CHAPTER XV

INFRARED SPECTRUM OF BARIUM THIOSULPHATE

AND

ITS VIBRATIONAL ANALYSIS

ABSTRACT

The infrared spectrum of Barium thiosulphate in the region 200 - 4000 cm$^{-1}$ is reported in this paper. The spectra has been analysed assuming $C_{3v}$ point group symmetry. The molecular constants have been evaluated, using the general quadratic valence force field.

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15.1 INTRODUCTION

Newman (1) has studied some complexes of $S_2O_3^-$, in an attempt to determine whether the ion functioning as a bidentate ligand is chelate or bridging. Ni $S_2O_4\cdot4H_2O$ shows three stretching modes and is assigned as probably chelate. $(NH_4)_2M_2(S_2O_3)_2$, where $M = Ag$ or Cu shows splitting of $\gamma_{as}$ and $\gamma_s (S-O)$, which could be interpreted as belonging to chelate ligand. Since no data is available for $S_2O_3^-$ ion in Ba, our present study is aimed at a vibrational analysis of $BaS_2O_3$.

15.2 EXPERIMENTAL

The infrared spectrum has been recorded in Perkin - Elmer IR 257 double beam grating spectrophotometer. The observed frequencies are reported in Table 1.

$S_2O_3^-$ ion gives rise to six fundamental vibrations, as is to be expected for a molecule of five atoms belonging to $C_{3v}$ symmetry. The assignment of the fundamental frequencies is made by analogy with those reported for $Na_2S_2O_3$. Siebert (2) has reported the Raman spectrum of thiosulphate ion. The frequencies reported by him (all in cm$^{-1}$) are
446 (ν₁, S-S stretching), 995 (ν₂, S-O symmetric stretching), 669 (ν₃, bending), 1123 (ν₄, S-O asymmetric stretching), 541 (ν₅, bending) and 335 (ν₆, bending). Our assignment of fundamental frequencies in cm⁻¹ are 409 (ν₁), 991 (ν₂), 631 (ν₃), 1128 (ν₄), 541 (ν₅) and 350 (ν₆). The S-O and S-S bond stretching frequencies and the bending frequency assignment is further supported by the earlier assignments made in S0₂⁻ ion (3) and S0₃ molecule (4). The fundamental frequencies account for the overtones and combination bands.

15.3 THEORETICAL CONSIDERATIONS

A normal coordinate analysis of Barium thiosulphate has been carried out following Wilson's F.G. matrix method (5), on the basis of C₃ᵥ point group using a general quadratic potential function and molecular constants. The theoretical background is briefly described.

15.3.1 Frequency distribution and symmetry coordinates:

The thiosulphate ion belonging to C₃ᵥ point group has been associated with six fundamental frequencies distributed as

\[ \Gamma = 3A₁ + 3E \]
The symmetry coordinates used in the present investigation are the same as those given in reference (6).

15.3.2 F matrix:

Using the most general quadratic potential function the F matrix elements have been obtained and they are given below.

**A_1** species:

\[
\begin{align*}
F_{11} &= f_D \\
F_{22} &= f_d + 2f_{dd} \\
F_{33} &= (3n^2d)^{-1}A \\
F_{12} &= \sqrt{3}f_{Dd} \\
F_{13} &= (nR\sqrt{3})^{-1}f_{Dg} \\
F_{23} &= (3n^2d)^{-\frac{1}{2}}B
\end{align*}
\]

**E** species:

\[
\begin{align*}
F_{44} &= f_d - f_{dd} \\
F_{55} &= 3f_d - r^{-2}A \\
F_{66} &= 2(f_\alpha - f_\alpha\alpha) \\
F_{45} &= -\sqrt{2}(3f_d + r^{-1}B)
\end{align*}
\]
\( F_{46} = \sqrt{2} (f'_{\text{d} \alpha} - f''_{\text{d} \alpha}) \)
\( F_{56} = 3 f'_{\alpha \Theta} + r^{-1} \mathbf{R} \mathbf{A} \)

where

\[ C_{\Theta} = -\sqrt{\frac{4 c^2 - 1}{3}} \]
\[ r = \sqrt{\frac{d}{D}} \]
\[ R = \sqrt{\frac{4 c^2 - 1}{c}} \]
\[ n = \sqrt{\frac{1}{6(D + R^2 d)}} \]
\[ S = \sqrt{D d} \]
\[ S_{\Theta} = 2s/\sqrt{3} \]
\[ S = \sin(\alpha/2) \]
\[ C = \cos(\alpha/2) \]
\[ t = \tan(\alpha/2) \]

D is the \( S - S \) bond length

d is the \( S - O \) bond length

\( \alpha \) is the \( O - S - O \) bond angle.

Further \( f_D, f_d, f_\Theta, f_\alpha \) are the stretching and bending force constants while \( f_{DD}, f_{dd}, f_{D\alpha} \) etc., are the interaction force constants.

15.3.3 G matrix ;

Using the \( S_k^t \) vector method (5) the G matrix elements are constructed. They are as follows.
\[ A_1 \text{ species:} \]
\[ G_{11} = \mu_X + \mu_Y \]
\[ G_{22} = 3 c_\theta^2 \mu_X + \mu_Z \]
\[ G_{33} = \frac{4 s^2 \mu_X + \mu_Z}{3n^2d} \]
\[ G_{12} = \sqrt{3} c_\theta \mu_X \]
\[ G_{13} = \frac{2 s \mu_X}{\sqrt{(3n^2d)}} \]
\[ G_{23} = \frac{2 s c_\theta \mu_X}{n\sqrt{d}} \]
\[ E \text{ species:} \]
\[ G_{44} = 2 s^2 \mu_X + \mu_Z \]
\[ G_{55} = \frac{3 (r^2 - c_\theta^2) \mu_X + 3 \mu_Y r^2 + 2 \mu_Z}{r^2} \]
\[ G_{66} = 4 s^2 t^2 \mu_X + \frac{(1 + 2c_\theta^2)}{c_\theta^2} \mu_Z \]
\[ G_{45} = -\sqrt{6} s \mu_X \frac{(r^2 - c_\theta)}{r} \]
\[ G_{46} = \sqrt{8} s^2 t \mu_X \]
\[ G_{56} = -\frac{\sqrt{3}}{7c} \left[ 2 s^2 (r^2 - c_\theta) \mu_X + c_\theta \mu_Z \right] \]
where \( \mu_X = \mu_Y = \mu_s \) and \( \mu_Z = \mu_0 \).
15.3.4 K matrix and the kinetic constants method:

Kinetic constants, the elements of kinetic energy matrix elements are obtained from G matrix elements. The symmetrized elements $K_{ij}$ (where $i, j = 1, 2, \ldots$) are related to the valence kinetic constants $k_D, k_d, k_{D\alpha}$, etc. The method of kinetic constants has been described in the earlier chapters. The essence of the method is to relate the off diagonal elements to the diagonal elements of the $F$ matrix through the constraint:

$$F_{ij} = \frac{K_{ij}}{K_{jj}} \quad (i < j; \ i, j = 1, 2, 3, \ldots)$$

The method has been successfully employed in solving the secular equation pertaining to the $3 \times 3$ vibrational problem of $A_1$ and $E$ species.

15.3.5 Compliance constants:

The constants which are invariant to the choice of coordinates are compliance constants. They are evaluated by Decius (7) method for this case.

15.3.6 Vibrational mean amplitudes:

The symmetrized mean square amplitude quantities at 298.16 K are evaluated using Cyvin's relation (8):

$$\Sigma = L \Delta \tilde{\alpha}$$
From the symmetrized vibrational mean square amplitudes, the bonded and non bonded valence mean square amplitudes are calculated using the following expressions:

\[
\begin{align*}
\sigma_D &= \Sigma_{11} \\
\sigma_d &= (\Sigma_{22} + 2\Sigma_{44})/3 \\
\sigma_\alpha &= (A R^2 + \Sigma_{66})/3 \\
\sigma_\theta &= \left\{ \frac{\Sigma_{55}}{3} + \frac{A}{3 r^2} \right\} \\
\sigma_{dd} &= \Sigma_{12}/\sqrt{3} \\
\sigma_{dd} &= (\Sigma_{22} - \Sigma_{44})/3 \\
\sigma_{\alpha\alpha} &= (\frac{A R^2}{3} - \frac{\Sigma_{66}}{6}) \\
\sigma_{\alpha\theta} &= \frac{\Sigma_{56}}{3} - \frac{AR}{3 r} \\
\sigma_{D\alpha\alpha} &= \Sigma_{13} n R \sqrt{d} \\
\sigma_{d\alpha\alpha} &= (RB + \sqrt{2}\Sigma_{46})/3 \\
\sigma_{d\alpha\alpha} &= RB (\frac{3}{3} - \frac{\Sigma_{46}}{3 \sqrt{2}}) \\
\sigma_{d\theta} &= -\left( \frac{\Sigma_{45}}{3 \sqrt{2}} + \frac{B}{3 r} \right)
\end{align*}
\]
where $A = 3 n^2 d \Sigma_{33}$

$B = \sqrt{3 n^2 d \Sigma_{23}}$

The non-bonded mean square amplitudes are given as follows.

$\sigma_p (y...Z) = \frac{1}{p} \left( a \sigma_{Dp} + b \sigma_{dp} + \varepsilon \sigma_{\nu} \right)$

$\sigma_q (z...Z) = 2 s \sigma_{dq} + c A$

where $A = 2 s \sigma'' + c \sigma\alpha$

$E = \frac{1}{p} \left( a \sigma_{D\theta} + b \sigma'' + \varepsilon \sigma_{\theta} \right)$

$\varepsilon = \sqrt{Dd}$

$s = \frac{2}{\sqrt{3}}$

$C_\theta = -\sqrt{\frac{4 \sigma^2 - 1}{3}}$

$a = (D - d C_\theta)$

$b = (d - D C_\theta)$

$p = \sqrt{(D^2 + d^2 - 2 Dd C_\theta)}$

$\sigma_{Dp} = \left( a \sigma_D + b \sigma_{Dd} + \varepsilon \sigma_{\nu} \sigma_{D\nu} \right)/p$

$\sigma_{D\theta} = -D \varepsilon \sigma_{D\alpha}/R \varepsilon$

$\sigma_{dq} = s (\sigma_d + \sigma_{dd}) + c \sigma''_{d\alpha}$
\[ \sigma_{d\phi} = (a \sigma_{Dd} + b \sigma_d + \varepsilon \varepsilon_{\alpha} \sigma_{d\varepsilon})/\rho \]

\[ \sigma''_{d\theta} = -D (\sigma''_{d\alpha} + 2 \sigma_{d\alpha}) - 2 \sigma_{d\phi} \]

Hence the mean amplitudes \( l_p, l_d, l_\alpha \) and \( l_\varepsilon \) are evaluated.

15.3.7 Coriolis coupling coefficients:

These vibration - rotation interaction constants arise from the following couplings.

i) First order: \( E x E \) with respect to the z axis.

ii) Second order: \( A_1 x E \) and \( E x E \) with respect to x axis and y axis.

The Coriolis matrix elements are calculated from the vector method of Meal and Polo (9) and they are listed below:

\( E x E (C^x) \)

\[ C_{45} = \frac{\mu_z}{r^2} \]

\[ C_{46} = -c_\theta \mu_z \sqrt{3/2}/c \]

\[ C_{56} = t \mu_z /r \]

\( E x E (C^z) \)

\[ C_{44} = 2 s^2 \mu_X \]

\[ C_{55} = \frac{3 (r^2 - c_\theta)^2 \mu_X + 3 r^2 \mu_Y}{r^2} \]
\[ c_{66} = 4 s^2 t^2 \mu_x - R^2 \mu_z \]
\[ c_{45} = -\frac{\sqrt{6}}{r} s (r^2 - c_0) \mu_x \]
\[ c_{46} = \frac{\sqrt{2}}{r} (2 s^2 \mu_x + \mu_z) \]
\[ c_{56} = -\frac{\sqrt{3}}{r} \left[ 2 s^2 (r^2 - c_0) \mu_x - \frac{c_0 R Z}{r} \right] \]
\[ A_1 \times B \] (C and C)
\[ c_{14} = \sqrt{2} s \mu_x \]
\[ c_{15} = -\sqrt{3} \left[ \frac{(r^2 - c_0)}{r} \mu_x + r \mu_y \right] \]
\[ c_{16} = 2 s t \mu_x \]
\[ c_{24} = \sqrt{6} s c_0 \mu_x \]
\[ c_{25} = -3 c_0 (r^2 - c_0) \mu_x + \frac{\mu_z}{r} \]
\[ c_{26} = \frac{\sqrt{2}}{r} c_{24} \]
\[ c_{34} = 4 s^2 \mu_x + \frac{\mu_z}{\sqrt{6} n^2 d} \]
\[ c_{35} = -2 s (r^2 - c_0) \mu_x \]
\[ c_{36} = \frac{\sqrt{2}}{r} c_{34} \]

where \( X \rightarrow S, \ Y \rightarrow S \) and \( Z \rightarrow 0 \).
From the $C$ elements, the Coriolis coupling coefficients $\zeta^\alpha$ are evaluated from the relation

$$\zeta^\alpha = L^{-1} C^\alpha (L^{-1})^T,$$

where $L$ is the normal coordinate transformation matrix.

15.3.8 Centrifugal distortion constants:

Using Cyvin's reformulated theory (40), the centrifugal distortion constants have been evaluated.
The expressions used are

$$t = \tilde{J} P^{-1} J,$$

where $J = K T_S$

The non vanishing $T_S$ matrix elements are given below.

$$T_{S1,xx} = T_{S1,yy} = 2 D,$$

$$T_{S2,xx} = T_{S2,yy} = 2 d (1 + 2 \alpha^2)/\sqrt{3},$$

$$T_{S2,zz} = 8 d s^2/\sqrt{3},$$

$$T_{S3,xx} = T_{S3,yy} = 2 \sqrt{d} c \phi s/\sqrt{3 n^2},$$

$$T_{S3,zz} = -4 \sqrt{d} s c \phi/\sqrt{3 n^2}.$$
Using the moments of inertia, the \( \tau \) elements are calculated and the centrifugal distortion constants \( D_j, D_k \) and \( D_{jk} \) are given in terms of \( \tau_{\alpha\beta\gamma\delta} \) elements.

\[
\begin{align*}
T_{S4a,xx} &= -4 d^2 s^2 / \sqrt{6} \\
T_{S4a,yy} &= 4 d^2 s^2 / \sqrt{6} \\
T_{S4a,zx} &= -\sqrt{8} d s c_\theta \\
T_{S5a,xx} &= -2 e s c_\theta \\
T_{S5a,yy} &= 2 e s c_\theta \\
T_{S5a,zx} &= 8 e s^2 / \sqrt{3} \\
T_{S6a,xx} &= 2 dt (1 + 2 c^2) / \sqrt{3} \\
T_{S6a,yy} &= -2 dt (1 + 2 c^2) / \sqrt{3} \\
T_{S6a,zx} &= -4 d s t c_\theta \\
T_{S4b,xy} &= 4 d^2 s^2 / \sqrt{6} \\
T_{S4b,yz} &= -\sqrt{8} d s c_\theta \\
T_{S5b,xy} &= 2 e s c_\theta \\
T_{S5b,yz} &= 8 e s^2 / \sqrt{3} \\
T_{S6b,xy} &= -2 dt (1 + 2 c^2) / \sqrt{3} \\
T_{S6b,yz} &= -4 d s t c_\theta
\end{align*}
\]
\[
\begin{align*}
D_J &= -\frac{\tau_{xxx}}{4} \\
D_{JK} &= -2D_J - \left( \frac{\tau_{xxzz} + 2\tau_{zzzx}}{2} \right) \\
D_K &= -D_J - D_{JK} - \frac{\tau_{zzzz}}{4}
\end{align*}
\]

For this type of axially symmetric molecules, \(R_5, R_6\) and \(6_J\) are zero.

15.4 RESULTS AND DISCUSSION

The kinetic constants, force constants, the compliance constants and the mean square amplitudes are given in Table 2. The major stretching force constants \(f_{S-O}\) and \(f_{S-S}\) are in the expected range. The present \(S-O\) stretching force constant compares reasonably with \(S-O\) stretching force constant \(7.934 \times 10^2\) N/m in \(S\text{O}^3^-\) ion (11). It is important to note that \(S-S\) bond is weak in thiosulphate which is reflected by a lower value of \(f_D(S-S)\) value in certain other molecules. As expected the interaction force constants \(f_{\alpha\alpha}, f'_{\alpha\alpha}, f'_{\alpha\alpha}, f'_{\alpha\Theta}\) and \(f'_{\alpha\Theta}\) are negative. The mean amplitudes of vibration \(l_{S-S}\) and \(l_{S-O}\) assume values characteristic of the bonds. The present value of \(l_{S-O}\) is \(3.8397 \times 10^{-2}\) \(\text{Å}\) which compares well with the literature values - \(3.617 \times 10^{-2}\) \(\text{Å}\) (12) and \(3.84 \times 10^{-2}\) \(\text{Å}\) (11).
The Coriolis coupling coefficients and the centrifugal distortion constants are presented in Table 3.

The zeta values shown in Table 3 obey the linear and quadratic sum rules by Boyd and Longuet-Higgins (13) and Oka (14) respectively.

1. \( \zeta_{44} + \zeta_{55} + \zeta_{66} = \frac{m}{2} \).

2. \( \zeta_{14}^2 + \zeta_{15}^2 + \zeta_{16}^2 + \zeta_{24}^2 + \zeta_{25}^2 + \zeta_{26}^2 + \zeta_{34}^2 + \zeta_{35}^2 + \zeta_{36}^2 = \frac{3\alpha}{2} + \frac{m}{4} \).

3. \( \zeta_{45}^2 + \zeta_{46}^2 + \zeta_{56}^2 = \frac{1}{2} - \frac{m}{4} \).

4. \( \zeta_{44}^2 + \zeta_{55}^2 + \zeta_{66}^2 + 2 \left[ (\zeta_{45}^2 + (\zeta_{46}^2 + (\zeta_{56}^2)^2) \right] = 2 + \frac{m^2}{4} \).

where \( m = \frac{I_z}{I_x} \).

The high values of \( \zeta_{34} \), \( \zeta_{36} \) and \( \zeta_{46} \) suggest the strong couplings between the species concerned. The centrifugal distortion constants have reasonable values with \( D_{JK} \) as negative as expected.
15.5 CONCLUSION

A complete vibrational analysis of thiosulphate ion using the vibrational frequencies obtained from the infrared spectrum is available in the present work on the basis of $C_{3v}$ symmetry. It may be added that the results obtained are in great support of the validity of the assignment of frequencies.

* * *
**TABLE - 1**

Infrared frequencies of Barium thiosulphate

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>(v_6) (Bending)</td>
<td>830</td>
<td>(2v_1)</td>
</tr>
<tr>
<td>400</td>
<td>(2v_6 - v_1)</td>
<td>991</td>
<td>(v_2) (S-O sym. strot)</td>
</tr>
<tr>
<td>409</td>
<td>(v_1) (S-S stretch)</td>
<td>1030</td>
<td>(2v_1 - v_3)</td>
</tr>
<tr>
<td>470</td>
<td>(2v_1 - v_6)</td>
<td>1085</td>
<td>(2v_5)</td>
</tr>
<tr>
<td>541</td>
<td>(v_5) (Bending)</td>
<td>1128</td>
<td>(v_4) (S-O asym. strot)</td>
</tr>
<tr>
<td>560</td>
<td>(v_2 - v_1)</td>
<td>1370</td>
<td>(v_1 + v_2)</td>
</tr>
<tr>
<td>651</td>
<td>(v_3) (Bending)</td>
<td>1410</td>
<td>(2v_1 + v_3)</td>
</tr>
<tr>
<td>720</td>
<td>(2v_6)</td>
<td>1680</td>
<td>(v_4 + v_5)</td>
</tr>
</tbody>
</table>
TABLE - 2
Kinetic constants ($k$), force constants ($f$), compliance constants ($n$), mean square amplitudes ($\sigma$) and the mean amplitudes ($l$) at 298.16 K of thiosulphate ion.

<table>
<thead>
<tr>
<th>Description</th>
<th>$k$ (10^{-26} \text{kg})</th>
<th>$f$ (10^2 \text{N/m})</th>
<th>$n$ (10^{-2} \text{m/N})</th>
<th>$\sigma$ (10^{-3} \text{Å}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>3.7921</td>
<td>2.2508</td>
<td>0.4224</td>
<td>3.1396</td>
</tr>
<tr>
<td>d</td>
<td>2.2401</td>
<td>7.7530</td>
<td>0.1305</td>
<td>1.4743</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.1555</td>
<td>0.1155</td>
<td>2.0074</td>
<td>11.5761</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0.1969</td>
<td>0.2587</td>
<td>0.7893</td>
<td>6.7795</td>
</tr>
<tr>
<td>Dd</td>
<td>0.2529</td>
<td>0.1501</td>
<td>-0.0129</td>
<td>-0.0804</td>
</tr>
<tr>
<td>dd</td>
<td>0.1446</td>
<td>0.1948</td>
<td>-0.0089</td>
<td>-0.0990</td>
</tr>
<tr>
<td>$\alpha \alpha$</td>
<td>0.0460</td>
<td>0.0280</td>
<td>0.8942</td>
<td>3.3578</td>
</tr>
<tr>
<td>$\alpha \theta$</td>
<td>0.0208</td>
<td>0.0687</td>
<td>0.1438</td>
<td>2.4495</td>
</tr>
<tr>
<td>D$x$</td>
<td>-0.1405</td>
<td>-0.0334</td>
<td>0.0432</td>
<td>1.3838</td>
</tr>
<tr>
<td>d$\alpha$</td>
<td>-0.1229</td>
<td>-0.0003</td>
<td>0.0430</td>
<td>1.3498</td>
</tr>
<tr>
<td>d$\alpha$</td>
<td>-0.0966</td>
<td>0.0951</td>
<td>-0.0357</td>
<td>0.4634</td>
</tr>
<tr>
<td>d$\theta$</td>
<td>0.1109</td>
<td>0.1636</td>
<td>-0.0352</td>
<td>0.7031</td>
</tr>
</tbody>
</table>

Mean amplitudes $l$ (10^{-2} \text{Å})

| Bonded | $l_D$ $\langle X - Y \rangle$ | 5.6032 | $l_d$ $\langle X - Z \rangle$ | 3.8397 |
| Non bonded | $l_p$ $\langle Y...Z \rangle$ | 1.6164 | $l_q$ $\langle Z...Z \rangle$ | 8.0706 |
TABLE - 3

Coriolis coupling constants
and
centrifugal distortion constants

\[ A_1 \times E(\zeta^x \text{ or } \zeta^y) \]

\begin{tabular}{ccc}
\( \zeta_{14} \) & \( \zeta_{15} \) & \( \zeta_{16} \) \\
\( \zeta_{24} \) & \( \zeta_{25} \) & \( \zeta_{26} \) \\
\( \zeta_{34} \) & \( \zeta_{35} \) & \( \zeta_{36} \) \\
0.3913 & -0.3552 & -0.4766 \\
-0.2899 & 0.6605 & -0.2405 \\
0.6864 & 0.3062 & 0.7001 \\
\end{tabular}

\[ E \times E(\zeta^z) \]

\begin{tabular}{ccc}
\( \zeta_{44} \) & \( \zeta_{45} \) & \( \zeta_{46} \) \\
\( \zeta_{55} \) & \( \zeta_{56} \) & \( \zeta_{56} \) \\
0.4164 & -0.2409 & 0.2931 \\
0.3122 & 0.8384 & 0.2072 \\
-0.4993 & -0.0638 & 0.5065 \\
\end{tabular}

Centrifugal distortion constants (KHz)

\[ D_J \quad D_{JK} \quad D_K \]

\begin{tabular}{ccc}
0.4186 & -0.2412 & 0.6976 \\
\end{tabular}
REFERENCES

8. S.J. Cyvin, Molecular vibrations and mean square amplitudes, (Elsevier Amsterdam), (1968).

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