The Electronic Structure of $[MnO_4]^{2-}$

By C. A. KOSKY
(*Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York* 11201)
and S. L. HOLT*
(*Department of Chemistry, University of Wyoming, Laramie, Wyoming* 82070)

Summary New features in the spectrum of $[MnO_4]^{2-}$ are reported.

CONSIDERABLE interest has been generated in the past few years in obtaining the correct description of the electronic structure of various tetrahedral oxyanions.[1] The accuracy of any calculation has been generally measured by how well it agrees with the spectrum of the oxyanion in question. Early attempts to obtain consistency between experimental and theoretical results relied mainly upon measurements of the optical spectra of various $[MX_4]^{x-}$ species prepared in aqueous media. Recent experimental efforts have considerably improved the quality of data available and have led to the questioning of various of the theoretical results.[1-4] Of considerable importance to this discussion has been the observation of the $e \rightarrow t_2$ (d–d) transition in $[CrO_4]^{3-}$ at *ca.* 7000 cm^{-1} lower than previously reported.[1,5-7] In an attempt to find further evidence to support the interpretation of the experimental result obtained for $[CrO_4]^{3-}$ we have measured the low-temperature absorption spectrum of the d^1 oxyanion, $[MnO_4]^{2-}$.

Tetlow[8] reported the spectrum of $[MnO_4]^{2-}$ in K_2SO_4. Conducting his measurements at 20°K he observed four highly structured bands, the most intense one occurring in the region of *ca.* 16,000—20,000 cm^{-1}, while much weaker maxima were found centred at *ca.* 23,000, 29,000, and 35,000 cm^{-1}. Nothing was observed to lower energies. In contrast, Carrington and Symons[9] noted a weak absorption band below 16,500 cm^{-1} which they assigned to the $e \rightarrow t_2$ (*d–d*) transition. This observation was later ignored[6] in a detailed treatment of the electronic structure of $[MO_4]^{x-}$ species.

We confirm the report of Carrington and Symons.[9] We have observed an absorption maximum in the 10,000—12,000 cm^{-1} (ϵ *ca.* 80) spectral range in alkaline solutions containing $[MnO_4]^{2-}$ and have also detected this band in single crystals of $Ba(MnO_4,SO_4)$ and $K_2(MnO_4,SO_4)$ (Figure). E.s.r. measurements in single crystals of $Ba(MnO_4,SO_4)$[10] indicate that $[MnO_4]^{2-}$ is the only paramagnetic species present, while $[MnO_4]^-$ has no absorption maxima in this region. We suggest that this transition arises from $[MnO_4]^{2-}$ and in accordance with our earlier interpretation of the polarized spectrum of $[CrO_4]^{3-}$ [1] as well as the accepted value of 11,000 cm^{-1} for Δ, $[MnO_4]^{3-}$ [11,12] that it is the $e \rightarrow t_2$ (*d–d*) excitation.†

We acknowledge the support of grants from the National Science Foundation.

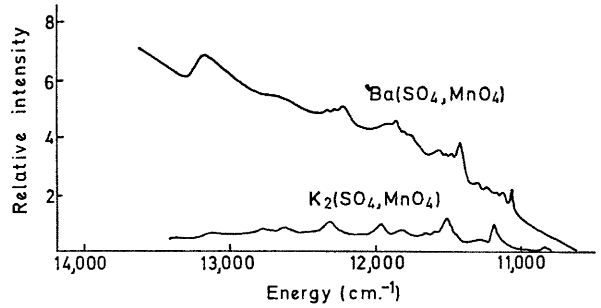

FIGURE. *The* 5°K *spectrum of* $[MnO_4]^{2-}$.

(*Received, April* 20*th*, 1970; *Com.* 559.)

---

† We have been recently informed that Day and his co-workers have also measured the low temperature spectrum of $K_2(MnO_4,SO_4)$ and have arrived at similar conclusions.

[1] See C. Simo, E. Banks, and S. L. Holt, *Inorg. Chem.*, 1970, **9**, 183, and references therein.
[2] S. L. Holt and C. J. Ballhausen, *Theor. Chim. Acta*, 1967, **7**, 313.
[3] J. C. Duinker and C. J. Ballhausen, *Theor. Chim. Acta*, 1968, **12**, 325.
[4] J. P. Dahl and H. Johansen, *Theor. Chim. Acta*, 1968, **11**, 8, 26.
[5] E. Banks, M. Greenblatt, and S. L. Holt, *J. Chem. Phys.*, 1968, **49**, 1431.
[6] A. Viste and H. B. Gray, *Inorg. Chem.*, 1964, **3**, 1113.
[7] N. Bailey and M. C. R. Symons, *J. Chem. Soc.*, 1957, 203.
[8] J. Tetlow, *Z. phys. Chem.* (*Leipzig*), (*B*), 1939, **43**, 198.
[9] A. Carrington and M. C. R. Symons, *J. Chem. Soc.*, 1960, 889.
[10] C. A. Kosky, B. R. McGarvey, and S. L. Holt, unpublished data.
[11] J. D. Kingsley, J. S. Prener, and B. Segall, *Phys. Rev.*, 1965, **137A**, 189.
[12] J. Milstein and S. L. Holt, *Inorg. Chem.*, 1969, **8**, 1021.