The 'Red Band' in the Spectrum of MnO_3Cl

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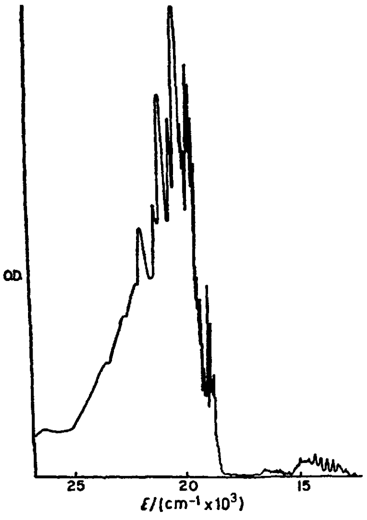
Summary The origin of the band in the red region of the absorption spectrum of $[Mn^{VII}X_4]$ species is clarified.

The assignment of the absorption spectra of various tetrahedral oxyanions has received considerable attention recently.[1] One particular problem is the origin of the maxima in 14,000—17,000 cm^{-1} region of the spectra of $[MnO_4]^-$, first reported by Teltow.[2] Based upon arguments involving the electron repulsion splitting of the $t_1^5e^1$ configuration Ballhausen[3] proposed that this band was due to both the ${}^1T_1 \leftarrow {}^1A_1$ and the ${}^3T_1$, ${}^3T_2 \leftarrow {}^1A_1$ transitions. More recently Day *et al.*,[4] Ballhausen *et al.*,[5] and Johnson *et al.*[6] have reinvestigated the absorption spectrum of $[MnO_4]^-$ in various perchlorate hosts and have assigned the 14,000 cm^{-1} band to the ${}^1T_1 \leftarrow {}^1A_1$, symmetry forbidden (in *Td*), transition. We present data which suggests that this assignment is not completely valid.

We have measured the gas-phase absorption of MnO_3Cl. The first two major regions of absorption in this spectrum are shown in the Figure. Both are consistent with what is observed for $[MnO_4]^-$ in $KClO_4$.



Figure

The MnO_3Cl molecule has C_{3v} symmetry, owing to the co-ordination of three oxygen atoms and one chlorine, and not through site-imposed symmetry or small Mn–O angular distortions. We should, therefore, expect electronic selection rules to be strongly obeyed. The symmetry-allowed transitions in C_{3v} are $E, A_1 \leftarrow A_1$ while any $A_2 \leftarrow A_1$ transition is symmetry-forbidden. Further, the correlations of state symmetries between *Td* and C_{3v} are $T_1 \rightarrow A_2 + E$, $T_2 \rightarrow A_1 + E$, and $A_1 \rightarrow A_1$. As a consequence, each ${}^1T_1$ state should give rise to one symmetry-allowed transition, ${}^1E_1 \leftarrow {}^1A_1$, which would be expected to have an intensity in the range of that observed for other spin- and symmetry-allowed transitions. Both regions of absorption below 18,000 cm^{-1} have intensities considerably below (*ca.* 1/50 for the 14,000 cm^{-1} manifold and >1/100 for the 16,000 cm^{-1} manifold) that observed for the band of $^1T_2 \leftarrow {}^1A_1$ parentage (18,000—25,000 cm^{-1}) (Figure). We therefore suggest that these data are consistent with an assignment of these maxima as arising from transitions of the type $^3X \leftarrow {}^1A_1$.

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[1] See C. A. Kosky, B. R. McGarvey, and S. L. Holt, *J. Chem. Phys.*, 1972, **56**, 5904 and references therein.

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