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HYPERSENSITIVE TRANSITIONS IN RARE-EARTH IONS

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A few years ago, it was noticed that the intensities of some absorption lines in the solution spectra of rare-earth ions are peculiarly sensitive to the solvent.¹ The source for the hypersensitivity was later studied in detail.² The selection rules for the lines in question, which all correspond to transitions within the 4f shell, are identical to those for pure quadrupole radiation; but the calculations revealed that the observed intensities are much too large by several orders of magnitude for this to be the explanation. Dynamic mechanisms depending on vibrations in the liquid were also rejected, as were sources depending on variations of covalency. It was concluded that the hypersensitivity owed its existence to the inhomogeneous polarizability of the solvent, which was visualized as enhancing the variation of the electric vector of the electromagnetic radiation across a rare-earth ion, thereby greatly increasing the intensities of quadrupole transitions.

Subsequent work has tacitly accepted this explanation,³ though some scepticism has recently been expressed.⁴ The purpose of this note is to air a certain uneasiness in the previous analysis,² and, in particular, to point out a new source for the hypersensitivity.

To obtain changes in intensity of lines satisfying quadrupole selection rules, it would only be necessary to vary the amplitudes of terms of the type Y_{lm} in the electric potential of the complex surrounding a rare-earth ion. These terms permit forced electric dipole transitions, and the combination of Y_{lm} with the dipole operator reduces to an effective quadrupole operator within the $4f$ shell. However, there is a classic argument for excluding the harmonics Y_{lm} from the Hamiltonian. Unlike all Y_{km} with $k > 1$, they possess nonvanishing derivatives at the origin, namely, the nucleus of the rare-earth ion. This implies the existence of an electric field at the nucleus, and hence that the rare-earth ion and its complex are not in equilibrium. Any static model, it seems, would necessarily have to exclude them: and for this reason they were rejected in previous work.^{1,2} However, this argument overlooks the fact that the electrons of the rare-earth ion may also produce an electric field at the nucleus that exactly cancels that coming from the neighboring ions. Evidently this asymmetrical electronic distribution within the rare-earth ion can be regarded as being produced by the external electric field; so, for calculating the mixing of the $4f$ orbitals with those of opposite parity, the terms Y_{lm} should be included in the Hamiltonian. Of course, not all arrangements of solvent molecules around the central rare-earth ion produce such terms. In Table I, the 32 point symmetries are divided into those that (a) possess no harmonics Y_{km} with k odd; (b) possess some harmonics Y_{km} with k odd, but none with $k = 1$; (c) possess harmonics Y_{km} with $k = 1$. (This table

is constructed from Table 5 of Prather.⁵⁾ On this basis, an enhanced pseudoquadrupole transition would indicate a symmetry type falling into category (c); and, from the estimates of the dynamic effects,² it would be necessary to assign this symmetry to the nearest neighbors to reproduce an order of magnitude change in the intensity. This does not rule out the mechanism depending on quadrupolar enhancement by dielectric inhomogeneity, which must, of course, contribute to some extent; but assigning the hypersensitivity principally to a simple change of point symmetry seems much more plausible.

It is interesting to note that the rare-earth double nitrates possess the point symmetry C_{3v} at a rare-earth site.⁶ On the present theory, but not necessarily on that depending on pseudoquadrupole transitions, we would expect the hypersensitive lines to be enhanced relative to the others. It is thus significant that the lines at 17300 cm^{-1} and 19320 cm^{-1} in Nd^{3+} , already classed as hypersensitive,¹ appear to be the most intense in the absorption spectrum of $\text{Nd}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$.⁷

Finally, it is to be noted that for Sm^{2+} at a site of C_{4v} symmetry in BaClF , there appears to be very strong evidence for terms of the type Y_{lm} in the Hamiltonian.⁸ This is consistent with the classification in Table 1.

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Table I. Classification of point groups.

(a) $C_i, C_{2h}, C_{4h}, C_{6h}, D_{2h}, D_{4h}, D_{6h}, D_{3d}, S_6, O, O_h, T_h.$

(b) $D_2, D_{2d}, D_3, D_{3h}, D_4, D_6, C_{3h}, S_4, T, T_d.$

(c) $C_s, C_1, C_2, C_{2v}, C_3, C_{3v}, C_4, C_{4v}, C_6, C_{6v}.$

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