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Vibrational Analysis of the Raman, Infrared and Electronic Spectra of Hexafluoromanganate(IV)*

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From the Raman, infrared and electronic spectra all of the fundamental vibrational frequencies were determined for both the ground state $^4A_{2g}$ and the excited ^2E_g. In addition some fundamental frequencies were established for the $^4T_{2g}$ and $^4T_{1g}$ excited states from low temperature absorption spectra.

Aus den Raman-, Infrarot- und Elektronenspektren wurden alle Grundschwingungsfrequenzen für den Grundzustand $^4A_{2g}$ und den angeregten ^2E_g-Zustand bestimmt. Ferner wurden noch einige der entsprechenden Größen für die angeregten Zustände $^4T_{2g}$ und $^4T_{1g}$ aus Tieftemperatur-Absorptionsspektren ermittelt.

Toutes les fréquences fondamentales de vibration ont été déterminées pour l'état fondamental $^4A_{2g}$ et l'état excité ^2E_g à partir des spectres Raman, infra-rouge et électronique. De plus, certaines fréquences fondamentales des états excités $^4T_{2g}$ et $^4T_{1g}$ ont été obtenues à partir des spectres d'absorption à basse température.

Introduction

A variety of molecular Cr(III) complexes exhibit a rich vibrational structure associated with the spin-forbidden $^2E \rightarrow {}^4A_2$ transition [1, 2]. Only in a few cases has a vibrational analysis been attempted [1–4]. In general it seems that an unequivocal vibrational analysis is made difficult by the complexity of the problem and the lack of reliable high resolution IR and Raman data for molecular Cr(III) complexes.

Since intra-ligand vibrations of polyatomic ligands also couple to electronic transitions of the *d* electrons of the complex ion, the most simple system for a theoretical and practical study of this kind would be an octahedral MA_6 species, where A is a monoatomic ligand such as a halide. However, no vibrational analysis of such complexes of Cr(III) has yet been made, since in emission only fluorescence is observed [2, 5] (which is structureless) and in the absorption spectra the $^2E \leftarrow {}^4A_2$ and $^4T_2 \leftarrow {}^4A_2$ transitions overlap [5, 6] thus obscuring any vibrational structure.

The hexafluoride complex of Mn(IV) (isoelectronic with Cr(III)) seems to be more suitable for this study since it does not have the disadvantages mentioned above: there is very strong phosphorescence [7] and the $^2E \leftarrow {}^4A_2$ and $^4T_2 \leftarrow {}^4A_2$ transitions are well separated. In addition, the Cs salt of the complex seems to be purely octahedral from both crystallographic [8] and optical data.

In this work the fundamental frequencies of the MnF_6^{2-} complex were determined from Raman, IR, electronic absorption and emission spectra. From

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* Dedicated to the memory of Prof. Hans-Ludwig Schläfer.

the data available an analysis of the observed vibrational structure in the transitions from the ${}^4A_{2g}$ ground state to the ${}^2E_g$, ${}^4T_{2g}$ and ${}^4T_{1g}$ excited states was attempted. The observed frequencies in the spectra are compared to the fundamental frequencies and combinations thereof which are predicted by group theory.

Experimental

Preparation. The complex K_2MnF_6 was prepared by the method described by Palmer [9]. The crude compound was purified by repeated crystallizations from 48% HF in Pt dishes at 40 °C. Cs_2MnF_6 and Rb_2MnF_6 were prepared from the potassium salt by cation exchange.

Raman Spectra. They were recorded on a Cary Model 81 Raman spectrophotometer using the 6328 Å line of a He/Ne laser of Spectra Physics. A special dewar was used to obtain spectra at 85 °K [10].

IR *Spectra.* The spectra in the region 200–500 cm^{-1} were taken on a Perkin-Elmer 421 and from 250 to 2000 cm^{-1} on a PE 457. The spectra were obtained in three different ways: pellets of the very finely powdered sample were either fused with polyethylene, pressed with KBr, or mulled with Nujol using AgCl windows.

Absorption Spectra. Single crystals were employed, grown from 48% HF by slow evaporation of the solvent. Depending on the optical density required the thickness of the crystals was varied from 30 μ to 1 mm. They were mounted in a conventional metal evacuable dewar and the spectrum was taken along the optical axis at different temperatures. At 300 °K and 85 °K a Cary 14 was used, but at 4.2 °K a different apparatus of higher resolution was required: the light of a quartz/iodine lamp was focussed on to the sample and the transmitted light analyzed by a Czerny-Turner grating type monochromator (Spex Instruments, 0.75 m, 10 Å/mm dispersion, blazed at 7500 Å) and detected by an RCA 1P28 photomultiplier (S5 characteristics). The signal was amplified with a Brookdeal LA350AC amplifier and displayed on a paper chart recorder.

Emission Spectra. The emission of Cs_2MnF_6 was measured using essentially the same apparatus (Czerny-Turner spectrometer) as described above except that the crystal (approx. 50 μ thick) was excited with the light of a PEK 110 mercury arc filtered through a 3 cm layer of conc. $CuSO_4$ in water and a 433 μ interference filter.

The emission spectrum of K_2MnF_6 dissolved in 20% HF (which forms a glass at liquid nitrogen temperature) was obtained with an apparatus of lower resolution. The sample, placed into a flat quartz cell, was excited as described above and the emitted light after passing through an orange filter C 3–67, was recorded with a Jarrell-Ash monochromator Model 82–400 (dispersion 33 Å/mm) and an RCA 1P28 photomultiplier.

Results

The Raman spectra of the K, Rb and Cs salts of H_2MnF_6 in the form of single crystals and as powders were obtained at room temperature and as powders at −85 °K. The spectra for the Cs and the K complexes are depicted in Figs. 1 and 2 and the band positions are listed in Tables 1 and 2, respectively. No

Table 1. *Observed frequencies (in cm^{-1}) in the Raman spectrum of* Cs_2MnF_6 *compared to frequencies observed in amission and absorption spectra (Laser excitation frequency 15803 cm^{-1})*

$\nu(R_1)$ Raman (300 °K) single crystal	$\nu(R_2)$ Raman (850 °K) powder	$\nu(R_1) + 15803$	$\nu(R_2) + 15803$	Absorption (300 °K) single crystal	Absorption (85 °K) single crystal	Emission (300 °K) single crystal	Emission (4.5 °K) single crystal	Assignment of $\nu(R_1)$ and $\nu(R_2)$
932		16735		—	16752	—		emission
870		16673		16660	16686	—		emission
835		16638		16621	16645	16633		emission
790 sh		16593		16582	—	16580		emission
685		16483		16488	—	16485		emission
557		16360		16349	16369	16359		emission
435		16238		16234	16259	16242		emission
266		16069		16067	16083	16072		emission
226		16024		—	16034	16028	16030	emission
+ 167		15970		—	—	15964	15969	emission
—	—	—	—	15784	—	15793	15801	—
− 111	—	15692	—	15681		15694	15696	emission
340 sh	335 sh	15453	15468			—	—	ν_5
396	389	15407	15414			15406	15414	emission
450 sh	415 sh	15353	15388			15378	15382	emission
503	503	15290	15290				15294	emission
587	587	15216	15216				15214	emission
611	610	15192	15193				15191	emission
695	693	15108	15110				15106	emission
850 sh	848	14953	14955				—	emission
895	892	14908	14911				14908	emission
975	971	14828	14832					emission
1010	1007	14793	14796					emission

sh shoulder.

Table 2. *Observed frequencies (in cm^{-1}) in Raman spectrum of* K_2MnF_6 *compared to frequencies observed in emission and absorption spectra (Laser excitation frequency* 15803 *cm*$^{-1}$*)*

$\nu(R_1)$ Raman (300 °K) single crystal	$\nu(R_2)$ (85 °K) powder	$\nu(R_1) + 15803$	$\nu(R_2) + 15803$	Absorption (300 °K) single crystal	Emission (85 °K) solution	Assignment of $\nu(R_1)$ and $\nu(R_2)$
1066		16869		16861		emission
966		16769		16767		emission
891		16694		16681		emission
732		16535		~16540 sh		emission
612		16415		16410		emission
486		16289		16283	16303	emission
345		16148		16147	—	emission
+ 270		16073		16071	16067	emission
—		—		15842	15848	—
—		—		15733	15723	—
− 310	311	15493	15492		—	ν_5
348	342	15455	15461		15456	emission
383 sh	393	15420	15411			emission
471	466	15332	15337			emission
507	507	15294	15294			ν_2
600	604	15203	15199			ν_1
667		15136				emission
867		14943				emission
906 sh		14897				$\nu_1 + \nu_5$
924 sh		14879				emission

sh shoulder.

difference was noted in the spectrum of a powder and a single crystal at room temperature. The spectrum of the Cs salt is in good agreement with that published recently [11]. The spectra (Raman and absorption) for the K and Rb salts are identical and the latter was not studied further.

Within experimental error no difference was observed in the IR spectra of the Cs and K complexes. The IR frequencies determined by three different methods (cf. experimental part) agree within 3%. The observed fundamentals are listed in Table 3.

The emission spectra and the relevant parts of the absorption spectra for the Cs and the K salts are depicted in Figs. 1 and 2 and the band positions are listed in Tables 1 and 2, respectively at the indicated temperatures. The band positions of the absorption spectrum of the Cs complex at 4.5 °K are given in Table 5. The presence of pair-lines in the emission spectrum of the Cs complex was tested by comparison with the emission spectrum of Mn^{4+} : Cs_2GeF_6 (mole ratio 5%). No significant difference was observed. Cs_2GeF_6 [12] has the same symmetry as Cs_2MnF_6.

Discussion

According to group theory an octahedral MA_6 species (with monoatomic ligands A) has three Raman-active vibrations ν_1, ν_2 and ν_5 of symmetry a_{1g}, e_g, and t_{2g}, respectively, two IR-active vibrations ν_3 and ν_4 (both t_{1u}) and one inactive vibration $\nu_6(t_{2u})$ [13].

In the Raman spectrum of an octahedral hexafluoride complex like K_2NiF_6, for example, three dominant bands at 562, 520 and 310 cm^{-1} are observed which have been assigned to the three fundamental vibrations ν_1, ν_2 and ν_5, respectively [14]. Although Ni(IV) is very similar to Mn(IV) (with respect to valency, mass, radius) the Raman spectrum of MnF_6^{2-} differs considerably; there are more bands with remarkably higher intensity, especially in the spectrum of the Cs salt, which was also noted recently by Matwiyoff *et al.* [11]. Furthermore, the Raman spectra of Cs_2MnF_6 and K_2MnF_6 differ in band positions and intensities (three comparatively narrow bands at 600, 507 and 310 cm^{-1} in the latter are not to be seen at all in the former) which was not observed in the spectra of the same salts of Ni(IV) [14, 15].

High intensities (on an absolute basis) can be caused by a resonance Raman effect [11, 16] or may be due to resonance emission. Such overlapping emission bands are observed, for example, in the Raman spectrum of some Cr(III) complexes [17] and resonance emission (phosphorescence) most probably is responsible for the observed anomalies in the Raman spectra of solid hexafluoromanganates. The complexes are strong phosphors [7] and they emit even at room temperature. Especially the Cs salt is very intense with the same emission quantum yield and lifetime at low (85 °K) and high (300 °K) temperatures [18]. Emission spectra, relevant parts of the absorption spectra together with the Raman spectra are displayed in Figs. 1 and 2. Two distinct features should be noted: (1) to almost every band in the Raman spectrum there corresponds a similar band in the emission spectrum and (2) some absorption bands are very close or overlap with the Raman excitation line.

From both emission and absorption studies, these particular bands were identified as "hot bands" of the spin-forbidden transition $^2E \leftarrow {}^4A_2$ [7]. In the spectra of the Cs complex, only the origin of this transition at 16030 cm^{-1} is common to both absorption and emission at 4.5 °K (cf. Table 4). Higher temperatures populate higher lying vibrational levels from which electronic transitions may occur, thus hot bands appear at 15681 and 15784 cm^{-1} at 300 °K. The latter band is relatively broad (approx. 35 cm^{-1} half-height width) and overlaps directly with the excitation line at 15803 cm^{-1}. The resulting emission superimposes on the (usually weak) Raman lines and obscures the Raman spectrum, hence the anomalies described above are observed. Lowering the temperature to 85 °K has no significant effect on the observed Raman spectrum. The hot band (now shifted to 15794 cm^{-1}) is still present and overlaps with the excitation line.

A different situation is encountered for the K salt. The intensity of the emission is considerably lower due to quenching by traces of Mn^{2+} [7] and there is less overlap with the excitation line. The hot band nearest to the excitation line is at 15842 cm^{-1} and is shifted to 15858 cm^{-1} when the temperature is lowered to 85 °K. This decreases the phosphorescence emission intensity and the three narrow lines (half height width approx. 5 cm^{-1}), before barely discernible from emission bands at room temperature, appear, slightly shifted and with relatively enhanced intensity. They are identified as the fundamental Raman frequencies $\nu_1 = 600$, $\nu_2 = 507$ and $\nu_5 = 310$ cm^{-1}. The relative intensities follow the common pattern $I(\nu_1) \gg I(\nu_2)$, $I(\nu_5)$ which is characteristic for most octahedral MA_6 complexes [19]. The assignments are made by comparison with Raman fre-

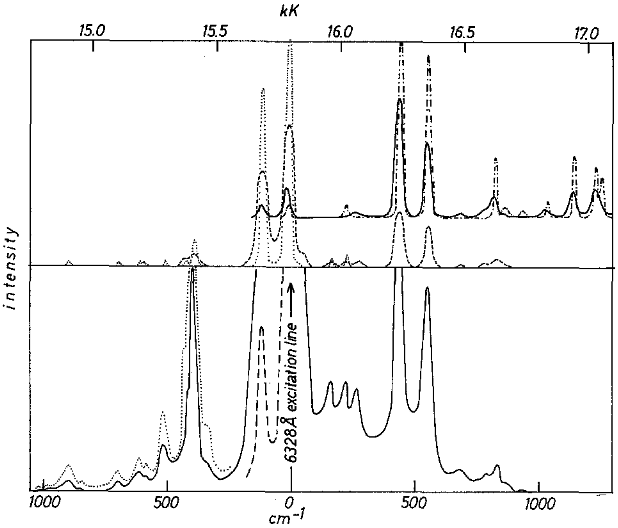

Fig. 1. Lower part: Raman spectra of Cs_2MnF_6 at 300 °K with sensitivity 2, slit 1 cm^{-1} ———, sensitivity 2, slit 0.1 cm^{-1} — — —, Raman spectrum at 85 °K with sensitivity 2, slit 5 cm^{-1} ....; upper part: Emission spectrum of Cs_2MnF_6 at 300 °K, slit 1 Å — — —, 4.5 °K, slit 1 Å ...., absorption spectrum at 300 °K ———, at 85 °K —·—·—

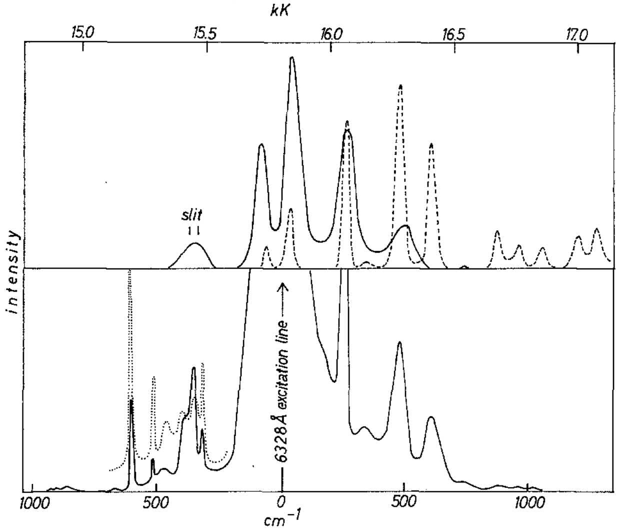

Fig. 2. Lower part: Raman spectra of K_2MnF_6 at 300 °K, sensitivity 200, slit 3.8 cm^{-1} ———, at 85 °K, sensitivity 2000, slit 10 cm^{-1} ....; upper part: Emission spectrum of K_2MnF_6 at 85 °K, slit 15 Å in a rigid glass ———, absorption spectrum at 300 °K — — —

quencies of similar complexes which are listed in Table 3. In solution (in dil. HF) the emission is very weak [18] and three bands only are observed in the Raman spectrum at 615(ν_1), 480(ν_2) and 282(ν_5) [11].

The IR spectrum is very similar to K_2NiF_6 [14] and no difference was observed between the spectrum of the K and Cs salts within experimental error. The

Table 3. *Fundamental frequency of some hexafluorides with tetravalent cations*

Complex	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	Refs.
$[MnF_6]^{2-}$	600	507	620	340	310	229	this work
$[NiF_6]^{2-}$	562	520	658	345	310	(220)[a]	[14, 15]
$[PdF_6]^{2-}$	578	558					[16]
$[PtF_6]^{2-}$	600	576	571	281	210	(184)[a]	[21, 14]
$[SiF_6]^{2-}$	656		753	485			[22, 20]
$[GeF_6]^{2-}$	627	454			318		[23]
$[SnF_6]^{2-}$	593		564		342		[24]

[a] Calculated frequencies.

spectrum consists of two strong peaks at 340 and 620 cm^{-1} which were assigned to the two infrared-active fundamental frequencies ν_4 and ν_3, respectively, and a weaker band at 1130 cm^{-1} which is probably the combination $\nu_3 + \nu_2$ (calc. 1127). The fundamental ν_4 is comparatively narrow (approx. 25 cm^{-1} half height width) whereas the ν_3 is much broader (over 100 cm^{-1}) and it seems that this is a general phenomenon of the hexafluoride complexes [14, 20].

The missing fundamental ν_6 is inactive and does not appear directly in either the Raman or IR spectrum. However, ν_6 can be determined from the emission spectrum by a vibrational analysis. The vibration ν_6 is antisymmetric (t_{2u}) and couples strongly with the $0-0$ transition to give rise to an intense emission band at 15801 cm^{-1}. The fundamental ν_6, determined in this way, is 229 cm^{-1}, which completes the assignment of fundamental frequencies for the complex MnF_6^{2-}. The fundamentals are summarized in Table 6, including their source. The frequency $\nu_7 = 61$ cm^{-1}, determined from the emission spectrum of Cs_2MnF_6 and 4.5 °K, is assigned to an (external) lattice mode. An analogous phonon band for the K complex was observed at 80 cm^{-1} from the origin. If ν_7 is a crystal lattice vibration, the frequency should be affected by a change of cation, as is observed when Cs is exchanged for K. The shift to higher energies is expected if one considers the different densities of the complexes ($\varrho(Cs_2MnF_6) = 3.73$, $\varrho(K_2MnF_6) = 3.98$ [8]).

In Table 4 the vibrational frequencies of Cs_2MnF_6 as observed in the emission spectrum and the relevant parts of the absorption spectrum at 4.5 °K are summarized and compared to the fundamental frequencies of the ground state or suitable combinations thereof. The combinations depend on the intensity mechanism operating which itself depends on the distortion of the crystal from O_h symmetry. An axial field, in the Cs complex, if present at all, has to be small because no splitting of the ^2E level in absorption or emission was detectable with the resolution employed (1 Å) and no measurable extinction was visible under the polarizing microscope. Furthermore, a splitting of approx. 10 cm^{-1} for this level was readily detected in the absorption spectrum of the K salt at 85 °K which is not cubic but hexagonal [8] and the half height width of the absorption bands is approximately twice the width of the appropriate bands of the Cs salt (≈ 10 cm^{-1} at 85 °K). Lack of data at lower temperatures and higher resolution preclude a further investigation of this complex at this point.

In perfect cubic symmetry, magnetic dipole transitions only are allowed. An example of a transition of this type is the $0-0$ transition of $^2E_g \to {}^4A_{2g}$ in Cr^{3+} : MgO which was established by Zeeman-effect studies [25]. The oscillator strength calculated from the absorption was found to be 7.2×10^{-9} [26]. The oscillator strength of the same transition for Cs_2MnF_6 calculated from the absorption spectrum of a single crystal at 85 °K is 4.2×10^{-9} which compares quite well with the value mentioned above suggesting that the same type of mechanism (magnetic dipole) is involved.

The intensities of the vibrational satellites are comparatively much stronger (for some by more than an order of magnitude) and they are dependent on temperature. For example, the band at 16244 cm^{-1} in the absorption spectrum (which is assigned as $\nu_{00} + \nu_6$ in Table 4) has an oscillator strength of 6.2×10^{-8} at 85 °K. Raising the temperature to 300 °K increases the oscillator strength by a factor of 2 to 1.24×10^{-7} (the increase calculated from the formula [27]:

$$f = f_0 \coth(h\nu/2kT), \qquad \nu = 229\ \text{cm}^{-1}$$

is 1.9) which is strong evidence that the intensities of the satellites are vibrationally induced. By this mechanism certain vibrations which can be determined by group theoretical methods couple with the $0-0$ transition to give rise to the observed vibrational structure. For an octahedral complex the vibrations predicted by group theory are the antisymmetric $t_{1u}(\nu_3$ and $\nu_4)$ and $t_{2u}(\nu_6)$ vibrations which couple to the $0-0$ transition of $^2E_g \leftarrow {}^4A_{2g}$. In Table 4 antisymmetric fundamentals and antisymmetric combinations of fundamentals are compared to the vibrations as observed in the emission and absorption spectrum of a single crystal of Cs_2MnF_6 at 4.5 °K. The pertinent results are:

1. The vibrational structure of the emission spectrum can within experimental error be satisfactorily explained by fundamental frequencies or combinations thereof predicted by group theory.
2. There is a "good" mirror-image relationship between the absorption and emission spectrum.

However, since the intensities of the emission bands are not corrected for response of the detecting instrument, the intensities of both spectra cannot be compared and the question "how good" cannot satisfactorily be answered. From an inspection of Fig. 1, it appears that the phosphorescence and the resonance emission spectra have intensity patterns which are similar to the intensity pattern of the absorption spectrum. In the case of such a mirror-image relationship the (natural) radiative lifetime τ_0 can be calculated from the experimental oscillator strength [28, 29] which is 1.6×10^{-2} sec (experimental 2.9×10^{-3} sec [7]). In view of the fact that the quantum yield of phosphorescence is not unity [18] $\tau_{\text{exp}} < \tau_0$ is expected and the predicted value of τ_0 is the right order of magnitude.

The bands at 17050, 17147 and 17434 cm^{-1} in the absorption spectrum could not be assigned to transitions associated with the ^2E_g state. Since they do not have a counterpart in the emission spectra (emission or resonance emission) they were assigned to vibronic transitions to the $^2T_{1g}$ state. This would place the origin of the $^2T_{1g}$ level at approx. 16810 cm^{-1}.

A similar approach was attempted to analyze the vibrational structure of the spin-allowed transitions. However, with the data available a detailed analysis of

Table 4. *Vibrational frequencies in emission and absorption spectrum of a single crystal of* Cs_2MnF_6 *at 4.5* °K

I(rel)	$\nu_{(Abs)}$	$\nu_{(Abs)} - \nu_{00}$	Assignment	Calc.	$\nu_{00} - \nu_{(Em)}$	$\nu_{(Em)}$	I(rel)
5.5	16034	0	$\nu_{00}(^2E_g)$	0	0	16030	5.3
1.2	16083	49	ν_7 [b]	—	61	15969	1.2
100.0	16259	225	ν_6	229	229	15801	100.0
73.4	16369	335	ν_4	340	334	15696	76.0
28.5	16645	611	ν_3	620	616	15414	10.6
4.2	16686	652	$\nu_4 + \nu_5$	650	648	15383	2.5
2.4	16752	718	$\nu_6 + \nu_2$	736	720	15310	1.4
7.4	16854	820	$\nu_6 + \nu_1$	829	816	15214	0.8
—	—	—	$\nu_4 + \nu_2$	847	839	15191	0.8
29.1	16965	931	$\nu_3 + \nu_5$	930	924	15106	0.5
24.2	17050	—	$^2T_{1g} + \nu_6$	—	—	—	—
17.6	17072	1038	$\nu_6 + \nu_2 + \nu_5$	1046	(1074 sh)[a]	—	—
8.0	17147 sh	—	$^2T_{1g} + \nu_4$	—	—	—	—
17.0	17159	1125	$\nu_3 + \nu_2$	1127	1122	14908	0.5
2.4	17241	1207	$3\nu_6 + \nu_2$	1194			
3.0	17274	1240	$2\nu_5 + \nu_3$	1240			
19.0	17352	1318	$3\nu_6 + 2\nu_5$	1307			
5.6	17396	1362	$\nu_4 + 2\nu_2$	1354			
12.8	17434	—	$^2T_{1g} + \nu_3$	—			
8.8	17470	1446	$\nu_3 + \nu_5 + \nu_2$	1437			
9.6	17548	1514	$3\nu_6 + \nu_5 + \nu_2$	1494			
8.8	17593	1559	$\nu_4 + 2\nu_1$	1540			
8.0	17646	1612	$3\nu_4 + \nu_1$	1620			
5.6	17662	1628	$\nu_3 + 2\nu_2$	1634			
2.4	17749	1715	$3\nu_6 + 2\nu_2$	1701			

[a] From Raman spectrum. — sh shoulder. — [b] ν_7 lattice mode.

the vibrational structure is difficult. Jahn-Teller instability, spin-orbit coupling (the single electron spin-orbit coupling parameter for the free Mn^{4+} ion is 415 cm^{-1}) and "solid state effects" like magnon sidebands (there are no data on magnetic susceptibilities of this complex) etc. have to be taken into consideration. Furthermore, fundamental frequencies derived for the excited state are not the same as those of the ground state because of the different geometrical configurations. Vibrational structure was observed in the transition $^4T_{1g} \leftarrow {}^4A_{2g}$ in the absorption spectrum at 85 °K (data are available at this temperature only) which has regular spacings of 480 and 580 cm^{-1} starting from the band centered at 27030 cm^{-1}. These spacings (cf. Table 5) were assigned to the vibrational modes ν_2 and ν_1, respectively which corresponds to a decrease of approx. 4% relative to the frequencies in the ground state. Whereas the ν_1 mode is symmetric and leaves the symmetry of the complex unchanged, the ν_2 mode causes a tetragonal distortion. The presence of this mode in a progression suggests that a Jahn-Teller distortion is present.

The rich vibrational structure in the $^4T_{2g} \leftarrow {}^4A_{2g}$ should permit a more complete study (Fig. 3) (the label $^4T_{2g}$ will be used in the remainder of the text although this state is probably split by spin-orbit coupling and/or a Jahn-Teller effect). As in the case of the structure in the $^2E_g \leftarrow {}^4A_{2g}$ transition the intensity of

Table 5. *Details of vibrational structure (in* cm^{-1}*) in* ${}^4T_{2g} \leftarrow {}^4A_{2g}$ *at 85 °K* (1), *at 4.5 °K* (2) *and in* ${}^4T_{1g} \leftarrow {}^4A_{2g}$ *at 85 °K* (3)

(1)	(2)	(3)
20355	—	27030
20447	—	
	20614	27510
	20627	27660
	20640	27780
	20687	
	20730	28090
20768	20799	
20826	20859	28570
	20938	
20969	21008	29150
	21181	
21304	21331	29630
	21368	
21404	21441	
21459	21492	
	21570 sh	
	21659 sh	
21791	21815	
21834	21882	
	21949	
	22017 sh	
	22237 sh	
22292	22306	
22336	22381	
	22422	
22495	22517	
22743	22779	
22831	22862	
22910	22931	
23245	23272	
23354	23386	
23447	23485	
23781	23815	
23923	23929	
24067	24067	
24301		

sh shoulder.

Table 6. *The fundamental frequencies of* MnF_6^{2-}

Vibration	Symmetry	Ground state			Excited states		
			${}^4A_{2g}$		${}^2E_g$	${}^4T_{2g}$	${}^4T_{1g}$
		(Raman)	(IR)	(emission)	(from absorption spectrum)		
ν_1	a_{1g}	600	—	(587)[a]	(605 ± 7)[a]	575 ± 15	580
ν_2	e_g	507	(510)[a]	(501 ± 9)[a]	(513 ± 20)[a]	482 ± 10	480
ν_3	t_{1u}	—	620	616	611	381?	—
ν_4	t_{1u}	—	340	334	335	232?	—
ν_5	t_{2g}	310	—	(312 ± 4)[a]	(316 ± 6)[a]	—	—
ν_6	t_{2u}	—	—	229	225	172??	—
ν_7	(lattice mode)	—	—	61	49	—	—

[a] From combinations.

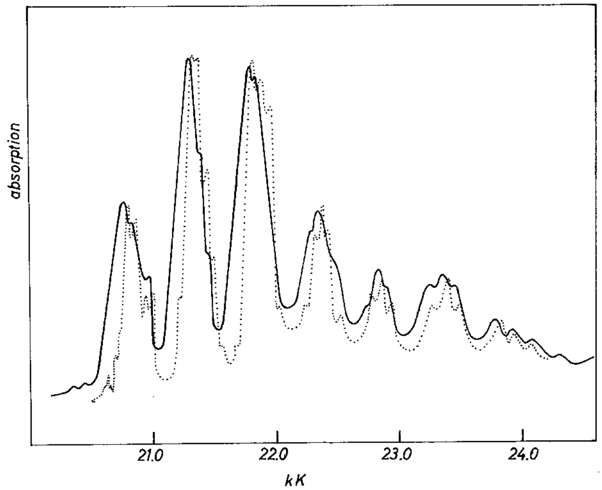

Fig. 3. Absorption spectrum of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition of Cs_2MnF_6 at 85 °K ———, at 4.5 °K ....

the bands are dependent on temperature suggesting that a vibronic intensity mechanism is operating. That the modes ν_1 and ν_2 are involved or combinations thereof can be seen from the progressions of regular spacings of 575 ± 15 and $482 \pm 10\,cm^{-1}$ originating at 20799, 20859 and 21008 cm^{-1} (Table 5). From position, spacing and intensity (oscillator strength approx. 10^{-5}) one is tempted to assign these three bands to the antisymmetric ν_6, ν_4 and ν_3 modes coupled to an electronic transition. The distance to the band lowest in energy which appears on the tail of the intense band at 20799 cm^{-1} is 172, 232 and 381 cm^{-1}, respectively, which would be quite small, especially for "ν_3".

The band lowest in energy, located at 20630 cm^{-1} could be an origin of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition considering its intensity and position: the band is weak and has an oscillator strength of approx. 10^{-6} which is in the range expected for a spin-allowed magnetic dipole transition ($f \sim 10^{-5}$) [30] and at higher temperatures hot bands appear on the low energy side of this "origin" (Fig. 3). Under increased resolution, however, the band splits into three components at 20614, 20627 and 20640 cm^{-1}, the first and the last appearing as shoulders.

Studies on K_2MnF_6 at 85 °K indicate that the origin of $^4T_2 \leftarrow {}^4A_2$ is split by 290 cm^{-1}. The strong static trigonal field of the crystal probably overrides the effects of spin-orbit coupling and Jahn-Teller instability. Progressions involving the symmetrical mode $\nu_1(a_1)$ only were observed [18].

A good starting point for a detailed analysis of the vibrational structure in the spin-allowed transitions of Cs_2MnF_6 would be a calculation of the spin-orbit and Jahn-Teller splittings which is left as a challenge to theorists.

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References

1. Forster, L. S.: Transition metal chemistry **5**, 1, ed. by R. L. Carlin. New York and London: M. Dekker 1969.
2. Witzke, H.: Ph. D. Thesis, University of British Columbia (1970).
3. Condrate, R. A., Forster, L. S.: J. chem. Physics **48**, 1514 (1968).
4. — — J. molecular Spectroscopy **24**, 490 (1960).
5. Schläfer, H. L., Gausmann, H., Zander, H. U.: Inorg. Chem. **6**, 1528 (1967).
6. Wood, D. L., Ferguson, J., Knox, K., Dillon, J. F., Jr.: J. chem. Physics **39**, 890 (1963).
7. Pfeil, A.: Spectrochimica Acta **26** A, 1341 (1970).
8. Bode, H., Wendt, W.: Z. anorg. Chem. **269**, 165 (1952).
9. Palmer, W. G.: Exp. Inorg. Chem. 484 (1962).
10. McQuaker, N. R.: Ph. D. Thesis, University of British Columbia (1970).
11. Matwiyoff, N. A., Asprey, L. B.: Chem. Comm. **1970**, 75.
12. Bode, H., Brockmann, R.: Z. anorg. Chem. **269**, 173 (1952).
13. Wilson, E. B., Jr., Decius, J. C., Cross, D. C.: Molecular vibrations. New York: McGraw-Hill 1955.
14. Reisfeld, M. J.: J. molecular Spectroscopy **29**, 120 (1969).
15. Classen, H. H.: J. chem. Physics **30**, 968 (1959).
16. Behringer, J.: Raman spectroscopy, ed. by H. A. Szymanski, p. 168. New York: Plenum Press 1967.
17. Siebert, H., Eysel, H. H.: J. molecular Structure **4**, 29 (1969).
18. Pfeil, A.: Unpublished results.
19. Woodward, L. A., Creighton, J. A.: Spectrochimica Acta **17**, 594 (1961).
20. Meyers, D. A., Cotton, F. A.: J. Amer. chem. Soc. **82**, 5027 (1960).
21. Woodward, L. A., Ware, M. J.: Spectrochimica Acta **19**, 775 (1963).
22. — Anderson, L. E.: J. inorg. nuclear Chem. **3**, 326 (1956).
23. Griffiths, J. E., Irish, D. E.: Inorg. Chem. **3**, 1134 (1964).
24. Kriegsmann, H., Kessler, G.: Naturwissenschaften **47**, 393 (1960).
25. Sugano, S., Schawlow, A. L., Varsanyi, F.: Physic. Rev. **120**, 2045 (1960).
26. Imbusch, G. F.: AEC Access No. 42155, Rept. No. ML-1190, available OTS (1964).
27. Liehr, A. D., Ballhausen, C. J.: Physic. Rev. **106**, 1161 (1957).
28. Birks, J. B., Dyson, D. J.: Proc. Roy. Soc. (London) A **275**, 135 (1963).
29. Strickler, S. J., Berg, R. A.: J. chem. Physics **37**, 814 (1962).
30. McCaffery, A. J., Mason, S. F.: Trans. Faraday Soc. **59**, 1 (1963).

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