An Apparent Resonance Effect in the Vibrational Raman Spectrum of Cs_2MnF_6†

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Summary The extremely intense bands observed in the vibrational Raman spectrum of Cs_2MnF_6 (s) may be due to a resonance Raman effect caused by the proximity of the He/Ne exciting line to a number of *d–d* transitions of Mn^{IV}.

THE polarizability derivatives associated with M–F vibrations (where M is a metal ion) are small and, consequently, the intensities of M–F vibrations detected in the Raman effect are generally weak.[1] In contrast, we have observed extremely intense bands in the Raman spectrum of Cs_2MnF_6. The Figure shows the striking difference between the Raman spectra of Cs_2MnF_6 and Cs_2NiF_6 whose spectrum is typical of those observed for most complex fluoro-anions of the transition elements. Both salts contain isolated MF_6^{2-} octahedra.[2] Two features in the spectra are especially noteworthy: (i) All bands in the spectrum of Cs_2MnF_6 are much more intense than those in the spectrum of Cs_2NiF_6. It should be emphasized that much smaller slit width and amplifier gain settings were used to obtain the spectrum of Cs_2MnF_6. (ii) In common with other octahedral F^- ion complexes, the NiF_6^{2-} ion exhibits only the ν_1, ν_2, and ν_5 fundamentals in the Raman spectrum. However, many overtone and combination bands are apparent in the spectrum of Cs_2MnF_6. The tentative assignments listed in the Table were made with the aid of the Raman spectra of 1 M-anhydrous HF solutions of Cs_2MnF_6 and K_2MnF_6. Those solutions exhibit only three Raman bands which can be attributed to MnF_6^{2-} vibrations:[3] ν_1 615, ν_2 480, and ν_5 282 cm^{-1}.

TABLE

Raman frequencies of solid Cs_2MnF_6

Observed frequencies (cm^{-1})	Tentative assignment	Calculated frequency
115	Lattice mode (ν_L)	—
346	$2\nu_2 - \nu_1$	345
397	$\nu_5 + \nu_L$	397
420	$\nu_1 + \nu_5 - \nu_2$	417
512	$\nu_5 + 2\nu_L$	512
595	$\nu_2 + \nu_L$	595
615	ν_1	615
707	$\nu_2 + 2\nu_L$	710
804	$\nu_1 + \nu_2 - \nu_5$	813
903	$\nu_1 + \nu_5$	897
965	$2\nu_2$	960
1012	$\nu_1 + \nu_5 + \nu_L$	1012
1065	$\nu_1 + 2\nu_5 - \nu_L$	1064
1095	$\nu_1 + \nu_2$	1095
1195	$2\nu_2 + 2\nu_L$	1190
1234	$2\nu_1$	1230
1345	$2\nu_1 + \nu_L$	1345
1357	$2\nu_2 + \nu_5 + \nu_L$	1357
1400	$2\nu_1 + \nu_5 - \nu_L$	1397

The high absolute intensities and the abnormal distribution of the relative intensities of the bands in the spectrum of Cs_2MnF_6 may be due to a resonance Raman effect.[4] The bands are probably too sharp to be due to resonance fluorescence.

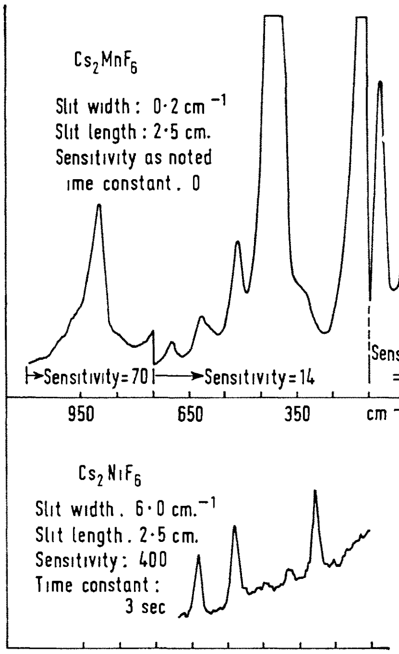

FIGURE. *Raman spectra of* Cs_2MnF_6 *and* Cs_2NiF_6 *obtained using he* 6328 Å *line of a* He/Ne *laser.*

The Raman spectra were obtained with a Model 81 Cary spectrometer using the 6328 Å line of a Spectra Physics He/Ne laser as the exciting line. The MnF_6^{2-} ion contains Mn^{IV} having a d^3 electronic configuration and, as required for the resonance effect, the ion exhibits a number of electronic transitions (*d–d*) near the exciting line. We have distinguished narrow weak bands at 6376, 6160, 6336, 6115, 6015, 5900, 5870, 5832, 5770, and 5741 Å in the electronic absorption spectra of Nujol and Fluorolube mulls of Cs_2MnF_6.[5] These bands, which are presumably due to the spin forbidden $^2T_{1g}$, $^2E_g \rightarrow {}^4A_{2g}$ transitions split by spin-orbit and vibronic coupling,[6,7] are well resolved but occur on the low-energy "tail" of an intense broad band centred at *ca.* 4650 Å. The latter, due to the spin-allowed $T_{2g} \rightarrow {}^4A_{2g}$ transition, exhibits vibrational fine structure (spacing *ca.* 520 cm^{-1} at 25°) probably associated with the ν_1 vibration of the $^4T_{2g}$ electronic state.

The vibronic theory of the resonance Raman effect requires that those vibrations which enable the electronic transition(s) responsible for the resonance effect, appear with enhanced intensities in the Raman spectrum.[4,8,9] In this regard, the prominence of the lattice vibration, ν_L, in the Raman spectrum is particularly interesting. Consequently, we are attempting to resolve in more detail the

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vibronic structure of both the spin-allowed and spin-forbidden electronic transitions of Cs_2MnF_6 (and other salts of the MnF_6^{2-} ion which also exhibit a resonance Raman effect) by studying its absorption spectrum at liquid-helium and liquid-nitrogen temperatures.

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