Excited states of cerium(III) in various local symmetries by UV absorption and luminescence spectra

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Abstract: Among trivalent lanthanides, cerium has the lowest-lying $5d^1$ configuration with up to five distinct Kramers doublet energies, strongly separated by chemical bonding of the same kind as known from Re, Os, Ir, Pt complexes with ground configuration $5d^9$, but with more moderate spin-orbit coupling effects in Ce. Lanthanides rather indifferently show all the coordination numbers N from 6 to 12 (11 for CeF_3) and elastic internuclear distances. Stokes shifts can only be superficially rationalized with one configurational coordinate out of many.

Gaseous Ce^{+3} has its three first excited J-levels at 2253 ($^2F_{7/2}$), 49737 ($^2D_{3/2}$), and 52226 cm^{-1} ($^2D_{5/2}$) above the groundstate $^2F_{5/2}$. In all four levels, one single electron moves on a background of the closed shells. The absorption spectra of cerium(III) compounds, and the Ce(III) sites dispersed in crystals and glasses, are only faintly influenced by the seven Kramers doublets of 2F (also because of superposed vibronic spectra) quite in contrast to ytterbium(III) with a narrow absorption structure a few hundred cm^{-1} around the only excited $4f^1$ level $^2F_{5/2}$ of gaseous Yb^{+3} at 10214 cm^{-1} . On the other hand, transitions from the odd-parity $4f$ to even-parity $5d$ levels in Ce(III) have oscillator strengths p as large as 0.01 to 0.1 to be compared with 10^{-7} to 10^{-5} for typical transitions [1] to excited $4f^q$ levels of lanthanides(III).

Freed [2] detected four strong, rather broad, absorption bands between 39000 and 48000 cm^{-1} in crystalline $[\text{CeLa}_{1-x}(\text{OH})_9](\text{C}_2\text{H}_5\text{OSO}_3)_3$. The aqueous solution shows five similar bands [3-5] close to 39600, 41700, 45000, 47400 and 50000 cm^{-1} . A 40 times weaker band at 33800 cm^{-1} was already [2] observed in undiluted ($x=1$) ethylsulfate and drew considerable attention [6,7] as due to another aqua ion, low-symmetry $\text{Ce}(\text{OH}_2)^{+3}$ formed by photochemical dissociation within a few nanoseconds, and itself luminescing at 31000 cm^{-1} with a life-time 27 ns (in aqueous solution 28000 cm^{-1} and 45 ns). Many Ce(III) complexes of anions in solution [4] show a strong absorption band in the region 30000 to 33000 cm^{-1} suggesting a coordination number $N = 8$ or lower.

The interpretation of the absorption and emission bands (usually split [8] slightly above 2000 cm^{-1} corresponding to 2F final states) is feasible in the Angular Overlap Model [9-11] considering the energies of the five $5d_3$ -like orbitals, and the spin-orbit coupling ζ_{5d} ($= 1000 \text{ cm}^{-1}$ in gaseous Ce^{+3}) as parameters derived from observations. If the symmetry of the cerium(III) close surroundings is sufficiently high, group-theory induces constraints on the four independent one-electron energy differences to the extent that only one parameter Δ subsists in $(3z^2-r^2)$ and (x^2-y^2) being equally strongly anti-bonding in regular octahedral MX_6 compared to the weakly anti-bonding (xy) , (xz) and (yz) of identical energy. It is rather rare for Ln(III) to have $N=6$ (as the two sites in cubic C-type Ln_2O_3 with point-groups C_{3i} and C_2) and much more unusual to show 0_h . The most clear-cut case is CeCl_6^{3-} and CeBr_6^{3-} in anhydrous acetonitrile [12], but lanthanides can also be incorporated [13] in elpasolite structure $\text{Cs}_2\text{NaLnX}_6$. The Δ in solution [12]

is above 15000 cm^{-1} (i.e. [10] $5\sigma^* = e_g$ approximated by $(\Delta/3)$ being at least 5000 cm^{-1} , to be compared [14,15] with 8300 cm^{-1} for the highly covalent IrCl_6 with the lower orbitals filled by $5d$, and considerably shorter distance $\text{Ir}-\text{Cl}$ than $\text{Ce}-\text{Cl}$. The strong $4f \rightarrow 5d$ absorption band [12] of CeCl_6 at 30300 cm^{-1} and of CeBr_6 at 29200 cm^{-1} is asymmetric, agreeing with the expected spin-orbit coupling splitting 1500 cm^{-1} .

In one sense, the (at most) five differing energies of $5d$ -like orbitals in Ce(III) might be compared with a $5d^1$ system having the first of the strong absorption maxima as an effective ground state, and e.g. excited states of the aqua ion at 2100 , 5400 , 7800 , and 10400 cm^{-1} . On the other hand, the electrostatic (tiny non-spherical part of the Madelung potential) model (essentially collapsed at the Solvay meeting on Chemistry in Brussels May 1956) would have considered the average energy of the states, 44700 cm^{-1} in Ce(III) aqua ions, as zero-point of reference. This represents 0.87 times the average energy of the five $5d$ states of Ce^{+3} and is frequently considered an indicator of the central field $U(r)$ being less steep in Ce(III) (for decreasing r) than in Ce^{+3} . One should rather not use here the word "nephelauxetic effect" (since the observed [15,17] decreases of Slater-Condon-Shortley parameters of interelectronic repulsion, as compared to the gaseous ion, contain two other effects, i.e. moderate delocalization of anti-bonding d orbitals and enhanced correlation effects [18,19] are of comparable importance for $U(r)$ modification). The A.O.M. approach [10,16] would encourage the zero-point to be put at a non-bonding orbital. If only σ -anti-bonding effects are considered, they are equiconsequential with a perturbation by Kronecker point charges, and would be the $3d$ electron energy in ground states of $\text{Cr}(\text{NH}_3)_6^{+3}$ and $\text{Co}(\text{NH}_3)_6^{+3}$ but the zero-point is well below in CrF_6 and $5d$ IrCl_6 because of neglect of π -anti-bonding known [20] to be about a third for oxo, fluoro, and chloro ligands in both the d -groups and [21] the $4f$ group. From this point of view, the $5d$ zero-point is likely to be close to 25000 cm^{-1} in CeCl_6 and evaluated not far from 30000 cm^{-1} in the Ce(III) aqua ion for e_g estimated [6,7] to 4800 cm^{-1} . Actually, the five strong bands are rationalized by the crystallographic structure of $\text{Ce(OH}_2)_9$ (point-group close to D_{3h}).

Recent interest has concentrated [22,23] on CeF_3 and $\text{La}_{1-x}\text{Ce}_x\text{F}_3$ all crystallizing in the tysonite structure with $N = 11$. Not only is symmetry low, but the $\text{Ce}-\text{F}$ distances vary significantly, seven between 240 and 246 pm ($2.46 \text{ \AA}$), two 262 and two 297 pm . Factually, the four absorption bands [22] at 40500 , 43100 , 45900 , and 48300 cm^{-1} occur at some 1000 cm^{-1} higher energy than of the aqua ion, and a narrow band in the excitation spectrum for 313 nm (32000 cm^{-1}) emission [22] at 52400 cm^{-1} , about 2200 cm^{-1} above the aqua ion [5]. A much stronger band in the excitation spectrum occurs at 161 nm (62000 cm^{-1}) with P of order 1 . CeF_3 , pure or syncrystallized in LaF_3 , can be used as scintillator [24-26] for detection of high-energy photons and "elementary" particles. The emission at 310 nm (for x up to 0.1) has a life-time 20 ns at 10 K , slightly shorter than the Einstein radiative life-time. Stoichiometric CeF_3 shows a broader emission at 360 nm with the longer life-time 30 ns at 300 K . As in so many stoichiometric compounds, energy migration may be very efficient, and both crystalline defects or traces of chemical impurities, such as one $\text{Ce}-\text{F}$ contact being replaced with a shorter $\text{Ce}-\text{O}$ bond, may provide the shifted luminescence.

Although the Stokes shift in CeF_3 is quite large, 8000 cm^{-1} for intrinsic emission (low x at 10 K), and 13000 cm^{-1} for the (defect ?) emission at 360 nm , some crystalline cerium(III) compounds [27] show the first absorption maximum at low energy, and Stokes shift corresponding to green luminescence. Thus, cubic garnets such as $\text{Y}_3\text{CeAl}_5\text{O}_{12}$ have $N = 6$ and 4 sites almost regular octahedra and tetrahedra, but the sites with $N = 8$ accommodating larger cations have very low local symmetry. The Ce(III) emission bands are at 18200 and 27800 cm^{-1} with excitation maxima at 22000 (Stokes shift 3800) and 29400 cm^{-1} . Tetragonal crystals $\text{Y}_{1-x}\text{Ce}_x\text{OCl}$; $\text{La}_{1-x}\text{Ce}_x\text{OCl}$; and $\text{La}_{1-x}\text{Ce}_x\text{OBr}$ show an emission maximum at 26300 , 27800 , and 22800 cm^{-1} , respectively, with Stokes shift slightly above 5000 cm^{-1} .

A more extreme case of red cerium(III) luminescence [28] is known from the hexagonal $\text{Ln}_2\text{O}_2\text{S}$ derived from A-type Ln_2O_3 by letting oxide on the axis ($N = 1+3+3 = 7$) be replaced by sulfide. The absorption peak of $\text{Gd}_{2-x}\text{Ce}_x\text{O}_2\text{S}^{-1}$ at 21500 cm^{-1} almost coincides with 21600 cm^{-1} of $\text{Y}_{2-x}\text{Ce}_x\text{O}_2\text{S}$ and 21500 cm^{-1} of $\text{Lu}_{2-x}\text{Ce}_x\text{O}_2\text{S}$, with luminescence maxima at 14300 and 15300 cm^{-1} , respectively, and concomitant Stokes shifts 7300 and 6200 cm^{-1} .

These published data invite the question how to handle N neighbor atoms scattered around a given Ce(III) at highly varying distances R (20 pm or $0.2\text{ \AA}$ is quite a lot) and under apparently arbitrary angles. The treatment [9,11] involving Kronecker point repulsive interaction with the $5d$ electronic density (having the angular dependence characterizing $l = 2$) takes over the empirical fact derived from spectra measured under high hydrostatic pressure that one-electron energy differences within a given l -shell (keeping the angular distribution constant) increase 5 to 8 percent for each percent of decrease of R . This has nothing to do with the pre-1956 electrostatic effect proportional with R^{-5} (for regularly octahedral MX_6) but is rather [11] an exponential decrease with increasing R , as typical for chemical bonding. If the Kronecker "charge" of each of N ligators is the same, the five eigenvalues of a d shell would probably spread out like a Poisson distribution. On the other hand, if the Kronecker "charges" are (at least as an average) inversely proportional to N , one expects the angular discrimination (inherent in positive l values) to become less and less influent for large N and then approach the result [11] known for icosahedral MX_{12} , not separating the five orbital energies of a d shell, but inducing three and four f orbitals to have two distinct energies.

Among the many models we accept without much reluctance in d and f group spectra, is the Born-Oppenheimer factorization for N (at least 3) nuclei having $(3N-6)$ mutually independent internuclear distances, and hence potential (hyper-) surfaces in a space with $(3N-5)$ dimensions [18,29,30]. We may be so accustomed to two-dimensional paper and blackboard surfaces that the concept of "configurational coordinate" has become a conditioned reflex. The odd-shaped luminescence bands, their exuberant Stokes shifts, their furtive crossing of potential surfaces at unexpected manifolds of internuclear distances, their energy transfer, non-radiative relaxation and, eventually, photochemical reactions [31,32] all belong to this scenario, including electron transfer bands in lanthanides Ln(III) and Ln(IV) , and detachment of a $5d$ electron in Ln(II) to a kind of "colour centre" [33].

Acknowledgements

I am grateful to Professor Renata Reisfeld for extended collaboration on interpretations of luminescence, to a great extent rendered feasible by the grant 20-32127.91 from the Swiss National Science Foundation.

I am also grateful to Professor Christian Pedrini, Université Lyon I, for most helpful information related to the "Crystal 2000" project with CERN.

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