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Oscillator Strengths for f → d Transitions in Lanthanide and Actinide Aqua Ions*

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Over the years, direct transitions in which an f electron is excited to a d state have been observed for a number of tripositive lanthanide and actinide aqua ions. Several authors, among them Reisfeld and Jϕrgensen [1], Carnall [2] and more recently Svetashev and Tsvirko [3], have noticed that the oscillator strengths P are rather small (of the order of 10^{-2} or even much less) for transitions that, on the face of it, are strongly allowed. The Thomas–Reiche–Kuhn sum rule for all transitions from the ground state of an ion gives a total P of N, the number of electrons of the ion. This should be taken literally (giving $P = 55$ for Ce^{3+}), but it is clear that contributions from excitations from closed shells are of no immediate interest. If all the electrons except those in the f shell are assumed to move in a central potential (thus neglecting the exchange effects that Fock [4] was aware of), and be insusceptible to excitation, P is reduced to a value equal to the number of f electrons. For Ce^{3+}, $P = 1$; but partial closure over just the d states (ignoring the g states, which contribute 12/7 to P) yields $P = -5/7$, the negative number coming from the ostensibly occupied d shells lying at deeper energies than the electrons in the open f shell. Thus the 3d and 4d states in Ce^{3+}, although occupied, must provide a formal contribution of at least −0.72 to the total P, and the observed transitions 4f → 5d make a very minor contribution to it. We find the two equivalent expressions

$$\sum_b P_{ab} = (2N/7)\chi\langle 4f|(\partial/\partial r) - 2r^{-1}|5d\rangle\langle 5d|r|4f\rangle \quad (1)$$

$$= -(2N/7)\chi\langle 4f|r|5d\rangle\langle 5d|(\partial/\partial r) + 4r^{-1}|4f\rangle \quad (2)$$

for the sum over all transitions from a state a of $4f^N$ to all states b of the single lanthanide configuration $4f^{N-1}5d$. In these formulas, the environmental factor χ is 1.19 (for aqueous solutions). The bras and kets denote R_{4f}/r or R_{5d}/r, the integration in the matrix elements being performed with the measure $r^2 dr$.

It may not be convenient to calculate the matrix elements of $\partial/\partial r$. If we are prepared to take the states of $4f^{N-1}5d$ as a degenerate set at an energy ΔE above the initial state a of $4f^N$, eqns. (1) and (2) become

$$\sum_b P_{ab} = (2N/7)\chi(\Delta E/E_0)\langle 4f|(r/a_0)|5d\rangle^2 \quad (3)$$

where $E_0 = 219\,475$ cm^{-1} and $a_0 = 0.5292$ Å. For Ce^{3+}, an extrapolation of the radial integrals of Carnall *et al.* [5] yields $\langle r/a_0\rangle_{4f,5d} = 0.828$. With $\Delta E \simeq 44\,000$ [2] and $N = 1$, we get $\Sigma_b P_{ab} = 0.047$, which is larger than the observed [2] figure of 0.022.

For $N > 1$, we may want to restrict b to just those states ψ coming from a parent ψ' of $4f^{N-1}$. This can be done by multiplying eqn. (3) by the squared coefficients of fractional parentage (cfp) $(4f^{N-1}\psi' + f|4f^N\psi)^2$. Thus the transitions $^7F \rightarrow (^8S)5d\,^7D$ of Tb^{3+} and Bk^{3+} gain a factor of 8 (compared to Ce^{3+}) from N, but lose a factor of 7 from the cfp. With adjusted radial integrals we calculate $P = 0.029$ for the Tb^{3+} band at 45 800 cm^{-1} and $P = 0.060$ for the Bk^{3+} band at 41 000 cm^{-1}. These overshoot the experimental [6] values of 0.0033 and 0.009 by an order of magnitude. A loss of the 5d or 6d wavefunctions to the ligands would explain the small observed figures, but the separation of ^9D and ^7D in Tb^{3+} $4f^7(^8S)5d$ is only slightly reduced in aqueous solutions (namely, to 7800 cm^{-1} from a free-ion [7] value of 9364 cm^{-1} for the relevant levels $^9D_5$ and $^7D_5$). A further complication is the small size of $P(^7F \rightarrow {}^9D)/P(^7F \rightarrow {}^7D)$, namely 2×10^{-3} [6], which is an order of magnitude less than the figure of 0.03 that specifies [7] the mixture of ^7D in ^9D.

No detailed discussion of these results can be given here. We note, however, that the Franck–Condon principle would reduce all calculated intensities by products of vibrational overlaps. Although this mechanism amounts to a mere redistribution of intensity among vibronic components, it should not be ignored. The breakdown of Russell–Saunders coupling would also redistribute intensity and lower the calculated P values for nominally allowed transitions.

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