The Electronic and Vibrational Spectra of the MnF_6^{2-} Ion

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Summary The luminescence spectrum of solid K_2MnF_6 indicates that some of the bands in the apparently anomalous Raman spectrum reported for Cs_2MnF_6 are due to $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence.

SOLID Cs_2MnF_6 was recently reported to give an extremely intense vibrational Raman spectrum.[1] Only one band was assigned as a fundamental but a large number of combinations was observed. This anomalous effect was tentatively attributed to resonance between the 15,803 cm^{-1} He/Ne laser excitation line and $^4A_{2g} \rightarrow {}^2E_g$ electronic transition. K_2MnF_6 and other Mn^{IV} compounds[2] luminesce strongly under mercury-arc excitation and comparison of these emission spectra with the anomalous Raman spectrum of Cs_2MnF_6 suggests that at least some of the bands reported in the *Raman* spectrum are due to $^2E_g \rightarrow {}^4A_{2g}$ *phosphorescence.*

Excitation of crystalline K_2MnF_6 with 436 nm radiation at room temperature gave a rather weak emission spectrum consisting of relatively sharp (< 30 cm^{-1} half-height width, instrumentally limited) lines (Table 1). The two lines at highest energy were greatly reduced in intensity on cooling the sample to 80° and are assigned as hot bands. The remaining sharp bands are slightly less intense at 80°K than they are at room temperature. In addition, a broad, asymmetric band centred at *ca.* 14,300 cm^{-1} appears at temperatures below 140°K and, on further cooling, rapidly increases in intensity. The sharp lines may be assigned to vibronic transitions from the ^2E_g state to the $^4A_{2g}$ ground state[3] (Table 1). The *O–O* band (which is electric dipole forbidden in O_h symmetry) will acquire some electric dipole intensity due to the C_{3v} site symmetry of the Mn^{4+} ion in this compound.[4]

TABLE 1

Vibronic structure of the $^2E_g \leftrightarrow {}^4A_{2g}$ *transition in* K_2MnF_6 *at* 295°K

Absorption (cm^{-1})	Emission (cm^{-1})	Assignment[a]
	15450	$O' \rightarrow \nu_3$
15720	15720	$O' \leftrightarrow \nu_4$
15850	15850	$O' \leftrightarrow \nu_6$
16080	16080	$O' \leftrightarrow O$
16280	16280	$O \leftrightarrow \nu_6'$
16400	16400	$O \leftrightarrow \nu_4'$
16690		$O \rightarrow \nu_3'$
16850		$O \rightarrow \nu_1' + \nu_3'$

[a] Primes denote ^2E_g state.

Allen, El-Sharkarwy, and Warren[5] did not detect any bands around 16,000 cm^{-1} in the reflectance spectrum of K_2MnF_6. However, the reflectance spectra of the samples of K_2MnF_6 used in this work showed a series of very sharp, very well resolved bands in this region. The positions and intensities of these bands closely paralleled those in the phosphorescence spectrum and are readily assigned to transitions to the vibrational levels of the ^2E_g state (Table 1). The derived vibrational frequencies in the $^4A_{2g}$ state are then (labelling as in O_h symmetry): $\nu_3(\tau_{1u})$ 630, $\nu_4(\tau_{1u})$ 360, $\nu_6(\tau_{2u})$ 230 cm^{-1} and those in ^2E_g state: $\nu_1(\alpha_{1g})$ 570, $\nu_3(\tau_{1u})$ 610, $\nu_4(\tau_{1u})$ 320, $\nu_6(\tau_{2u})$ 200 cm^{-1}. In confirmation of these assignments the i.r. and Raman spectra gave the following frequencies in the $^4A_{2g}$ state: Raman ν_1 600, $\nu_2(\epsilon_g)$ 510, $\nu_5(\tau_{2g})$ 308; i.r. ν_3 630, ν_4 338, ν_6 260 cm^{-1}. ν_6 appeared as a weak broad bond in the i.r. spectrum, presumably because of the C_{3v} site symmetry of the complex. ν_2 and ν_5 also appeared weakly in the i.r. spectrum. Exact agreement between the ground-state vibrational frequencies as measured by the i.r. spectra and the $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence spectrum would not be expected due to the different selection rules for the split components of the O_h triply degenerate modes in C_{3v} symmetry. The 15,803 cm^{-1} He/Ne laser-excited Raman spectrum of K_2MnF_6 was quite normal (except for two weak features discussed later) being even weaker than that reported for K_2NiF_6.[1]

The broad emission band centred at *ca.* 14,300 cm^{-1} is assigned as the $^4T_{2g} \rightarrow {}^4A_{2g}$ fluorescence transition. In support of this, Mn^{IV} compounds with *Dq* less than *ca.* 2000 cm^{-1} show only fluorescence;[2] *Dq* in K_2MnF_6 is *ca.* 2200 cm^{-1}. This band has some poorly resolved vibrational structure and a sharp feature at 14,700 cm^{-1} which may be related to the band at 19,300 cm^{-1} in the reflectance spectrum.

Following the assignments in the potassium salt and estimating the (electric dipole forbidden) $^2E_g \leftrightarrow {}^4A_{2g}$ *O′–O* band in Cs_2MnF_6 to be close to 16,025 cm^{-1}, it is possible to assign some of the more prominent features of the emission and absorption spectra given in ref. 1 as shown in Table 2. The main excitation process is probably $^4A_{2g}$ $(O + \nu_6) \rightarrow {}^2E_g(O')$. Not all of the features of the spectra are at present explicable on this model, but some of the remaining bands may be due to transitions from hot bands or to a breakdown of the simple vibronic coupling model due to the proximity of the Jahn–Teller split components of the $^4T_{2g}$ state to the ^2E_g state. In addition, some of the transitions may be due to resonance enhanced Raman scattering.

TABLE 2

Assignments of some of the vibronic structures of $^2E_g \leftrightarrow {}^4A_{2g}$ *transition in* Cs_2MnF_6.[a]

Absorption	Emission	Assignment[b]
	14791	$O' \rightarrow \nu_1 + \nu_3$
	14838	$O' \rightarrow 2\nu_1$
	15096	$O' \rightarrow \nu_1 + \nu_4$
	15188	$O' \rightarrow \nu_1 + \nu_6$
	15383	$O' \rightarrow \nu_3$
15684	15688	$O' \leftrightarrow \nu_4$
15782		$O' \rightarrow \nu_6$
(16025)	16025)	$O \leftrightarrow O'$
16353		$O \rightarrow \nu_4'$
16625		$O \rightarrow \nu_3'$
16949		$O \rightarrow \nu_1' + \nu_4'$

[a] Data from ref. 1. [b] Primes denote ^2E_g state.

In addition to the bands reported above, the room temperature Raman spectrum of K_2MnF_6 shows weak bands at *ca.* 350 cm^{-1} and *ca.* 75 cm^{-1} which are probably the 15,450 cm^{-1} and 15,720 cm^{-1} emission lines. The difference between the 15,803 cm^{-1} excited luminescence spectra of K_2MnF_6 and Cs_2MnF_6 is due mainly to the much lower efficiency of the $^2E_g \rightarrow {}^4A_{2g}$ emission in the former case. This may be caused by small differences in the energies of the levels derived from the $^4T_{2g}$ state in the two compounds.

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[1] N. A. Matwiyoff and L. B. Asprey, *Chem. Comm.*, 1970, 75.
[2] C. D. Flint, to be published.
[3] C. D. Flint, *J. Mol. Spectroscopy*, 1969, **32**, 514.
[4] H. Bode and W. Wendt, *Z. anorg. Chem.*, 1952, **269**, 165.
[5] G. C. Allen, G. A. M. El-Sharkarwy, and K. D. Warren, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 725.