with temperature in the bending region (Fig. 3) broadly corroborates the discontinuous changes depicting the PT at 284, 256.5 and near 233K. Figures 2-3 show that (I) minor changes are taking place at 284K, which indicate that 2nd or higher order PT is taking place. This observation may be attributed to the axial compression of water molecules resulting due to distortion of $\text{ClO}_4^-$ ion in crystal hydrates, below 284K, without structural change,\(^1\) (II) the sharp changes at 256.5K indicate that 1st order PT is taking place; changes in band shapes (Fig. 2) indicate that structural change\(^1\) is taking place. Our observations support\(^4\) that the space group $\text{C}_2\text{v}$ of $\text{ZnH}_2$ at HT changes to space group $\text{C}_2\text{h}$ below 256.5K, which is consistent with group theoretical calculations and experimental observations\(^1\) in tutton salt having the same octahedral aquo-complex, (III) the discontinuity in between 243-223K shows that this PT is 2nd or higher order. The change in FWHMI in the stretching region indicates that the PT near 233K is order-disorder type.\(^14\)

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References