

Spectral intensities in cubic systems. I. Progressions based upon parity vibrational modes

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The well-resolved emission and absorption spectra of centrosymmetric coordination compounds of the transition metal ions have been used widely to provide the experimental data against which to test theoretical models of vibronic intensities. With reference to the $2E_g \rightarrow 4A_{2g}$ luminescence transition, at a perfect octahedral site in Cs_2SiF_6 , over than one hundred vibronic lines are observed with line widths of a few wavenumber spread over some 3000 cm^{-1} . This paper reports a thorough examination of both the electronic and vibrational factors, which influences the observed vibronic intensities of the various assigned and identified lines in the spectra of the MnF_6^{2-} complex ion in the Cs_2SiF_6 cubic lattice. The origin and nature of higher order vibronic interactions are analysed on the basis of a symmetrized vibronic crystal field-ligand polarization model.