SHORT COMMUNICATIONS

SITE SPLITTING OF THE MnO₄⁻ VIBRATIONAL MODES IN A KClO₄ LATTICE

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The present study of the infrared spectrum of potassium permanganate in a solid solution of potassium perchlorate was prompted by a recent reinvestigation and interpretation of the electronic spectrum of potassium permanganate in solid potassium perchlorate solution.¹

The site symmetry of the MnO₄⁻ ion in the KClO₄ lattice is known² to be C₃. Hence, it would be expected that the triply degenerate F₂ vibrational modes of MnO₄⁻ would be split into triplets. Also, the A₁ and E modes, which are infrared inactive in Tₐ symmetry, might be expected to be observed here.

<table>
<thead>
<tr>
<th>KMnO₄ (%) w/w</th>
<th>v₁ (at c. 300 K)</th>
<th>v₂ (at c. 300 K)</th>
<th>v₃ (at c. 80 K)</th>
<th>v₄ (at c. 300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.59</td>
<td>a</td>
<td>931, 915, 909</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>a</td>
<td>932, 917, 911</td>
<td>b</td>
<td>a</td>
</tr>
<tr>
<td>2.0</td>
<td>847</td>
<td>932, 916, 909</td>
<td>935.5, 918.5, 912.5</td>
<td>394, 404</td>
</tr>
<tr>
<td>3.2</td>
<td>847</td>
<td>932, 917, 910</td>
<td>b</td>
<td>387, 394, 404</td>
</tr>
</tbody>
</table>

ₐ Not observed, probably because of insufficient concentration of KMnO₄.

b Not investigated.

Most of the above expectations have been verified (see Table 1). Both the v₃ (F₂) and v₁ (F₂) modes were found to be triplets and the v₁ (A₁) mode was detected. The v₂ (E) mode was not observed. This is not surprising in view of previous studies³⁻⁵ of the infrared spectrum of KMnO₄. In each case, it was found that the v₂ (E) mode is not observed in the infrared and is of only medium intensity in the Raman spectrum.⁶

The observed frequencies seemed to be independent of the concentration of KMnO₄ in KClO₄ over the concentration range studied.

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² Teltow, J., Z. phys. Chem. (B), 1938, 40, 400.

In the case of the $v_3 (F_2)$ triplet, the frequencies of the triplet were found to rise with a decrease in temperature, but the spacing between them remained constant.

The detailed vibrational fine structure, found by Holt and Ballhausen, in two of the four band systems they observed (particularly the one between 18000 and 23000 cm$^{-1}$), would be expected to correlate with our findings. However, their assignment of peaks found in the 18000–23000 cm$^{-1}$ band system does not bear this out. Thus a re-examination of this band system seems warranted.