

## SHORT COMMUNICATIONS

### SITE SPLITTING OF THE $\text{MnO}_4^-$ VIBRATIONAL MODES IN A $\text{KClO}_4$ 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.<sup>1</sup>

The site symmetry of the  $\text{MnO}_4^-$  ion in the  $\text{KClO}_4$  lattice is known<sup>2</sup> to be  $C_s$ . Hence, it would be expected that the triply degenerate  $F_2$  vibrational modes of  $\text{MnO}_4^-$  would be split into triplets. Also, the  $A_1$  and  $E$  modes, which are infrared inactive in  $T_d$  symmetry, might be expected to be observed here.

TABLE 1  
VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) OF  $\text{KMnO}_4$  IN A  $\text{KClO}_4$  LATTICE AT VARIOUS CONCENTRATIONS  
 $\nu$  values at 300 K are  $\pm 2 \text{ cm}^{-1}$ , at 80 K  $\pm 1 \text{ cm}^{-1}$

$\text{KMnO}_4$ (% w/w)	$\nu_1$ (at c. 300 K)	$\nu_3$ (at c. 300 K)	$\nu_3$ (at c. 80 K)	$\nu_4$ (at c. 300 K)
0.59	a	931, 915, 909	b	a
1.1	a	932, 917, 911	b	a
2.0	847	932, 916, 909	935.5, 918.5, 912.5	a, 394, 404
3.2	847	932, 917, 910	b	387, 394, 404

a Not observed, probably because of insufficient concentration of  $\text{KMnO}_4$ .

b Not investigated.

Most of the above expectations have been verified (see Table 1). Both the  $\nu_3$  ( $F_2$ ) and  $\nu_4$  ( $F_2$ ) modes were found to be triplets and the  $\nu_1$  ( $A_1$ ) mode was detected. The  $\nu_2$  ( $E$ ) mode was not observed. This is not surprising in view of previous studies<sup>3-5</sup> of the infrared spectrum of  $\text{KMnO}_4$ . In each case, it was found that the  $\nu_2$  ( $E$ ) mode is not observed in the infrared and is of only medium intensity in the Raman spectrum.<sup>6</sup>

The observed frequencies seemed to be independent of the concentration of  $\text{KMnO}_4$  in  $\text{KClO}_4$  over the concentration range studied.

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<sup>1</sup> Holt, S. L., and Ballhausen, C. J., *Theor. chim. Acta*, 1967, **7**, 313.

<sup>2</sup> Teltow, J., *Z. phys. Chem. (B)*, 1938, **40**, 400.

<sup>3</sup> Krebs, B., and Mueller, A., *J. molec. Spectrosc.*, 1967, **22**, 290.

<sup>4</sup> Pinchas, S., Samuel, D., and Petranu, E., *J. inorg. nucl. Chem.*, 1967, **29**, 335.

<sup>5</sup> Manzelli, P., and Taddei, G., *J. chem. Phys.*, 1969, **51**, 1484.

<sup>6</sup> Hendra, P. J., *Spectrochim. Acta (A)*, 1968, **24**, 125.

In the case of the  $\nu_3$  ( $F_2$ ) 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,<sup>1</sup> in two of the four band systems they observed (particularly the one between 18000 and 23000  $\text{cm}^{-1}$ ), would be expected to correlate with our findings. However, their assignment of peaks found in the 18000–23000  $\text{cm}^{-1}$  band system does not bear this out. Thus a re-examination of this band system seems warranted.