LETTERS TO THE EDITOR

TABLE I. Depolarization cross sections and mean reorientation angles averaged over all rotational states for \( I^s \)-M collisions.

<table>
<thead>
<tr>
<th>( M )</th>
<th>( \Delta \sigma' = 0 )</th>
<th>( \Delta \sigma' = 0 )</th>
<th>( \Delta \sigma' = +1 )</th>
<th>( \Delta \sigma' = -1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>2.9</td>
<td>5.3</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>( \text{He} )</td>
<td>3.7</td>
<td>7.0</td>
<td>12.9</td>
<td>9.4</td>
</tr>
<tr>
<td>( \text{Ne} )</td>
<td>22.7</td>
<td>22.8</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

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7 S. Mrozowski, Bull. Intern. Cracow 346 (1933); 295 (1937).

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Force Constants of the Metaborate Ion in Alkali Halides*

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Previous infrared studies\(^1\) of the metaborate ion as a substitutional impurity in alkali halide lattices have yielded generally concordant values for the bending and antisymmetric stretching fundamental frequencies as well as the strongest combination mode which is the Fermi doublet \( v_1 + v_3 \) and \( 2v_2 + v_3 \). Isotopic species reported include \(^{10}\text{B}^{16}\text{O}_2^-\), \(^{11}\text{B}^{16}\text{O}_2^-\), and \(^{10}\text{B}^{18}\text{O}_2^-\).\(^{11}\)

The cyanate ion\(^\text{a}\) in similar hosts exhibits a splitting of the \( v_1 + v_3 \) and \( 2v_2 + v_3 \) doublet which is almost identical with the splitting of \( v_1 \) and \( v_2 \) which are observable for the unsymmetric linear triatomic molecule, but forbidden in the infrared spectrum of metaborate. In cyanate, the sums of the observed values of \( v_2 \) and either of the observed values of \( v_1 \) and \( v_2 \) are about 20 cm\(^{-1}\) greater than the respective members of the \( v_1 + v_3 \) and \( 2v_2 + v_3 \) doublet. By transferring this anharmonicity correction from cyanate to metaborate we can predict the positions of the infrared inactive \( v_1 \), \( 2v_2 \) frequencies as follows (KBr host):

\begin{align*}
\text{(i) } & ^{10}\text{B}^{16}\text{O}_2^-: \\
& (2v_2 + v_3) - v_1 + 20 = 3251 - 2029 + 20 = 1242 \text{ cm}^{-1}, \\
& (v_1 + v_3) - v_2 + 20 = 3095 - 2029 + 20 = 1086 \text{ cm}^{-1}, \\
\text{(ii) } & ^{11}\text{B}^{16}\text{O}_2^-: \\
& (2v_2 + v_3) - v_1 + 20 = 3145 - 1958 + 20 = 1207 \text{ cm}^{-1}, \\
& (v_1 + v_3) - v_2 + 20 = 3022 - 1958 + 20 = 1084 \text{ cm}^{-1}.
\end{align*}

With the search area for these previously unknown energy levels rather narrowly circumscribed, we proceeded to examine the \( v_2 \) region of the spectrum of single crystals of KBr and KCl doped with metaborate in order to find the difference frequencies (hot bands) for the transitions \( 01'0 \rightarrow 10'0 \) and \( 01'0 \rightarrow 02'0 \) which...
The intensity ratio for this Fermi doublet is approximately 2.5 to 1 for $^{11}$BO$_2^-$ and 3.3 to 1 for $^{13}$BO$_2^-$.

Subsequent to the infrared studies which have just been described, we were able to observe several of the combination bands and which gives also the calculated positions of $\nu_1$ and $2\nu_2$ which, since they are obtained by the Ritz principle, involve no assumptions about anharmonicity; it is seen that the results found are in good agreement with the prediction based upon the transferred anharmonicity correction.

TABLE I. New transitions and energy levels of metaborate ion in alkali halide hosts ($T=305^\circ$K).

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Final state</th>
<th>KBr</th>
<th>KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$00^00$</td>
<td>$02^+1$</td>
<td>$1103.5$</td>
<td>$1135.5$</td>
</tr>
<tr>
<td>$00^00$</td>
<td>$10^01$</td>
<td>$3145$</td>
<td>$3251$</td>
</tr>
<tr>
<td>$00^00$</td>
<td>$01^00$</td>
<td>$588.6$</td>
<td>$609.5$</td>
</tr>
<tr>
<td>$01^00$</td>
<td>$10^01$</td>
<td>$613.5$</td>
<td>$631.5$</td>
</tr>
<tr>
<td>$00^00$</td>
<td>$02^01$</td>
<td>(1202.1)</td>
<td>(1241)</td>
</tr>
<tr>
<td>$00^00$</td>
<td>$10^01$</td>
<td>(1078.6)</td>
<td>(1083.5)</td>
</tr>
<tr>
<td>$\nu_1$ (unperturbed)</td>
<td></td>
<td>$1103.5$</td>
<td>$1135.5$</td>
</tr>
</tbody>
</table>

* All frequencies are observed in the infrared spectrum except those marked "*", which were observed in the Raman effect, and those enclosed in parentheses, which were calculated using the Ritz principle.

are infrared allowed and have been detected in cyanate studies. The results are summarized in Table I which includes some previously unreported data on the combination bands and which gives also the calculated positions of $\nu_1$ and $2\nu_2$ which, since they are obtained by the Ritz principle, involve no assumptions about anharmonicity; it is seen that the results found are in good agreement with the prediction based upon the transferred anharmonicity correction.

Subsequent to the infrared studies which have just been described, we were able to observe several of the crystal samples with Laser excited Raman techniques. The lines found in this way are also reported in Table I. The intensity ratio for this Fermi doublet is approximately 2.5 to 1 for $^{11}$BO$_2^-$ and 3.3 to 1 for $^{13}$BO$_2^-$, the lower frequency in each case being stronger. By neglecting the effects of anharmonicity except via the Fermi resonance, we have estimated the unperturbed value of $\nu_1$ as shown in the last line of the table. Since sufficient levels of metaborate are not yet known to correct for anharmonicity, we have calculated the force constants using the observed values of $\nu_1$ given in the table together with previously reported values for $\nu_2$. The BO stretching constant turns out to be $f_{BO} = 11.4$ mdyn/Å and the interaction constant is $f' = 2.2$ mdyn/Å (KBr host). Similar calculation of the force constants of the isoelectronic molecules CO$_2$ and NO$_2^+$ yields for $f_{BO} = 15.5$ and $d_{NO} = 17.5$ mdyn/Å. Although the spectroscopic measurements come from different phases for the isoelectronic sequence BO$_2^-$, CO$_2$, NO$_2^+$, the trend of increasing bond strength with increasing nuclear charge of the central atom is clear.

It may also be of interest to note that the value of $\nu_1 = 1104.5$ (KBr average) is found to be larger than $\nu_1 = 1070$ in the neutral BO$_2$, just as $\nu_1 = 1335$ (average of Fermi doublet) in CO$_2$ is greater than $\nu_1 = 1280$ in CO$_2^+$. Thanks are due to Dr. J. Willis of the Cary Instrument Company and to Mr. Bob Reed of Spex Industries for having demonstrated the feasibility of detecting the Raman modes.

Raman Spectroscopy, Rotational Isomerism, and the "Rotator" Phase Transition in n-Alkanes

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(Received 13 January 1972)

Many n-alkanes exhibit a first-order solid-solid phase transition a few degrees below their melting points. The earliest molecular interpretation of this phenomenon was given by Muller and later studies have tended to reinforce his view that the phase transition is associated with the onset of hindered rotation of the extended alkane chains about their long axes. Recently Pechhold and his co-workers have proposed a "kinkblock" model in which the phase transition is associated with the occurrence of rotational isomers belonging to a particular class, the so-called kink-isomers. Since the n-alkanes and their polar derivatives...