Normal Coordinate Analysis and Mean Amplitudes of Vibration of Halate Ions
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A normal coordinate analysis of halate ions, viz. $\text{ClO}_3^-$, $\text{BrO}_3^-$, $\text{Br}^{18}\text{O}_3^-$ and $\text{IO}_3^-$ has been carried out using a general valence force field and Wilson's $F-G$ matrix approach. Mean amplitudes of vibration for bonded halogen-oxygen and non-bonded oxygen-oxygen distances have been reported using Cyvin's method and Müller's $L$-matrix formalism. Effects of isotopic substitution and isotope frequency shifts are also examined.

Introduction

Normal coordinate analysis and studies of mean amplitudes of vibration of halate ions, viz. $\text{ClO}_3^-$, $\text{BrO}_3^-$ and $\text{IO}_3^-$ including their isotopic substitutions, have been very limited because of scanty experimental data on infrared and Raman spectra of halate ions. Force constant computations for the chlorate ion were carried out by Bates $^1$, Venkateswarlu and Malathy Devi $^2$ and Hollenberg and Dows $^3$ using solid state frequencies.

Force constant computations of isotopic molecules and ions are helpful in understanding the relative role of apical and terminal atom substitution. An example for the two categories is provided by the recent vibrational analysis of halate ions by Gardiner et al. $^4$. In their analysis, the isotopic species of chlorate and bromate ions provide at least one example of each category — $^{37}\text{ClO}_3^-$ and $^{35}\text{ClO}_3^-$ belong to the former category while $\text{Br}^{18}\text{O}_3^-$ and $\text{Br}^{18}\text{O}_3^-$ to that of latter. The effect of these isotopic substitutions can be examined in two different symmetry species each of which contains three different independent force constants. Similarly, it is interesting to observe the effect of these substitutions on the mean amplitude quantities. A study of isotope frequency shifts is also important for the ions in question from the force field point of view.

Vibrational and Structural Data

The infrared and Raman spectra of various metal chlorates were recorded in solid state by Rocchiccioli $^5$, Hollenberg and Dows $^6$, Sterzel and Schnee $^6$ and Bates $^1$. These ions were also studied in melts by Wilmshurst $^7$ and by James and Leong $^8$. Similar studies for $\text{KClO}_3$ and $\text{NaClO}_3$ have very recently been reported by Quest $^9$. Infrared spectra have been reported by Rocchiccioli $^{10}$ and Campbell and Turner $^{11}$ for the bromate ion in polycrystalline metal salts. The infrared and Raman spectra of metal iodates were reported by Descent and Waddington $^{12}$, Rocchiccioli $^{16}$ and Sherwood and Turner $^{13}$ in solids and by Shen et al. $^{14}$ in aqueous solution.

Ideally, fundamental frequencies of free gaseous ions should be used in force constant or mean amplitude calculations. However, in the absence of such information, frequencies obtained from measurements in solution provide a better approximation as compared to solids. In the present work, aqueous solution spectra recently reported by Gardiner et al. $^4$ have been utilised. The structures of all the halate ions of group VII B are established to possess pyramidal structure as has been shown by Ramdas $^{15}$, Wykoff $^{16}$ and Keve et alias $^{17}$. The relevant selection rules for point group $C_{3v}$ yield its vibrational representation $^{18}$ — $I = 1 + 2A_1 + 2E'$. All the transitions are allowed both in Raman and infrared (Table 1).

Table 1. Vibrational frequencies (in cm$^{-1}$) for halate ions.

<table>
<thead>
<tr>
<th>Ions</th>
<th>$r_1(A_1)$</th>
<th>$r_2(A_1)$</th>
<th>$r_3(E')$</th>
<th>$r_4(E')$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{35}\text{ClO}_3^-$</td>
<td>933</td>
<td>608</td>
<td>977</td>
<td>477</td>
</tr>
<tr>
<td>$^{37}\text{ClO}_3^-$</td>
<td>925</td>
<td>604</td>
<td>966</td>
<td>476</td>
</tr>
<tr>
<td>$\text{Br}^{18}\text{O}_3^-$</td>
<td>805</td>
<td>418</td>
<td>805</td>
<td>358</td>
</tr>
<tr>
<td>$\text{Br}^{18}\text{O}_3^-$</td>
<td>805</td>
<td>401</td>
<td>769</td>
<td>358</td>
</tr>
<tr>
<td>$\text{IO}_3^-$</td>
<td>805</td>
<td>358</td>
<td>775</td>
<td>329</td>
</tr>
</tbody>
</table>

Structural parameters —

- $\text{Cl} - \text{O} = 1.447$ Å, $\text{O} - \text{Cl} - \text{O} = 107.1^\circ$ (Ref. 15)
- $\text{Br} - \text{O} = 1.68$ Å, $\text{O} - \text{Br} - \text{O} = 108.7^\circ$ (Ref. 16)
- $\text{I} - \text{O} = 1.802$ Å, $\text{O} - \text{I} - \text{O} = 104.5^\circ$ (Ref. 17)
Evaluation of Force Constants

Wilson’s F-G matrix method was used to carry out the normal coordinate analysis. The kinetic energy matrix was computed using Wilson’s S, vector method. The elements of the F-matrix related to the various valence force constants in each symmetry species can be written as
\[ F_{ij} = r_i f_{rr} + f_{rr}^* \]
where \( f_r \) and \( f_a \) are the bond stretching and angle bending force constants respectively while \( f_{rr} \) and \( f_{aa} \) are their mutual interactions, \( f_{rr}^* \) denotes the interaction between \( Ar \) and \( Aa \) having a common bond and \( f_{ra} \) denotes the interaction between \( Ar \) and \( Aa \) having no common bond; \( \Delta \) represents changes in bond lengths or bond angles.

Evaluation of Mean Amplitude Quantities

The elements of symmetrised mean square amplitudes were obtained from Cyvin’s secular equation
\[ \sum G^{-1} - \Delta_i E = 0 \]
where \( G \) represents the inverse of the kinetic energy matrix, \( E \) is the unitary matrix and \( \Delta_i = (\hbar/\beta)^2 v_i c \coth(\hbar v_i c/2kT) \); \( \hbar, c, k \) have their usual meaning. Based on Cyvin’s principle, Sundaram has extended the method for the evaluation of mean amplitude quantities for \( XY_3 \) pyramidal molecules. The same procedure has been used. In a regular pyramidal \( XY_3 \) type molecule, there are two types of distances, viz. bonded \( X-Y \) and non-bonded \( Y \ldots Y \). Here we report the corresponding mean amplitudes of vibration for bonded \( U(X-Y) \) and non-bonded \( U(Y \ldots Y) \) distances corresponding to each pair of atoms along with that arising due to angle bending of two adjacent bonds. Other mean amplitude quantities arising due to the interactions of bond stretch and angle bending of various coordinates have not been reported.

Solution of the \((2 \times 2)\) Eigen Value Problem

For a unique solution of the \( n = 2 \) secular determinant in the vibrational eigen value problem an additional constraint apart from vibrational frequencies is needed. In the present case the same situation exists since both the species \( A_1 \) and \( E' \) are of second order. Several investigators have proposed different constraints to overcome this difficulty but the L-matrix approximation of Müller has been found to be most satisfactory in calculating a reasonable set of force constants as well as mean amplitudes where the coupling of masses is small. Briefly, for \((2 \times 2)\) secular equations considering \( \Lambda_{ij} = 0; \ j \geq i \), the elements of the \( F \) and \( \Sigma \) matrices can be obtained by the relations:
\[ F_{11} = \frac{\dot{\lambda}_1 - \dot{\lambda}_2}{G_{11} \det(G)}, \quad F_{12} = -\frac{G_{12} \dot{\lambda}_2}{\det(G)} \]
\[ F_{22} = \frac{G_{11} \dot{\lambda}_2}{\det(G)} \]
where \( \dot{\lambda}_1, \dot{\lambda}_2 \) are the eigen values for the isotopic and the normal molecule respectively, \( L_0^{-1} \) stands for the corresponding normal coordinate transformation coefficients and \( \Delta G \) is the change in the G-matrix which can be determined using the relation in matrix form
\[ G = G^0 + \Delta G \]

Calculation of Isotope Shifts

Wilson, Decius and Cross have developed a direct relation between isotope shift and L-matrix elements using perturbation theory. Accordingly
\[ \dot{\lambda}_k = \dot{\lambda}_k^0 + \dot{\lambda}_k^0 \sum (L_0^{-1})_{kl} + 2(L_0^{-1})_{kk} \Delta G_{kl} \]
where \( \dot{\lambda}_k \) and \( \dot{\lambda}_k^0 \) are the eigen values for the isotopic and the normal molecule respectively, \( L_0^{-1} \) stands for the corresponding normal coordinate transformation coefficients and \( \Delta G \) is the change in the G-matrix which can be determined using the relation in matrix form
\[ G = G^0 + \Delta G \]
For second order eigen value problems the Eq. (3) can be written as
\[ \Delta \dot{\lambda}_k/\dot{\lambda}_k^0 = (L_0^{-1})_{kk} \Delta G_{11} + 2(L_0^{-1})_{kk} \Delta G_{12} + (L_0^{-1})_{kk} \Delta G_{22} \]
It is known that in cases where \( n = 2 \) and where the coupling of masses is small \( (m_i > m_j) \), \( \Delta G = 0 \) is a good approximation. Thus, Eq. (3) can be further simplified under this approximation to yield
\[ \Delta \dot{\lambda}_1/\dot{\lambda}_1^0 \text{ and hence} \]
\[ \Delta \dot{\lambda}_1/\dot{\lambda}_1^0 = \Delta G_{11}/\dot{\lambda}_1^0 \]
\[ \Delta \dot{\lambda}_2/\dot{\lambda}_2^0 = (1/|G|) [(G_{12}^2/\dot{\lambda}_1^0) (\Delta G_{11}) - 2 G_{12}^0 \Delta G_{12} + G_{11}^0 \Delta G_{22}] \]
(7)
Using the above formulation the isotope shifts for the (\(^{35}\text{Cl}O_3^- - ^{37}\text{Cl}O_3^-\)) and (\(^{16}\text{Br}O_3^- - ^{18}\text{Br}O_3^-\)) systems have been examined.

### Results and Discussion

The G.V.F.F. constants calculated with the help of L-matrix approximation are presented in Table 2. The symmetrised force constants which are obtained with the help of the \(L_{12} = 0\) approximation of Müller have been verified by P.E.D. method. Evaluating the same constants with \(L_{21} = 0\), it is observed that the off-diagonal elements \(F_{ij} (i \neq j)\) are numerically much higher than those of \(L_{12} = 0\) or P.E.D., though the other elements are comparable. The stretching force constants \(f_r\) for \(\text{ClO}_3^-\), \(\text{BrO}_3^-\) and \(\text{IO}_3^-\) are 6.30, 5.16 and 5.24 mdyn/Å respectively, indicating that the force constants for (Br—O) and (I—O) bonds are comparable.

Chantry et al.\(^{28}\), on the basis of their Raman intensity measurements observed that the bond orders in isoelectronic and isostructural ions were in the order \(\text{ClO}_3^- > \text{BrO}_3^- \approx \text{IO}_3^-\). Lippincott and Nagarajan\(^{29}\) have reported bond orders of 0.91, 0.78 and 1.00 for \(\text{ClO}_3^-\), \(\text{BrO}_3^-\) and \(\text{IO}_3^-\), respectively, on the basis of their Raman polarizability studies. Although the calculation of the bond orders from force constants is tedious, it may be safely concluded that in \(\text{ClO}_3^-\), it should be larger in magnitude than in \(\text{BrO}_3^-\) or \(\text{IO}_3^-\) and that they should be nearly identical for \(\text{BrO}_3^-\) and \(\text{IO}_3^-\). It is likely that \(\sigma\) and \(\pi\) bonding contributions may influence the molecular constants of the halate ions. Due to poorer overlap of 4d orbitals of bromine and 5d or 4f orbitals of iodine with a 2p orbital of oxygen, the bond orders are nearly equal for \(\text{BrO}_3^-\) and \(\text{IO}_3^-\) as emphasised by Chantry and Plane, but the force constants and mean amplitude values show different behaviour due to the presence of 4f orbitals in iodine.

In general, as shown in Table 4, the root mean square amplitude quantity \((\sigma_d)^{1/2}\) due to the non-bonded oxygen pair is greater than that of the bonded halogen-oxygen pair \((\sigma_r)^{1/2}\). The quantity due to bending \((\sigma_s)^{1/2}\) is, in general, found very much greater than those for the halogen oxygen...
pairs, whether bonded or non-bonded. Actually, this situation is reversed in the case of the corresponding force constants. It may be mentioned here that the calculated mean amplitudes in the present case do not depend on the bond distance among the structural parameters but mainly on the valence bond angle. The bond angles for ClO$_3^-$ and BrO$_3^-$ are comparable and hence the stretching mean amplitudes are nearly equal in the two cases.

In comparing the mean amplitudes of vibration of ClO$_3^-$, BrO$_3^-$ and IO$_3^-$ with those of ClO$_4^-$, BrO$_4^-$ and IO$_4^-$, we observe a uniform decrease in mean amplitude quantities for bonded as well as non-bonded distances with a corresponding increase in force constants. Further, the obtained values of mean amplitudes of vibration at room temperature for the bonded atom pairs Cl-O, Br-O and I-O are approximately the same, i.e. about 0.039, and for the non-bonded atom pair O-O the value is approximately 0.06 Å. In all the halate ions the peripheral oxygen atoms has a fixed electronegativity value while the electronegativity of the central atom decreases (Cl>Br>I) as the mass of the central atom increases. This may be one of the possibilities that the influence of atomic weights of central atoms on mean amplitudes be significantly governed by electronegativities of the central atoms. However, it is more reasonable to say that mean amplitudes for halogen-oxygen (bonded) and oxygen-oxygen (non-bonded) distances are highly characteristic. This means that the interaction force constants $F_{ij}$ ($A_j$) and $F_{34}$ ($E'$), governed by valence the force constants $f_{ij}$ and $f_{ij}'$, are more predominant than the masses of the constituent atoms. These parameters adjust in such a way that in chloro, bromo and iodo-species, the mean amplitudes are identical.

Using the perturbation theory and Müller's formalism for the calculation of isotope frequency shifts and making use of the relations (5) and (7) under the approximation $L_{ii} = 0 (j > i)$, the isotope frequency shifts (in cm$^{-1}$) for the $A_1$ and $E'$ symmetry species of BrO$_3^-$ were found to be

$$
\Delta v_1(A_1) = 30.0 \\
\Delta v_2(A_1) = 16.6 \\
\Delta v_3(E') = 36.2 \\
\Delta v_4(E') = 22.2
$$

Since the force field used here is approximate and no exact force field data for these systems are available, the agreement between the calculated and observed (values in parentheses) frequency shifts

<table>
<thead>
<tr>
<th>Ions</th>
<th>Distance</th>
<th>Quantity</th>
<th>$T = 0$ K</th>
<th>$T = 298$ K</th>
<th>$T = 500$ K</th>
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<tbody>
<tr>
<td>$^{35}$ClO$_3^-$</td>
<td>X...Y bonded</td>
<td>$(\sigma)_1$</td>
<td>0.039</td>
<td>0.040</td>
<td>0.042</td>
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<td></td>
<td>non-bonded</td>
<td>$(\sigma)_d$</td>
<td>0.0058</td>
<td>0.066</td>
<td>0.068</td>
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<td>$^{37}$ClO$_3^-$</td>
<td>X...Y bonded</td>
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<td>0.089</td>
<td>0.097</td>
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<tr>
<td></td>
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<td>$(\sigma)_d$</td>
<td>0.054</td>
<td>0.057</td>
<td>0.068</td>
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<tr>
<td>Br$^{18}$O$_3^-$</td>
<td>X...Y bonded</td>
<td>$(\sigma)_1$</td>
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<tr>
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<td>0.039</td>
<td>0.042</td>
</tr>
<tr>
<td>IO$_3^-$</td>
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<td>0.070</td>
<td>0.082</td>
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<td></td>
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<td>$(\sigma)_d$</td>
<td>0.053</td>
<td>0.065</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Table 4. Mean amplitudes of vibration (in Å) for bonded halogen-oxygen and non-bonded oxygen-oxygen distances of halate ions.

* Values in parentheses are mean amplitudes values of the corresponding distances in perhalate ions (Ref. 30, 31).
is limited but the magnitude of these values essentially shows the basic soundness of the calculations. The method is less valid for ClO₅⁻ (larger mass coupling).

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