# Excitation and Luminescence Spectra of Dipotassium Hexafluoromanganate(IV)

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Measurement of the excitation and luminescence spectra of the salt $K_2[MnF_6]$ prepared by different methods shows that the intense emission observed at low temperatures between 14 700 and 13 500 cm$^{-1}$ is caused by a Mn$^{IV}$ species present as impurity. The $^2E$ state of the impurity is populated by energy transfer from the $^2E$ state of the $[MnF_6]^{2-}$ ion thereby almost quenching the emission from the latter. The nature of this impurity is discussed. The previously reported absorption band at 19 300 cm$^{-1}$ is not present in the excitation spectrum and is attributed to another impurity. All the expected electronic and vibronic origins of the $^4A_2 \rightarrow {}^2E$ and $^4A_2 \rightarrow {}^2T_1$ transitions of the $[MnF_6]^{2-}$ ion have been identified.

THE electronic spectrum of dipotassium hexafluoromanganate(IV) has been investigated several times [1-6] but there is little agreement between the spectra obtained. The differences probably arise because the salt exists in two or three crystallographic modifications [6,7] and may contain several different impurities. Novotny and Sturgeon [6] have discussed some of the differences that occur in the absorption spectra. In this paper we report excitation and luminescence spectra of the salt $K_2[MnF_6]$ prepared by different methods which enable several of the remaining problems to be resolved.

## EXPERIMENTAL

Several samples of the salt $K_2[MnF_6]$ were prepared by the method of Palmer [8] using 40% aqueous hydrofluoric acid. Recrystallisation from 40% hydrofluoric acid did not produce any change in the 80 K luminescence spectrum of the product provided that the temperature of the reaction mixture was kept at 0 °C during the reduction stage (compare ref. 3). Other samples of the salt were prepared by the same method but using progressively more dilute hydrofluoric acid (30, 25, 20, and 15%). The products from these reactions were darker in colour and gave 80 K luminescence spectra in which the ratio of the intensity of the emission from the $[MnF_6]^{2-}$ ion to that of the broad impurity emission steadily decreased. **CAUTION.** We attempted to prepare the salt $K_2[MnF_6]$ using more concentrated hydrofluoric acid (60—90%). When a small quantity of powdered potassium permanganate was added to this acid there was a flash of light and a great deal of heat was evolved. The solid products were dark, impure samples of the salt $K_2[MnF_6]$. This potentially hazardous reaction clearly has no synthetic value and it was not investigated further. The salt was also prepared by direct fluorination of $K_2[MnCl_6]$ at 350 °C.

Luminescence spectra [9] and decay curves [10] were measured using the apparatus previously described. Excitation spectra were obtained using a modulated XBO 150 xenon arc and 600 mm monochromator as excitation source, and a 250 mm monochromator and EMI 9558QA photomultiplier as detector. The resulting signal was amplified using phase-sensitive techniques.

## RESULTS AND DISCUSSION

*Luminescence Spectra.*—The 80 K 436 nm-excited luminescence spectrum of the salt $K_2[MnF_6]$ prepared by Palmer's method is shown in Figure 1. The weak, sharp emission near 16 000 cm$^{-1}$ resembles the $^2E_g \rightarrow {}^4A_{2g}$ luminescence of cubic $Cs_2[MnF_6]$ except that the 0′–0 line was relatively more intense.[11] The three

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[1] C. K. Jorgensen, *Acta Chem. Scand.*, 1958, **12**, 1539.

[2] G. C. Allen, G. A. M. Sharkarwy, and K. D. Warren, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 725.

[3] A. Pfiel, *Spectrochim. Acta*, 1970, **A26**, 1341.

[4] A. Pfiel, *Theoret. Chim. Acta (Berlin)*, 1971, **20**, 159.

[5] C. D. Flint, *Chem. Comm.*, 1970, 482.

[6] D. S. Novotny and G. D. Sturgeon, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 455.

[7] H. Bode and W. Wendt, *Z. anorg. Chem.*, 1952, **269**, 173.

[8] W. G. Palmer, 'Experimental Inorganic Chemistry,' Cambridge University Press, Cambridge, 1954, p. 484.

[9] C. D. Flint and P. Greenough, *J.C.S. Faraday II*, 1972, **68**, 897.

[10] C. D. Flint and P. Greenough, *J. Chem. Phys.*, 1972, **56**, 5771.

[11] C. D. Flint, *J. Mol. Spectroscopy*, 1971, **37**, 414.

strongest lines to low energy of this origin (Table 1) are readily identified as the vibronically active vibrations $\nu_3(\tau_{1u})$, $\nu_4(\tau_{1u})$, and $\nu_6(\tau_{2u})$. In addition there were two low-energy lattice vibrations (not necessarily zero wave-vector modes) and bands at 299, 521, and 749 cm$^{-1}$ from the origin. The energy of these bands suggests that they are assigned as $\nu_5(\tau_{2g})$, $\nu_2(\varepsilon_g)$, and $(\nu_6 + \nu_2)$ respectively, but the room-temperature Raman spectrum of the salt $K_2[MnF_6]$ prepared by the same method gave the wavenumbers of $\nu_5$ and $\nu_2$ as 308 and 510 cm$^{-1}$. The differences between these values and those determined from the luminescence spectrum are several times the experimental error and are not due to a shift of the bands with temperature, since they could be detected in the same position (but less well resolved) in 196 and 295 K luminescence spectra. The most probable explanation is that these three weak bands involve coupling of the electronic excitation to $\nu_5$ and $\nu_2$ at one or more special points of the Brillouin zone other than the centre.

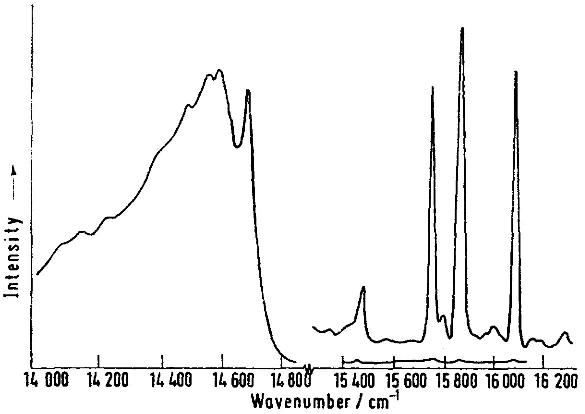

FIGURE 1 Luminescence spectrum of the salt $K_2[MnF_6]$ (wet preparation) at 80 K

TABLE 1

Vibronic intervals (cm$^{-1}$) in the 80 K $^2E_g \rightarrow {}^4A_{2g}$ luminescence of solid $K_2[MnF_6]$

| Wet prepn. Interval from 0′–0 at 16 097 cm$^{-1}$ | Fluorination prepn. Interval from 0′–0 at 16 094 cm$^{-1}$ | Assignment |
|---|---|---|
| −337 | *−345* | $\nu_4'$ |
| −296 | −318 | |
| −216 | *−230* | $\nu_6'$ |
| | −128 | Lattice vibrations |
| −84 | −87 | |
| | −67 | |
| 0 | 0 | |
| | 56 | Lattice vibrations |
| 92 | 79 | |
| 135 | 117 | |
| 229 | 221 | $\nu_6\ (\tau_{2u})$ |
| 299 | 301 | $\nu_5\ (\tau_{2g})$ (see text) |
| 344 | 330 | $\nu_4\ (\tau_{1u})$ |
| | 403sh | |
| 521 | 525 | $\nu_2\ (\varepsilon_g)$ (see text) |
| 625 | 624 | $\nu_3\ (\tau_{1u})$ |
| 677 | 676 | $(87 + \nu_1)$ |
| 749 | 745 | $(\nu_6 + \nu_2)$ (see text) |
| | 822 | $[\nu_6 + \nu_1\ (\alpha_{1g})]$ |
| | 857 | $(\nu_4 + \nu_2)$ |
| | 933 | $(\nu_4 + \nu_1)$ |

The broader luminescence showed an origin and some structure at 80 K (Figure 1). The decay curve of this emission was exponential with a half-life of $120 \times 10^{-6}$ s and a rise time of less than $2 \times 10^{-6}$ s. The half-life of the 16 000 cm$^{-1}$ emission was also less than $2 \times 10^{-6}$ s. At 5 K the 14 500 cm$^{-1}$ band was resolved into a large number of vibronic bands (Figure 2). Pfiel[3,4] attributed this broader luminescence to the $^4T_1(G) \rightarrow {}^6A_1$ transition of an octahedrally co-ordinated Mn$^{II}$ impurity. For reasonable values of $Dq$ in this environment the energy separation of the $^4T_1(G)$ and $^6A_1$ states decreases rapidly with $Dq$. The equilibrium metal–ligand distance is therefore appreciably smaller in the $^4T_1(G)$ than in the $^6A_1$ state. Electronic origins of the $^4T_1(G) \rightarrow {}^6A_1$ transition of Mn$^{II}$ are therefore weak and in practice a broad featureless band is observed. The observed luminescence spectrum is thus inconsistent with the impurity being a Mn$^{II}$ species. Recrystallisation of the salt $K_2[MnF_6]$ from 40% hydrofluoric acid to which manganese(II) nitrate had been added failed to change the relative intensity of the 16 000 and 14 500 cm$^{-1}$ emissions.

The position, lifetime, and structure of the broader emission shows that it is not $^4T_2 \rightarrow {}^4A_2$ fluorescence[5] but strongly suggests that it is due to a $^2E \rightarrow {}^4A$ transition of a $d^3$ ion present as impurity. A careful search to high energy of the electronic origin in the 80 K luminescence spectrum failed to reveal any trace of a second origin, any splitting of the $^2E$ state being less than 10 or more than 400 cm$^{-1}$. The luminescence band was more than 1 000 cm$^{-1}$ wide and since the highest vibrational wavenumbers likely to be present are less than 650 cm$^{-1}$, it must involve vibronic bands corresponding to two or more vibrational quanta. The potential surfaces of the initial and terminal electronic states are thus slightly different but not sufficiently so

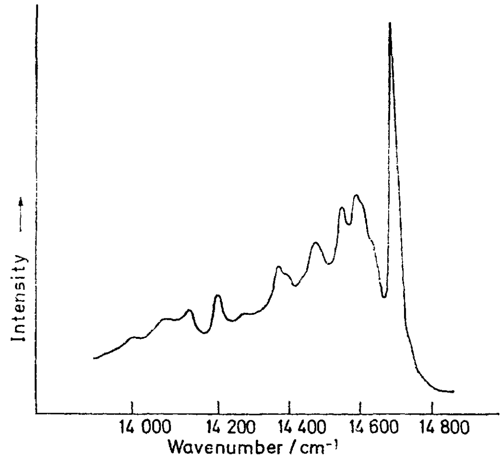

FIGURE 2 Impurity emission from the salt $K_2[MnF_6]$ (wet preparation) at 5 K

as to cause the intensity of the combination bands to approach that of the electronic and vibronic origins. This small difference will arise in the impurity if the $^2E$ state lies close to the $^4T_2$ state (or one of its components) as has been shown to occur [12] in the salt $K_2Na[(Cr,Ga)F_6]$. Indeed the impurity 5 K luminescence spectrum has a remarkable overall similarity to that reported for this salt. The intensity of emission decreased rapidly as the temperature was raised so that above 140 K it could not be detected. This is also consistent with the $^2E$ state being close to a quartet state which is rapidly non-radiatively depopulated. These considerations, and the observation that the intensity of the impurity emission relative to that of the $[MnF_6]^{2-}$ emission increases as the concentration of the hydrofluoric acid used in its preparation is decreased, suggest that the impurity is a hydrolysis product of the ion $[MnF_6]^{2-}$, possibly $[MnF_5(OH)]^{2-}$, $[MnF_4(OH)_2]^{2-}$, or the corresponding aquo-ions.

Direct fluorination of the salt $K_2[MnCl_6]$ produced a sample of $K_2[MnF_6]$, which had an 80 K luminescence spectrum consisting of a weak $^2E \rightarrow {}^4A$ electronic origin and three strong vibronic bands (the $2\tau_{1u}$ and $\tau_{2u}$ vibrations of the $[MnF_6]^{2-}$ ion). The appearance of the spectrum in the 16 000 cm$^{-1}$ region was similar to that of the salt $Cs_2[MnF_6]$ and indicated that the product was mainly the cubic form [6,7] of $K_2[MnF_6]$. In the course of a few hours, the luminescence spectrum near 16 000 cm$^{-1}$ changed until it was similar to that of the salt $K_2[MnF_6]$ prepared by the wet method but considerably more intense. There were also some small (but significant) differences in the positions of some of the sharp lines. This change occurred at a similar rate both when the sample was kept at 80 K in the vacuum space of the cryostat and when it was stored at room temperature in an unsealed Polythene tube. The *X*-ray powder pattern of the aged fluorinated salt and that obtained by the wet method were not identical. Impurity emission in both the freshly prepared (cubic) fluorinated sample and the aged fluorinated sample (which is probably the hexagonal form [6,7]) was much weaker, both absolutely and relative to emission from the $[MnF_6]^{2-}$ ion in the same salt, than that in the sample prepared by the wet method (the trigonal form [6,7]). The low intensity of the impurity emission of the fluorinated product further suggests that it is due to a hydrolysis product.

Table 2 gives two possible assignments of the vibronic structure of the impurity emission on the assumption that it is due to a $^2E \rightarrow {}^4A$ transition of a fluoro-complex of $Mn^{IV}$. Assignment (I) would be more appropriate for a hydroxo-complex since the $OH^-$ ion is isoelectronic with $F^-$, but assignment (II), which involves large splittings of the octahedral fundamental vibrations, enables more lines to be accounted for and might be better for an aquo-complex. In each case vibrational frequencies similar to those observed in the $[MnF_6]^{2-}$ ion may be observed. Vibration intervals comparable to $\nu_2$ and $\nu_1$ of the $[MnF_6]^{2-}$ ion appear strongly and this further emphasises the similarity with the salt $K_2Na[(Cr,Ga)F_6]$. The most unsatisfactory feature of these assignments is that they fail to account for the bands at 90 and 103 cm$^{-1}$, which seem to be of too low energy to be internal modes and of too high intensity to be ascribed confidently to lattice vibrations. Attempts to locate the transition in absorption were unsuccessful but Allen *et al.*[2] have reported a very weak broad band at 14 300 cm$^{-1}$ in the reflectance spectra of their sample of $K_2[MnF_6]$. The broad weak emission band reported for the salt $Cs_2[MnF_6]$ is probably caused by a similar impurity.

TABLE 2

Vibronic structure of the 5 K impurity luminescence from solid $K_2[MnF_6]$

| Wave-number/ cm$^{-1}$ | Interval from 0′–0 | Possible assignments (I) | Possible assignments (II) |
|---|---|---|---|
| 14 706 | 0 | zero phonon line | zero phonon line |
| 14 643 | 63 | | |
| 14 616 | 90 | | |
| 14 603 | 103 | | |
| 14 556 | 150 | | $\nu_6$ |
| 14 480 | 226 | $\nu_6$ | $\nu_6$ |
| 14 399 | 307 | $\nu_5$ | $\nu_5$ |
| 14 372 | 334 | $\nu_4$ | $\nu_4$ |
| 14 278 | 428 | | $\nu_4$ |
| 14 205 | 501 | $\nu_2$ | $\nu_2$ |
| 14 128 | 578 | $\nu_1$ | $\nu_1$ |
| 14 098 | 608 | $2\nu_5 = 614$ | $2\nu_5 = 614$ |
| 14 063 | 643 | $\nu_3$ or $(\nu_4 + \nu_5) = 641$ | $\nu_3$ or $(\nu_4 + \nu_5) = 641$ |
| 14 025 | 681 | $3\nu_6 = 678$, $103 + 578$ | $3\nu_6 = 678$ |
| 13 974 | 732 | $(\nu_6 + \nu_2) = 727$ | or $(\nu_6 + \nu_1) = 728$ |
| 13 889 | 817 | $(\nu_6 + \nu_1) = 804$ | |
| 13 862 | 844 | $(\nu_4 + \nu_2) = 835$ | |
| 13 780 | 926 | $(\nu_4 + \nu_1) = 912$ or $(\nu_4 + \nu_2) = 929$ | |
| 13 702 | 1 004 | $2\nu_2 = 1\,004$ or $(\nu_4 + \nu_1) = 1\,006$ | |
| 13 626 | 1 080 | $(\nu_2 + \nu_1) = 1\,079$ | |
| 13 554 | 1 152 | $2\nu_1 = 1\,156$ or $(\nu_3 + \nu_2) = 1\,144$ | |
| 13 477 | 1 229 | $(\nu_6 + 2\nu_2) = 1\,228$ or $(\nu_3 + \nu_1) = 1\,221$ | |

*Excitation Spectrum.*—The $^2E \rightarrow {}^4A$ emission of the $[MnF_6]^{2-}$ ion in the salt $K_2[MnF_6]$ prepared by the wet method was too weak for a satisfactory excitation spectrum to be obtained. However by observing the intensity of the broader *impurity* emission as a function of excitation wavelength a very satisfactory spectrum was obtained consisting of a large number of sharp lines between 15 800 and 17 820 cm$^{-1}$ (Figure 3, Table 3) and a single broad structureless band at *ca.* 22 000 cm$^{-1}$. The sharp-line excitation spectrum did not resemble the impurity emission but was readily assigned as $^4A \rightarrow {}^2E$ and $^4A \rightarrow {}^2T_1$ transitions of the $[MnF_6]^{2-}$ ion. The origin of the $^4A \rightarrow {}^2E$ excitation transition coincided with that of the $^2E \rightarrow {}^4A$ $[MnF_6]^{2-}$ emission and the $\nu_6$, $\nu_4$, and $\nu_3$ vibrational frequencies in the $^2E$ state are similar to those observed in the $^4A$ state by luminescence and i.r. spectroscopy. Remaining strong lines in this region are assigned as the three origins of the $^4A \rightarrow {}^2T_1$ transition and one quantum of the $\nu_6$, $\nu_4$, and $\nu_3$ vibrations based on each of these origins (Table 3). The separation of the three origins of the $^2T_1$ state are 26 and 68 cm$^{-1}$.

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[12] J. Ferguson, H. J. Guggenheim, and D. L. Wood, *J. Chem. Phys.*, 1971, **54**, 504.

The closer pair are assigned as components of the $\Gamma_8(O_h^*)$ state split in the second order by the small trigonal field. This splitting is expected to be about an order of magnitude larger than the separation of the second-order spin–orbit coupling is very similar to the $\Gamma_6$–$\Gamma_8$ separation[13] in the ion $[CrF_6]^{3-}$. Vibrational frequencies in the $^2T_1$ states are almost identical to those in the $^2E$ and $^4A$ states. In addition to the strong bands, there were several weak lines which can be assigned as the first members of progressions in $\nu_1$ based on the vibronic origins. The intensity of these pro-

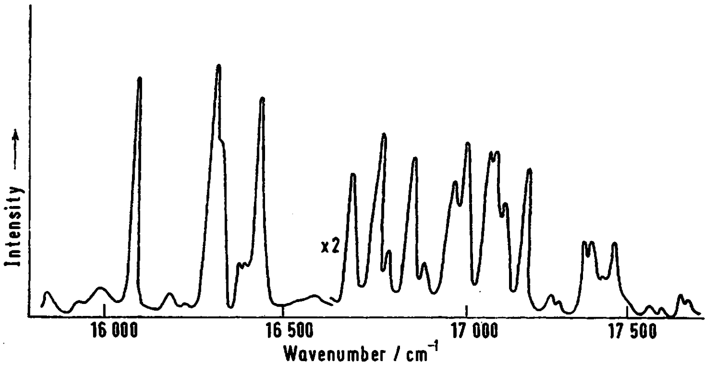

FIGURE 3 80 K Excitation spectrum of the salt $K_2[MnF_6]$ (wet preparation) monitored at 14 706 cm$^{-1}$

TABLE 3

$^4A_{2g}\rightarrow{}^2E_g,{}^2T_{1g}$ Excitation spectrum of solid $K_2[MnF_6]$ at 80 K, monitored at 14 706 cm$^{-1}$

| Wavenumber/cm$^{-1}$ | $^4A_{2g}\rightarrow{}^2E_g$ Interval from 0–0′ | $^4A_{2g}\rightarrow{}^2T_{1g}$ interval from 0–0′ | | | Assignment[a] |
|---|---|---|---|---|---|
| 15 860 | −215 | | | | $^4A_2+\nu_6\rightarrow{}^2E$ |
| 16 085s | 0 | | | | $^4A_2\rightarrow{}^2E$ |
| 16 179 | 94 | | | | $\rightarrow{}^2E$ + lattice |
| 16 226 | 141 | | | | |
| 16 308s | 223 | | | | $\rightarrow{}^2E+\nu_6'$ |
| 16 327sh | 242 | | | | |
| 16 377 | 292 | | | | |
| 16 396 | 311 | | | | |
| 16 431s | 346 | | | | $\rightarrow{}^2E+\nu_4'$ |
| 16 499 | 414 | | | | |
| 16 559 | 474 | | | | |
| 16 589 | 505 | | | | |
| 16 600 | 515 | | | | |
| 16 647 | 562 | | | | |
| 16 700s | 615 | | | | $\rightarrow{}^2E+\nu_3'$ |
| 16 756sh | | | | | |
| 16 781s | | 0 | | | $\rightarrow\Gamma_8(^2T_1)$ |
| 16 807 | | | 0 | | |
| 16 875s | | | | 0 | $\rightarrow\Gamma_6(^2T_1)$ |
| 16 912 | 827 | | | | $\rightarrow{}^2E+\nu_1'$ |
| 17 000s | | 220 | | | $\rightarrow\Gamma_8+\nu_6'$ |
| 17 030s | 945 | | 227 | | $\rightarrow{}^2E+\nu_4'+\nu_1'$ |
| 17 100s | | | | 225 | $\rightarrow\Gamma_6+\nu_6'$ |
| 17 117s | | 336 | | | $\rightarrow\Gamma_8+\nu_4'$ |
| 17 144m | | | 337 | | |
| 17 215s | | | 340 | | $\rightarrow\Gamma_6+\nu_4'$ |
| 17 265 | | | | | |
| 17 304 | 1 219 | | | | $\rightarrow{}^2E+\nu_3'+\nu_1'$ |
| 17 334 | | | | | |
| 17 397m | | 616 | | | $\rightarrow\Gamma_8+\nu_3'$ |
| 17 422m | | | 615 | | |
| 17 458 | | | | | |
| 17 489 | | | | 614 | $\rightarrow\Gamma_6+\nu_3'$ |
| 17 544 | | | | | |
| 17 606 | | 825 | | | $\rightarrow\Gamma_8+\nu_6'+\nu_1'$ |
| 17 637 | | | 830 | | |
| 17 712 | | 931 | | 837 | $\rightarrow\Gamma_8+\nu_4'+\nu_1'\rightarrow\Gamma_6+\nu_6'+\nu_1'$ |
| 17 746 | | | 939 | | |
| 17 819 | | | | 944 | $\rightarrow\Gamma_6+\nu_1'+\nu_1'$ |

[a] Labels as in $O_h$.

components of the $^2E$ state so that our failure to resolve the splitting of the latter is not unexpected. The separation of the upper component of the $^2T_1$ state $[\Gamma_6(O_h^*)]$ from the centre of the lower pair due to

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[13] A. D. Liehr, *J. Phys. Chem.*, 1963, **67**, 389.

gressions relative to their vibronic origins was much greater in the $^2E$ than in the $^4A_2$ state, presumably as a result of interaction between vibronic levels of the $^2E$ and $^2T_1$ states. The 22 000 cm$^{-1}$ excitation band is assigned as the $^4A \rightarrow {}^4T_2$ transition of the $[MnF_6]^{2-}$ ion.

The excitation spectrum shows that the $^2E$ state of the luminescent impurity is populated from the $^2E$ state of the $[MnF_6]^{2-}$ ion. This excitation transfer is fast since it almost quenches the $[MnF_6]^{2-}$ emission, even though the concentration of the impurity is so low that the electronic absorption and i.r. spectra give no indication of its presence. The $^4A \rightarrow {}^2E$ transition of the impurity would be expected to be a broad band between 14 700 and 16 000 cm$^{-1}$. It therefore overlaps with the $^2E \rightarrow {}^4A$ transition of the $[MnF_6]^{2-}$ ion and this may partly explain the efficiency of the process.[14] Allen *et al.*[2] reported a very weak broad band at 14 300 cm$^{-1}$ in the reflectance spectrum of their sample of the salt $K_2[MnF_6]$, which may be due to the luminescent impurity. The band at 19 300 cm$^{-1}$ in the absorption spectrum [2,5,6] does not appear in the excitation spectrum; it is probably caused by another impurity which does not transfer excitation to the $[MnF_6]^{2-}$ ion or to the hydrolysis-product impurity.

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[14] D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836.