The Infra-red Spectrum of Synthetic Haidingerite, CaHAsO$_4$·H$_2$O *

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Synthetic Haidingerite, dicalcium arsenate monohydrate was studied by infra-red techniques from 4000—400 cm$^{-1}$. All the observed bands have been assigned and the data are discussed in the light of known crystallographic structure.

The spectra structure correlations of complex phosphates formed in the system CaO—P$_2$O$_5$—H$_2$O have received considerable attention and the observed bands have been assigned$^{1-5}$. However, no data on the corresponding arsenates have been published. The earlier infra-red spectroscopic reports of the ortho-arsenates are mainly on alkali and alkaline earth metals either without or with only the general assignments for the observed bands$^{6-10}$.

It is the purpose of this communication to report the infra-red spectrum for dicalcium arsenate monohydrate in the range 4000—400 cm$^{-1}$ at 300 °K and to assign the bands and to discuss them in terms of the crystal structure.

Structure

Haidingerite, dicalcium arsenate monohydrate belongs to the ortho-rhombohedral crystallographic class, and its crystal structure is now well characterized by X-ray diffraction methods. BINAS$^{11}$ investigated the structure of Haidingerite and found that his crystallographic data confirmed the earlier work of FISCHER$^{12}$ except for the space group. Almost simultaneously CASSIEN et al.$^{13}$ determined its crystal structure and their results are comparable with those of BINAS$^{11}$, except for the co-ordination around calcium atoms, which have six nearest neighbours.

More recently the structure was determined using three-dimensional least square analysis for refinement by CALLERI and FERRARI$^{14}$ and agreed to that proposed by BINAS$^{11}$. According to these authors Haidingerite structure is made up by double-layers of AsO$_4$ groups normal to (010); inside the double-layers calcium atoms co-ordinate six oxygen atoms bound to arsenic and a seventh one belonging to a water molecule. One of the arsenate groups' oxygen is not calcium co-ordinated, and it evidently belongs to an OH group. This oxygen atom is hydrogen bonded simultaneously to an oxygen atom of the arsenate tetrahedra of its own layer, except for the space group.

<table>
<thead>
<tr>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>Z</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.946</td>
<td>16.14</td>
<td>7.930</td>
<td>8</td>
<td>D$_{5h}$/Pnma</td>
</tr>
<tr>
<td>6.925</td>
<td>16.19</td>
<td>7.928</td>
<td>8</td>
<td>D$_{5h}$/Pnma</td>
</tr>
<tr>
<td>6.935</td>
<td>16.15</td>
<td>7.940</td>
<td>8</td>
<td>D$_{5h}$/Pnma</td>
</tr>
<tr>
<td>6.904</td>
<td>16.16</td>
<td>7.935</td>
<td>8</td>
<td>D$_{5h}$/Pnma</td>
</tr>
</tbody>
</table>

Table 1. Crystallographic data of Haidingerite.

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14 M. CALLERI and G. FERRARI, Period. Miner. 36, 1 [1967].
and also to an oxygen atom of a water molecule of the adjacent double layer. Water molecules form a second hydrogen bond with an oxygen atom of its own layer. The unit cell characteristics and space group are summarized in Table 1.

Results

The values of the observed frequencies and qualitative intensities are listed in Table 2, together with band assignments.

Assignments and Discussion

The highest available symmetry for the dibasic ortho-arsenate $\text{HAsO}_4^{2-}$ ion is $C_{3v}$, where the hydroxyl group is considered to be free to rotate about its As—O bond. The hexatomic $\text{HAsO}_4^{2-}$ ion has $(3n - 6) = 12$ degrees of vibrational freedom, out of which 9 are associated with the $\text{AsO}_4$ grouping, with the following selection rules: $3A_1$ (i.r., R) + $3E$ (i.r., R) where i.r. = infra-red and R = Raman active. The remaining three vibrational degrees of freedom are associated with the motions of the hydroxyl group.

On the basis of the centro-symmetric space groups of Haidingerite, site group analysis after the method of Halford shows that $\text{HAsO}_4^{2-}$ ions and $\text{H}_2\text{O}$ molecules are located on the sites of $C_4$ symmetry. The detailed features of the spectrum are now described according to the reduction of symmetry $C_{3v}$ for $\text{HAsO}_4^{2-}$ and $C_{2v}$ for $\text{H}_2\text{O}$ to $C_1$.

The above analysis shows that all the degeneracies are removed and 9 arsenate skeletal and 3 water infra-red active absorption are to be expected. In addition three $\text{HAsO}_4^{2-}$ modes are also predicted.

The observed frequencies of the spectral bands are assigned following the assignment data of Chapman and Thirlwell for the dibasic orthophosphate $\text{HPO}_4^{2-}$ anion. The numbering of normal modes is according to Herzberg. Arsenate skeletal modes are found at 896, 890, 851 and at 752 cm$^{-1}$. These values could be assigned to the components $v_6$ and $v_6''$ of the doubly degenerate $\text{AsO}_3$ stretch; the non-degenerate $\text{AsO}_3$ stretch, $v_2$ and the $\text{As—O(H)}$ symmetric stretch, $v_3$. Arsenate bending modes are observed at 490, 463 and 452 cm$^{-1}$. These correspond to the non-degenerate $\text{As—O—As}$ bending motion $v_4$ and to the components of the doubly degenerate bending mode $v_7$. Though it is not easy to assign these frequencies unambiguously in the absence of the calculated frequencies on the force constant data, the latter pair (i.e. 463 and 452 cm$^{-1}$) most probably

<table>
<thead>
<tr>
<th>$\nu$ [cm$^{-1}$]</th>
<th>$\nu$ [cm$^{-1}$]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3395 v s</td>
<td>2395 w, b</td>
<td>$v_1$ and $v_3$ OH stretching modes for water.</td>
</tr>
<tr>
<td>3205 sh, b</td>
<td>2290 w, b</td>
<td>$(\text{HAsO}_4)$, OH stretching mode.</td>
</tr>
<tr>
<td>2915 w</td>
<td>2040 w</td>
<td>Overton band, $2\text{OH}(\text{HAsO}_4)$ (?).</td>
</tr>
<tr>
<td>2300 w, b</td>
<td>1776 w</td>
<td>$v_2$, $\text{H—O—H}$ deformation for water.</td>
</tr>
<tr>
<td>1639 m, b</td>
<td>1215 w, b</td>
<td>$v_2$, $\text{H—O—D}$ deformation.</td>
</tr>
<tr>
<td>1385 —</td>
<td>1440 v s</td>
<td>Combination band ($\sim$ 890 + $\sim$ 490 = $\sim$ 1380).</td>
</tr>
<tr>
<td>1097 m, b</td>
<td>855 sh</td>
<td>$\delta_{\text{OH}}(\text{HAsO}_4)$, in plane $\text{As—O—H}$ deformation, $v_3$(e).</td>
</tr>
<tr>
<td>1025 m, b</td>
<td>800 w</td>
<td>$v_6$, $\nu''_6$ components of $v_6$ (e), $\text{AsO}_3$ degenerate stretch.</td>
</tr>
<tr>
<td>886 sh</td>
<td>902 sh</td>
<td>$v_3$, $\text{As—O(H)}$ symmetric stretch (a).</td>
</tr>
<tr>
<td>889 v s</td>
<td>890 v s</td>
<td>$r_2$, $\text{As—O(H)}$ symmetric stretch; and also $\gamma\text{OH}(\text{HAsO}_4)$ out of plane $\text{As—O—H}$ deformation, $v_5$(e).</td>
</tr>
<tr>
<td>851 v s</td>
<td>850 v s</td>
<td>$r_2$, $\text{As—O(H)}$ symmetric stretch.</td>
</tr>
<tr>
<td>752 sh</td>
<td>745 v v</td>
<td>$r_4$ and $r_7$ and $r''_4$, $r''_7$ $\text{O—As—O}$ bending modes (e and a respectively).</td>
</tr>
<tr>
<td>622 sh</td>
<td>722 v v</td>
<td>$\gamma\text{OH}$ water.</td>
</tr>
<tr>
<td>490 sh</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>463 s</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>452 s</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2. Observed infra-red spectrum and assignments for $\text{CaHAsO}_4\cdot\text{H}_2\text{O}$, $\text{CaDAsO}_4\cdot\text{D}_2\text{O}$. w = weak, m = medium, s = strong, b = broad, v = very, sh = shoulder.

15 S. R. Halford, J. chem. Physics 14, 8 [1946].
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belongs to \( v_7' \) and \( v_7'' \). The components of the
doubly degenerate antisymmetric O—As—O angle
mode \( v_8 \) are not observed as they are expected to
fall beyond the range studied presently. In dicalcium
phosphate dihydrate (brushite) these com-
ponents were observed at 252 and 238 cm\(^{-1}\) by
Berry et al.\(^3\); and were not reported by Petrov
et al.\(^5\) who studied the region only down to 300
cm\(^{-1}\). Little significant changes in frequency were
noted on deuteration for any of these HAsO\(_4\)\(^2-\)
fundamentals.

In the observed spectrum the absorptions at 2915,
2300, 1097 and 1025 cm\(^{-1}\) are associated with the
HAsO\(_4\)\(^2-\) hydroxyl groups, since they show sensitivity
to deuterium substitution. Out of these the bands at 2915 and 2300 cm\(^{-1}\) are assigned on
\( \nu_\text{oH}(\text{HAsO}_4) \) modes, and those at 1097 and 1025
\( \nu_\text{oH}(\text{HAsO}_4) \) are due to \( \delta_\text{oH}(\text{HAsO}_4) \) vibrations. Blinc and Hadzi\(^1\) have reported the bands at \( \sim 2700 \)
and \( \sim 2350 \) cm\(^{-1}\) for KH\(_2\)AsO\(_4\) which were assigned to
hydroxyl stretching vibrations. The experimental value of 2300 cm\(^{-1}\) in the present study is close to
2350 cm\(^{-1}\), but the value at 2915 cm\(^{-1}\) appears at
comparatively higher wave number and require comments. The O—H stretching frequencies can be
evaluated from the linear hydrogen bonded O---O distances using the relationship derived by Naka-
moto et al.\(^1\). A hydrogen bond of length 2.71 Å,
as is present in Haidingerite\(^13\) would predict hy-
droxyl stretching frequency at about 2950 cm\(^{-1}\),
making the above assignment. The weak band at 2300 cm\(^{-1}\) is probably an overtone band but this is
doubtful at present. The band assignable to
\( \gamma_\text{oH}(\text{HAsO}_4) \) should lie close to 750 cm\(^{-1}\), but is
probably masked by As—O(H) skeletal stretching
vibration. As the spectrum of the deuterated sample
could not be extended beyond NaCl region no de-
finitive conclusion can be drawn about this vibration.

The vibrational frequencies assignable to stretching
modes of water molecules are found at 3395
and 3205 cm\(^{-1}\). In case of dicalcium phosphate di-
hydrate, two intense doublets were found, one with
the components around 3548 and 3490 cm\(^{-1}\) and
the other with the components around 3281 and
3163 cm\(^{-1}\). These are assigned to two non-equiva-
talent species of water. In Haidingerite these are
only type of water molecules present\(^11,14\) and hence
the assignment is quite simple. Further the broad
nature of the bands and the frequency range where
they appear, clearly suggest that the water molecules
are involved in hydrogen bonding. Both these con-
clusions are in accordance with the crystal structure.
Bands at \( \sim 1650 \) cm\(^{-1}\) are assigned as \( \delta_\text{oH} \) modes
for water molecules and \( \gamma_\text{oH} \) vibration is found at
622 cm\(^{-1}\). (Very weak broad band centred around
1640, which is not reported in the Table 2, appears
consistently in the deuterated sample. This may
probably be due to bending vibration of the
residual water left because of incomplete deutera-
tion or rehydration of the sample).

Thus only one broad band of medium intensity
at 1385 cm\(^{-1}\) remains unexplained. This band does
not have a deuterated analogue, and whether it is
sensitive to deuteration or not remains to be seen
as this region is masked by Nujol bands. However
it seems likely that it owes its origin to the allowed
combination mode \( v_6(e) + v_4(e) = \sim 890 + \sim 490 \)
\( = \sim 1380 \) cm\(^{-1}\). The strong sharp band at around
1440 cm\(^{-1}\) in deuterated sample is easily explained
as H—O—D bending mode, suggesting partial deutera-
tion.

Experimental

Synthetic Haidingerite was prepared by the method
of Iyer\(^2\). (Ca = 20.55%; As = 37.66%). (Theoretical,
Ca = 20.24%; As = 37.83%) Infra-red spectra
in the range 4000—400 cm\(^{-1}\) were recorded using
Perkin-Elmer 21 at 300 °K. Nujol mull and KBr disc
techniques were employed. For deuteration the com-
 pound was refluxed with D\(_2\)O for several hrs in a
closed chamber.

\(^{18}\) R. Blinc and R. Hadzi, Molecular Physics 1, 391 [1958].
\(^{19}\) K. Nakamoto, M. Margoshes, and R. E. Rundale, J.
Amer. chem. Soc. 77, 6480 [1955].