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Independent-Systems Mechanisms for f–f Transition Probabilities in Lanthanide Coordination Compounds*

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The Laporte-forbidden f–f electronic transitions of lanthanide coordination compounds acquire an electric-dipole probability by two mechanisms in the general independent-systems model, where overlap between the charge distributions of the metal ion and the ligands is neglected. A first-order electric-dipole transition moment arises, either from the mixing of the f–f with f–d and f–g electron promotions under the electrostatic field of the ligands, or from transient dipoles induced in the ligand groups by an allowed even-multipole electric moment of the f–f excitation. The electrostatic field and the ligand polarization mechanisms make complementary intensity contributions to the f–f transitions of a given Ln(III) complex, dependent upon the rank of the leading electric multipole moment. The polarization mechanism contributes principally to the intensities of the ligand-hypersensitive 2^2-pole f–f transitions, whereas the electrostatic mechanism is predominant for the 2^6-pole transition intensities, and makes the more important contribution in the 2^4-pole cases. Applied initially to Ln(III) complexes containing monoatomic ligands, which have an effective isotropic polarizability, the ligand polarization mechanism is found to depend, on extension to the corresponding polyatomic ligand cases, upon the anisotropy of the ligand polarizability tensor in complexes belonging to the higher non-centric symmetries.

Introduction

The f–f transitions of lanthanide and actinide coordination compounds are of the general type, $\Delta l = 0$, which includes the d–d excitations of transition metal complexes and the p–p promotions of heteroatoms in organic chromophores additionally. The probabilities of electronic transitions in the $\Delta l = 0$ class, or Δl even generally, are sensitive to the particular stereochemistry and to the polarizability of the ligand groups in the molecular environment of the open-shell metal ion or the organic heteroatom chromophore. Over a series of compounds containing a common metal ion or heteroatom chromophore, the oscillator strength covers a range of more than two orders of magnitude, dependent upon the symmetry of the ligand array and the electronic softness of the ligand groups. The oscillator strength range is common to the organic p–p type [1], a number of the d–d class in transition metal complexes [2], and to the quasi-quadrupolar f–f transitions of lanthanide coordination compounds [3, 4]. For chiral stereochemistries, the rotational strengths of the $\Delta l = 0$ transitions are even more sensitive than the corresponding dipole or oscillator strengths to the particular location and to the electronic properties of the ligand groups in the molecular environment of the chromophore [5].

Independent-Systems Mechanisms for Electronic Transition Probabilities

The localised-systems model for electronic transition probabilities, in which electron exchange between the chromophore and the ligands is neglected, assumed two forms during the 1930s, in connection with the theory of optical activity. The one-electron theory of Condon, Altar and Eyring [6] postulated a mixing of the electronic transitions of the chromophore under a static dissymmetric field due to the ligand groups. In contrast, Kirkwood [7] developed a quantum mechanical form of the classical polarizability theories of optical activity, based upon the view that the leading transition moment of the chromophore dynamically induces, and couples to, a secondary electric transition dipole in each ligand group.

Both of the independent-systems mechanisms were applied to the p–p type excitations of organic chromophores, notably the $n \rightarrow \pi^*$ carbonyl transition of chiral ketones. Following previous studies [8, 9], Watanabe and Eyring [10] and Bouman and Moscowitz [11] developed the static coupling model on the basis that, at the oxygen atom, the $2p_y \rightarrow 2p_x$ component of the carbonyl $n \rightarrow \pi^*$ transition near 300 nm is mixed with the corresponding Rydberg excitation, $2p_y \rightarrow 3d_{yz}$, under the field due to the

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incompletely-screened nuclei of the substituent atoms.

In the corresponding development of the dynamic coupling model, Höhn and Weigang [12] proposed that the leading electric moment of the carbonyl $n \rightarrow \pi^*$ transition, the xy-component of a quadrupole at the oxygen atom, induces a secondary electric dipole transition moment in a substituent group, dependent on the polarizability of the group and its location in the molecular frame of the carbonyl chromophore. The electric dipole induced in the substituent group, in conjunction with the zero-order magnetic dipole moment, gives the carbonyl $n \rightarrow \pi^*$ transition a rotational strength conforming to the empirical octant rule [12] and enhances the corresponding dipole strength [13].

The parallel development of the localised-systems model for the f–f and d–d transition probabilities in the lanthanide and transition-metal coordination compounds was confined largely to the static coupling mechanism, however, adopting the general procedure employed for the crystal-field interpretation of the observed Stark-splittings of the corresponding transition energies. Following the pioneer studies of Van Vleck [14] and others [15, 16], the static coupling mechanism for the Laporte-forbidden [17] transition probabilities was placed upon a quantitative basis for both the transition metal [18, 19] and the lanthanide [20, 21] coordination compounds.

The oscillator strengths of the d–d excitations in octahedral transition metal complexes are accommodated by the vibronic form of the static coupling mechanism [18], whereas the values calculated for the corresponding electronic transitions in analogous tetrahedral complexes are too small by some two orders of magnitude [19]. A further anomaly became apparent from studies of the temperature dependence of the d–d absorption intensities. The d–d oscillator strengths of octahedral transition metal complexes are found to increase as the temperature is raised, in accord with the vibronic static coupling mechanism. The intensity enhancement is due to the larger excursions from O_h symmetry with increasing temperature, owing to the increasing population of the higher vibrational levels of the non-totally symmetric modes in the electronic ground state of the complex [22]. A similar trend is expected for tetrahedral complexes, but the contrary behaviour is observed [23].

Stereochemical Ligand Hypersensitivity

In the parallel application of the static coupling mechanism and its vibronic extension to the f–f transition probabilities of lanthanide coodination compounds [20, 21] an exceptional set of hypersensitive f–f excitations was identified, following the selection rules for electric quadrupole transitions [3]. The oscillator strength of a hypersensitive f–f excitation, such as the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of a Nd(III) complex near 590 nm, covers a range of some three magnitude orders, dependent upon the stereochemical symmetry of the ligand set, the polarizability of the ligands, and the metal–ligand bond lengths [4]. At the lower end of the range, exemplied by Nd^{3+} as a guest ion in the LaF_3 host lattice, static coupling estimates give the 590 nm transition an intensity compatible with experiment [24], but the corresponding estimates for other Nd(III) complexes are too small, particularly for the trihalides NdX_3 in the vapour phase at the higher end of the range [25].

In the initial survey of the possible sources of f–f hypersensitivity, an inhomogeneous dielectric mechanism was suggested, based upon the quasidiatomic model of a lanthanide ion coordinated to a ligand with a polarizability larger than that of the surrounding medium [3]. The ligand increases the spatial gradient of the electric field vector of the radiation across the lanthanide ion, and so enhances the f–f electric quadrupole transition probability [3]. Although intensity data were available for a number of lanthanide coordination compounds, the inhomogeneous dielectric mechanism was applied to no specific cases, and its potential as a dynamic coupling alternative to the standard static crystal field mechanism was not fully appreciated until recently [26, 27].

Indeed an alternative or supplementary static coupling mechanism for f–f hypersensitivity was proposed, involving the addition of the first-rank harmonics Y_{1m} to the crystal field in order to form, with the electric dipole operator, an effective electric quadrupole operator within the 4f shell [28]. Crystal field potentials of the Y_{1m} form are non-zero only in metal complexes with the symmetries C_{pv} or lower, and the proposal is of limited application to the open-shell metal coordination compounds with dihedral symmetries, although a number of D_3 and D_{3h} complexes have quadrupolar d–d or f–f transitions with relatively large oscillator strengths. In such cases the Y_{1m} potentials are only effective vibronically, dependent upon the amplitudes of the non-totally symmetric vibrational modes of the complex.

The largest f–f oscillator strength reported as yet is that of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of NdI_3 in the vapour phase [25]. From an analysis of the infrared spectra of the neodymium halides in the gas phase at 1000 °C it is concluded that these molecules have a D_{3h} equilibrium nuclear configuration [29]. The conclusion is questioned from the results of an electron diffraction study of the lanthanide triiodides in the vapour phase near 800 °C, showing that NdI_3 has a bond angle of 112° in this temperature region [30]. At the elevated temperatures required for gas-phase spectroscopic [25, 29] and electron diffraction [30, 31] measurements the higher vibrational levels of the low-frequency out-of-plane bending mode, 98 cm^{-1} for NdI_3 [29], and the other modes, are extensively populated in the electronic ground state of the molecule, and the amplitudes of the nuclear motions are relatively large. The method of gas-phase electron-diffraction, with a time constant of only *ca.* 10^{-20} s, records the instantaneous relative atomic positions at, or near to, the turning points of the vibrational amplitudes [32]. Gas-phase electron diffraction studies of a number of lanthanide trihalides record instantaneous bond angles at temperatures 800–1000 °C in the range from 108° (GdI_3) [30] to 115.5° ($LaBr_3$) [31]. The vibrational amplitudes of the lanthanide trihalides at elevated temperatures and the metal–halide bond lengths, measured by electron diffraction, provide the structural data required for the application of the static coupling and the dynamic polarization mechanisms proposed to account for f–f hypersensitivity.

Isotropic Ligand Polarization

The problems of the static coupling mechanism for the probabilities of $\Delta l = 0$ transitions were particularly evident in the treatment of the d–d rotational strengths of chiral transition metal complexes. Sugano [33], in a critique of the pioneer study of Moffitt [34], showed that a first-order static coupling d–d rotational strength in a chiral complex containing an octahedral chromophore required a pseudoscalar crystal field which, at the minimum, is a ninth-power function of the electronic coordinates. While more satisfactory in principle, the corresponding second-order [35] and higher-order [36] perturbation treatments provided computed rotational strengths at variance with experimental observations.

The productive application of the complementary dynamic coupling mechanism for the estimation of dipole and rotational strengths to the p–p excitations of chiral ketones [12, 13], prompted an extension of the mechanism to d–d [37] and f–f [4] transition probabilities in open-shell metal ion coordination compounds. The extension provided a quantitative analysis for the d–d rotational strengths of the chiral tris-diamine complexes of cobalt(III) [38], and for the relatively large d–d dipole strengths [39], and the singular negative temperature coefficient of those strengths [40], in the tetrahedral halide-ion complexes of cobalt(II). In addition, the d–d Faraday transition probabilities determined from the magnetically-induced circular dichroism spectra of tetrahedral cobalt(II) complexes, while anomalous in sign according to static-coupling crystal field theory [41–43], are accommodated by the dynamic-coupling mechanism [44, 45]. Applied initially to investigate the large oscillator strengths of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ f–f transition of neodymium(III) in the gaseous trihalides [46, 47], the dynamic ligand polarization mechanism is found to account for a wide range of hypersensitive f–f intensities [48–50], including the dipole strengths vibronically-induced in centrosymmetric lanthanide coordination compounds [51, 52].

The Laporte-forbidden $\Delta l = 0$ electronic promotions, according to the ligand-polarization model, acquire a first-order electric dipole probability from the correlated resultant of electric dipoles induced in the individual ligands by an allowed even-multipole electric moment of the metal ion excitation. The allowed electric 2^{λ}-pole moments of a $\Delta l = 0$ transition lie in the range, $2 < \lambda < 2l$, that is, a quadrupole only for p–p promotions, the 2^2- and 2^4-pole for d–d excitations, and the 2^6-pole additionally in the case of f–f transitions. Owing to the dependence of the potential between an electric 2^{λ}-pole and a dipole on $R_L{}^{-\lambda-2}$, where R_L is the metal–ligand bond length, the dynamic polarization mechanism is the most effective for transitions with an electric quadrupole as the leading moment [46, 47].

For isotropic ligands, such as the halide ions, or with ligands taken to have the mean polarizability $\bar{\alpha}_L(\nu_{om})$ at the metal ion transition frequency, the first-order electric dipole moment, μ^{γ}_{om}, of the metal ion excitation, $M_o \rightarrow M_m$, with the electric quadrupole component, $\theta^{\alpha\beta}_{om}$, as its leading moment, is given by the relation,

$$\mu^{\gamma}_{om} = -\sum_{L} \theta^{\alpha\beta}_{om} G^{L}_{\alpha\beta\gamma} \bar{\alpha}_L(\nu_{om}) \qquad (1)$$

where the sum is taken over the ligands, L. The geometric tensor $G^{L}_{\alpha\beta\gamma}$ represents the radial and angular terms governing the potential between the electric quadrupole component, $\theta^{\alpha\beta}_{om}$, centred on the metal ion, and the induced dipole, with γ-polarization, located in the ligand, L. The Greek suffixes (α, β, γ) denote Cartesian components (x, y or z) in the coordinate frame of the metal complex.

The development of equation (1) for a given $|f^N J\rangle \rightarrow |f^N J'\rangle$ quadrupolar transition of the metal ion in a complex with a single set of symmetry-related ligands affords an expression for the dipole strength of the transition as a function of the L–M–L bond angle, with a constant M–L bond length [26, 45, 48]. Relative to a unit dipole strength for the corresponding monocoordinate diatomic M–L case, a trigonal ML_3 complex has a ligand polarization dipole strength which varies with the cosine of the L–M–L bond angle, c, according to the function, $3[1 - 3c + 5c^3]$, over the stereochemical range from D_{3h} to C_{3v}. For trigonal complexes ML_3, notably, the lanthanide trihalides in the vapour phase, the dipole strength is an optimum for the bond angle of 117°, but the ligand polarization intensity is only 1% smaller at the D_{3h} equilibrium nuclear configuration, and 6% smaller for the bond angle of 108° [45], which represents the largest out-of-plane vibrational amplitude measured by gas-phase electron diffraction for a lanthanide trihalide at 1000 °C [30]. The corresponding expression for the regular four-coordinate complexes over the general D_{2d} range, $\{-60[c + 2c^2 + c^3]\}$, shows that the ligand polarization dipole strength is optimum for an exact tetrahedral stereochemistry. The decrease in the dipole strengths of the quadrupole-allowed d–d transitions of the cobalt(II) tetrahalides is due to the larger vibrational excursions from regular T_d symmetry with an increase in temperature [40, 45].

The ligand polarization dipole strength of a quadrupolar transition in a four-coordinate metal complex is optimum at the highest symmetry, tetrahedral, over the D_{2d} range as only the xy-, yz-, and zx-components of the transition quadrupole moment at the metal ion coulombically correlate the electric dipole moments induced in the ligands to give a non-vanishing resultant first-order electric dipole transition moment for all variants of D_{2d} stereochemistry (Fig. 1). The corresponding dipole strength in a trigonal three-coordinate complex is not optimum at the highest symmetry, trigonal planar, over the C_{3v} range, however, since only the xy- and $(x^2 - y^2)$-components of the transition quadrupole moment, due to the $\Delta M_J = \pm 2$ transition components, produce an analogous coulombic correlation for a D_{3h} stereochemistry (Fig. 2). An out-of-plane bending deformation to C_{3v} symmetry gives rise to additional contributions to the resultant first-order electric-dipole transition moment from similar correlations of the dipoles induced in the individual ligands by the yz- and zx-components ($\Delta M_J = \pm 1$) and the z^2-component ($\Delta M_J = 0$) of the electric quadrupole transition moment located on the metal ion.

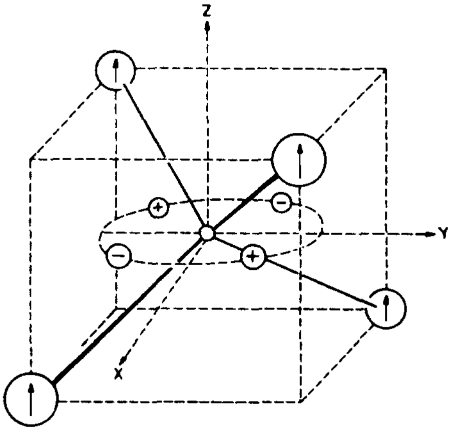


Fig. 1. The Coulombic correlation of the z-component of the electric dipole induced in each of the ligands of a tetrahedral metal complex by the xy-component of a quadrupole moment centred on the metal ion.

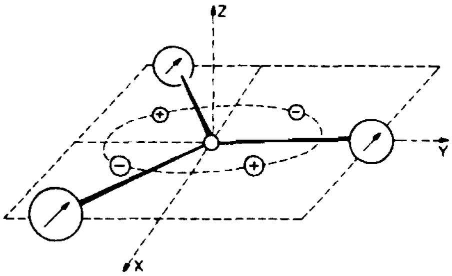
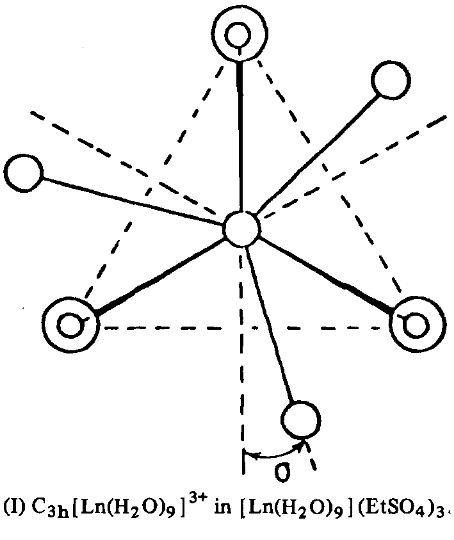


Fig. 2. The Coulombic correlation of the x-component of the electric dipole induced in each of the ligands of a trigonal metal complex by the xy-component of a quadrupole moment centred on the metal ion.

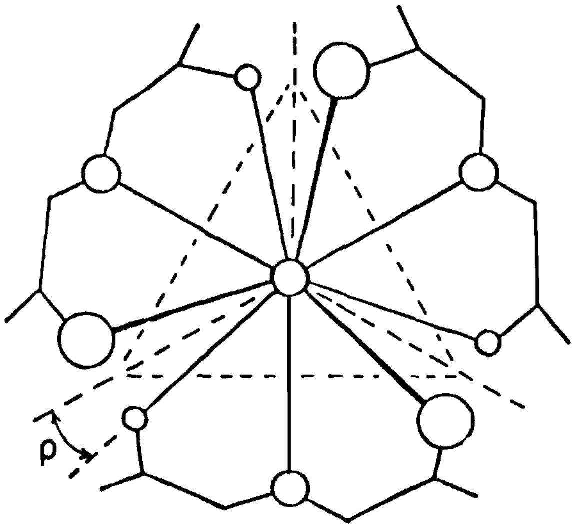
Anisotropic Ligand Polarization

New features of the dynamic polarization mechanism emerged from the analyses of the single-crystal polarized spectra of the trigonal europium(III) complexes, $[Eu(H_2O)_9](EtSO_4)_3$ (I), $Na_3[Eu(ODA)_3]\cdot NaClO_4\cdot 6H_2O$ (II), and $Gd(Eu)Al_3(BO_3)_4$ (III) [53, 54]. The $[EuO_9]$ cluster in each of the complexes (I) and (II) is made up of two ligand sets, a trigonal planar $[ML_3]$ group and a superimposed trigonal prism $[ML_6]$ group, the latter being regular (D_{3h}) in the nonahydrate (I), but distorted (D_3) in the complex (II), where each tridentate ODA ligand consists of the dianion of oxy-diacetic acid $[O(CH_2CO_2)_2]^{2-}$. The two D_{3h} ligand sets in the nonahydrate (I) are displaced by a small angle, *ca.* 5°, from the staggered configuration, so that the $[EuO_9]$ chromophore has C_{3h} symmetry overall. The six-coordinate $[EuO_6]$ cluster of the borate (III) has the D_3 distorted trigonal prism symmetry [54].

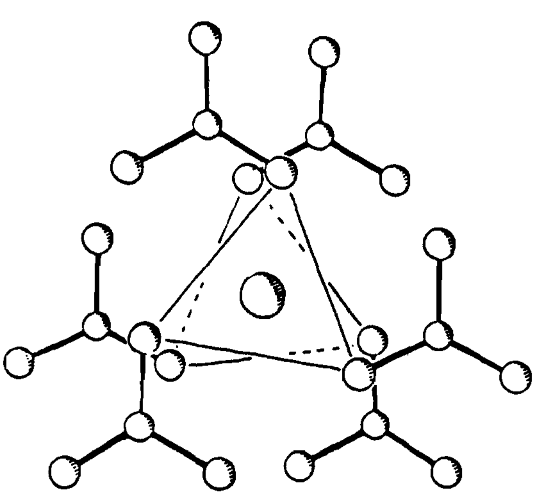
The application of equation (1) to the $\Delta M_J = \pm 2$ component of the $^7F_0 \rightarrow {}^5D_2$ f–f transition of Eu(III) at a trigonal site, where the (xy) and $(x^2 - y^2)$ components of an electric quadrupole are the leading



(I) $C_{3h}[Ln(H_2O)_9]^{3+}$ in $[Ln(H_2O)_9](EtSO_4)_3$.



(II) D_3 9-coordinate $[Ln(ODA)_3]^{3-}$ in $Na_3[Ln\{O(CH_2CO_2)_2\}_3]\cdot NaClO_4\cdot 6H_2O$.



(III) D_3 6-coordinate $[Ln(BO_3)_6]^{3-}$ in $Gd(Ln)Al_3(BO_3)_4$.

transition moments, shows that the contribution of both the $[ML_3]$ and the $[ML_6]$ ligand set to the first-order electric dipole transition moment is substantial. The two contributions are out of phase, however, so that the net resultant is small in the complexes (I) and (II). With only the $[ML_6]$ trigonal prism ligand set, the complex (III) has a $\Delta M_J = \pm 2$ dipole strength larger by an order of magnitude than the corresponding strength of either the complex (I) or (II) [54] (Table I). In contrast, the pure magnetic-dipole transition, $^7F_0 \rightarrow {}^5D_1$, is ligand-insensitive, and has a similar dipole strength in each of the Eu(III) complexes, (I), (II) and (III) (Table I).

The treatment of the $\Delta M_J = \pm 1$ component of the $^7F_0 \rightarrow {}^5D_2$ f–f transition of Eu(III), with the (yz) and (zx) components of an electric quadrupole as the leading moments at a trigonal site, requires a consideration of the anisotropy of the ligand polarizability. The $\Delta M_J = \pm 1$ component is observed in the spectra of the D_3 complexes (II) and (III), but not in that of the C_{3h} nonahydrate (I), as expected on group-theoretical grounds. The mean polarizability approximation of the dynamic coupling mechanism (eqn. 1) fails to account for the observed $\Delta M_J = \pm 1$ dipole strengths. These are accommodated by the inclusion of the ligand anisotropy through the relation,

$$\mu^{\gamma}_{om} = -\sum_{L} \theta^{\alpha\beta}_{om} G^{L}_{\alpha\beta\delta} \alpha^{L}_{\gamma\delta}(\nu_{om}) \qquad (2)$$

where $\alpha^{L}_{\gamma\delta}(\nu_{om})$ refers to the $\gamma\delta$-component of the polarizability tensor of the ligand L in the global coordinate frame of the complex at the transition frequency ν_{om}.

The electric dipole polarizability tensor of a ligand is made up of the three irreducible sets, $\underset{\sim}{\alpha}^{(0)}$, $\underset{\sim}{\alpha}^{(1)}$, and $\underset{\sim}{\alpha}^{(2)}$. The scalar mean polarizability, $\underset{\sim}{\alpha}^{(0)}$, enters into eqn. (1), whereas the five symmetric polarizability components, forming an irreducible second rank tensor $\underset{\sim}{\alpha}^{(2)}$, are of primary concern in eqn. (2). The three antisymmetric components, transforming like an axial vectorial set, $\underset{\sim}{\alpha}^{(1)}$, are significant for resonance transition probabilities, *e.g.* the resonance Raman effect [55], and the interactions between simultaneous transitions, electronic at the metal ion and vibrational in the ligand, detected by infrared circular dichroism spectroscopy [56].

TABLE I. The Frequency $\bar{\nu}$ (cm^{-1}) and the Dipole Strength D_{om} (10^{-66} C^2 m^2) of the Magnetic-Dipole $^7F_0 \rightarrow {}^5D_1$ Transition and the Electric Quadrupole $^7F_0 \rightarrow {}^5D_2$ Transition of Europium(III) Observed in the Axial (ax) and in the Orthoaxial Polarized (π, Parallel; σ, Perpendicular), Single-Crystal Spectra of $[Eu(H_2O)_9](EtSO_4)_3$ (I), $Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ (II), and $Gd(Eu)Al_3(BO_3)_4$ (III).

Transition		Polarization	(I)		(II)		(III)	
			ν	D_{om}	ν	D_{om}	ν	D_{om}
$^7F_0 \rightarrow {}^5D_1$	($\Delta M = \pm 1$)	π + ax	19020	30	18981	31	18966	38
	($\Delta M = 0$)	σ	19024	26	18965	24	18995	23
$^7F_0 \rightarrow {}^5D_2$	($\Delta M = \pm 2$)	σ + ax	21499	10	21433	14	21419	230
	($\Delta M = \pm 1$)	σ + ax			21484	62	21491	220

In general, the principal axes of the polarizability ellipsoid of a ligand group are not parallel to the global axes of the coordination compound, with an origin at the metal ion. The polarizability component of the ligand, $\alpha^{L}_{\gamma\delta}$ in eqn. (2), is transformed into the corresponding components which are diagonal in the local axes by means of the standard rotation matrix, or the equivalent matrix of direction cosines for the Cartesian forms. The first order electric dipole transition moment of eqn. (2) is stereochemically dependent, not only upon the bond lengths and angles of the ligand atoms directly coordinated to the metal ion, expressed in the geometric tensor, $G^{L}_{\alpha\beta\delta}$, but also upon the orientation of the bonds from the coordinated atoms to other ligand groups, expressed in the angular matrix transforming $\alpha^{L}_{\gamma\delta}$ to the local diagonal form, $(\alpha_{\|} - \alpha_{\perp})_L$ for cylindrical local bond symmetry.

The angular matrix changes the selection rules for the dynamic polarization mechanism. The general condition for a non-vanishing first-order electric dipole transition moment requires, in both eqns. (1) and (2), that μ^{γ}_{om} and $\theta^{\alpha\beta}_{om}$ transform under the same representation row of the point group to which the coordination compound belongs. In addition, the geometric tensor $G^{L}_{\alpha\beta\gamma}$ is required to be invariant under the operations of the group for each ligand in eqn. (1) [46, 47]. The second condition is not necessary in eqn. (2) where, with a non-totally symmetric geometric tensor $G^{L}_{\alpha\beta\delta}$, invariance to the operations of the group is restored by the angular transformation matrix in the combination $[G^{L}_{\alpha\beta\delta}\alpha^{L}_{\gamma\delta}]$, which is required to be totally symmetric [54, 57].

Thus eqn. (2) is less restrictive than eqn. (1). The former relation accounts for the observed $\Delta M_J = \pm 1$ dipole strengths of the $^7F_0 \rightarrow {}^5D_2$ transition of Eu(III) in the D_3 complexes (II) and (III) [54], and the d–d rotational strength of trigonal Cu(II) complexes, appearing when the chromophoric symmetry is reduced from C_{3v} to C_3 [58]. For some coordination symmetries, eqn. (2) adds no qualitatively new features to eqn. (1), as in the cases of the D_{3h} equilibrium configuration of the gaseous Nd(III) trihalides, the $C_{3h}[Eu(H_2O)_9]^{3+}$ complex ion (I), and complexes with regular T_d symmetry. For other coordination symmetries, notably D_4, only the anisotropy of the ligand polarizability makes a non-zero contribution to the first-order electric dipole transition moment (eqn. (2)), and the isotropic contribution (eqn. (1)) vanishes [54].

Complementary Static and Dynamic Coupling Intensity Contributions

The theory of f–f transition probabilities due to Judd [20] and Ofelt [21] provides, for a given lanthanide coordination compound, a set of three dipole strength parameters, Ω_λ (λ = 2, 4 or 6), which may be compared with the corresponding observed quantities. Although the Judd-Ofelt theory was formulated on the electrostatic crystal field basis [20, 21], the intensity parameterisation is general for all one-electron mechanisms [59]. The empirical intensity parameters are obtained from the manifold of $J \rightarrow J'$ bands, each with the dipole strength $D_{JJ'}$, observed in the f–f spectrum of the Ln(III) complex through the relation,

$$D_{JJ'} = (2J + 1)^{-1}\sum_{\lambda}\Omega_\lambda|(J'\|U^{(\lambda)}\|J)|^2 \qquad (3)$$

The reduced matrix elements in eqn. (3), $(J'\|U^{(\lambda)}\|J)$, refer to the unit tensor $U^{(\lambda)}$ operating within the $4f^N$ configuration and express the fractional even 2^λ-pole moment of the $J \rightarrow J'$ transition. The corresponding dipole strength parameters, Ω_λ, represent the square modulus of the first-order electric dipole moment of the f–f excitation, whether of a crystal field or another origin, associated with the zero-order electric 2^λ-pole moment (λ = 2, 4 or 6) of the transition. With a set of the reduced matrix element of $U^{(\lambda)}$, a least-squares analysis of the manifold of $J \rightarrow J'$ intensities in the spectrum of a given Ln(III) complex provides the three empirical Ω_λ(obs) parameters [60, 61].

The crystal field and the ligand polarization mechanisms for f–f transition probabilities are independent within the localised-systems model, and the first-order electric dipole moments given by the two mechanisms for a particular excitation are vectorially additive. The expression for the total dipole strength parameter, Ω_λ(tot), of the $J \rightarrow J'$ manifold exhibited by a particular Ln(III) complex contains terms corresponding, not only to the square modulus of each first-order electric dipole moment, Ω_λ(CF) for the crystal field contribution and Ω_λ(LP) for the ligand polarization contribution, but also to a pseudoscalar cross term, Ω_λ(CT), between the static and the dynamic component of the first-order electric-dipole transition moment,

$$\Omega_\lambda(\text{tot}) = \Omega_\lambda(\text{CF}) + \Omega_\lambda(\text{LP}) + \Omega_\lambda(\text{CT}) \qquad (4)$$

The cross term, Ω_λ(CT), is non-vanishing for a first-order static field and dynamic coupling electric dipole moment with the same polarization, connected with a common component of a given zero-order electric 2^λ-pole moment of the metal ion transition [62–64].

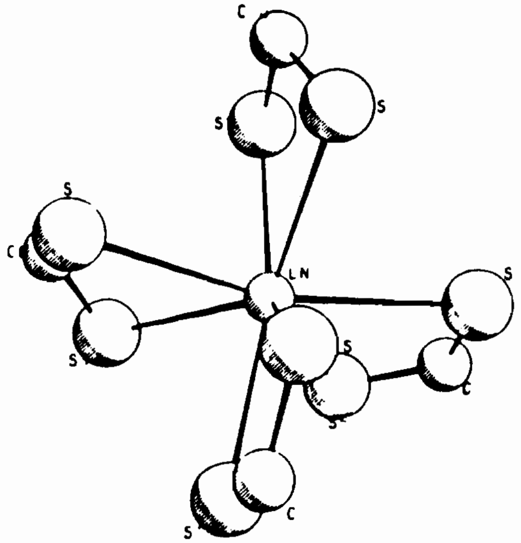
The ligand polarization dipole strength parameter, Ω_λ(LP), represents essentially the square modulus of the first-order electric-dipole transition moment of eqns. (1) and (2) and the analogous expressions for the corresponding zero-order electric 2^4- and 2^6-pole moments of the metal ion transition. The crystal field dipole strength parameter, Ω_λ(CF), is made up of two principal terms, one dependent solely on the metal ion, $P_{\lambda k}$, which expresses the mixing of a f–f transition possessing a leading 2^λ-pole moment with a dipolar 4f → 5d or 4f → ng transition, and the other dependent only on the ligands, B^k_m, representing the odd-parity electrostatic crystal field experienced by the metal ion,

$$\Omega_\lambda(\mathrm{CF}) = (2\lambda + 1) \sum_{k=1}^{7} \sum_{m=-k}^{k} |P_{\lambda k} B^k_m|^2 (2k+1)^{-1} \quad (5)$$

The order k of the crystal field parameter B^k_m is restricted to the values, $k = (\lambda \pm 1)$, with $\lambda = 2, 4$ or 6.

Estimates of the crystal field and the ligand polarization contributions to the overall dipole strength of particular $J \rightarrow J'$ f-electron transitions in the complexes $[\mathrm{Ln(H_2O)_9}]^{3+}$ (I) and $[\mathrm{Ln(ODA)_3}]^{3-}$ (II), for the Ln(III) cases of Pr, Eu, Tb and Ho, indicate that the crystal field contribution is generally dominant, the ligand polarization contribution being of comparable significance only for the hypersensitive quadrupolar transitions [62, 63]. In complexes of the structural types (I) and (II), the ligand polarization contribution to the first-order electric-dipole transition moment is minimised by negative interference, due to the out-of-phase relation between the individual contributions of the $[\mathrm{ML_3}]$ and the $[\mathrm{ML_6}]$ ligand sets [53, 54]. Moreover, for D_3 and higher dihedral coordination polyhedra, such as the complex (II), only the anisotropic polarizability contributions (eqn. 2) are non-zero for $\Delta M_J = \pm 1$ transitions [53, 54], and these contributions were not taken into account in the estimates [62, 63].

The eight-coordinate tetrakis(dithiocarbamate) Ln(III) complexes, $\mathrm{Na[Ln(Et_2dtc)_4]}$ (IV), provide a more comprehensive comparison of the relative crystal field and ligand polarization contributions to the overall dipole strength parameters, Ω_λ (eqn. 4), for the majority of the lanthanides [64]. Crystals of the coordination compounds, $\mathrm{Na[Ln(Et_2dtc)_4]}$, are isomorphous over the lanthanide range La to Yb, and the crystal structure of the La(III) complex, determined by X-ray diffractometry, shows that the $[\mathrm{LaS_8}]$ cluster has the stereochemical form of a distorted dodecahedron, in which the four $\mathrm{CS_2}$ chelate groups are arranged at the vertices of a quasi-tetrahedron (IV) [65]. The transition frequencies and the dipole strengths over the generally accessible f–f manifold have been determined for the majority of the $\mathrm{Na[Ln(Et_2dtc)_4]}$ complexes [65], allowing an extraction of the three dipole strength parameters, Ω_λ with $\lambda = 2, 4$ or 6, for each member of the series (IV) [64]. The values of Ω_λ(obs) thus obtained are listed in Table II, together with the



(IV) ψ-Td array of $\text{-}\mathrm{CS_2}^-$ ligand groups in $\mathrm{Na[Ln(S_2C\text{-}NEt_2)_4]}$

TABLE II. The Observed and the Calculated Dipole Strength Parameters, Ω_λ, of the f–f Transitions in the Series of $\mathrm{Na[Ln(Et_2dtc)_4]}$ Complexes, (IV). The Observed Ω_λ are Minimised Root-Mean-Square Values Based upon the Spectroscopic Data Reported by M. Ciampolini, N. Nardi, P. Colamarino and P. Orioli, *J. Chem. Soc. Dalton Trans.*, 379 (1977). The Individual Crystal Field Contributions Ω_λ(CF) are Listed for each Calculated Ω_λ, together with the Particular Ligand Polarization Contribution, Ω_2(LP). The Calculated Total, Ω_λ(tot), Sums the CF and LF Contributions with the CF-LP Cross Term.

Ln(III)	Ω_λ(obs)/10^{-61} (Cm)^2			Ω_λ(calc)/10^{-61} (Cm)^2						
	Ω_2	Ω_4	Ω_6	Ω_2(CF)	Ω_2(LP)	Ω_2(tot)	Ω_4(CF)	Ω_4(tot)	Ω_6(CF)	Ω_6(tot)
Pr(f^2)	7.19	3.83	2.56	1.31	18.72	27.83	2.04	4.13	2.92	2.98
Nd(f^3)	10.73	2.87	2.77	1.35	16.83	25.60	1.25	3.06	1.80	1.84
Sm(f^5)	4.71	3.71	1.27	0.82	13.89	19.94	1.11	2.23	1.37	1.40
Dy(f^9)	9.50	1.22	1.17	0.87	10.32	15.74	1.17	1.89	1.40	1.41
Ho(f^{10})	9.75	2.85	1.16	0.74	9.73	14.60	0.96	1.60	1.12	1.13
Er(f^{11})	9.46	0.62	0.81	0.76	9.19	13.99	0.98	1.57	1.14	1.15
Tm(f^{12})	8.51	3.00	0.82	0.78	8.69	13.46	1.01	1.57	1.14	1.15
Yb†(f^{13})				0.69	8.21	12.55	0.86	1.35	0.97	0.98

†The observed and the calculated values of the total dipole strength of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of the Yb(III) complex (IV) are 3.67 and 3.66, respectively, in units of 10^{-62} (Cm)^2.

corresponding calculated total value, Ω_λ(tot), and the more significant of the three constituent components (eqn. 4).

The calculated estimates of the total dipole strength parameters, Ω_λ(tot) for the series of Ln(III) complexes (IV) are in fair agreement with the corresponding empirical values Ω_λ(obs) only for $\lambda = 4$ and 6, the Ω_2(tot) estimates being too large (Table II). The calculated values listed do not take into account the opposing effects of the screening of the 4f electrons by the outer $5s^2rp^6$ shell [26] and the antiscreening due to the effective reduction of the charge on the Ln(III) ion from tripositive in the complex, or to other nephelauxetic effects. In principle [24], the Hartree-Fock radial expectation values for the 4f electrons of the Ln(III) ion, $\langle r^\lambda \rangle_{HF}$, require scaling by a screening, σ_λ, and an antiscreening, τ_λ, factor to give the effective value, $\langle r^\lambda \rangle_{eff}$, where,

$$\langle r^\lambda \rangle_{eff}/\langle r^\lambda \rangle_{HF} = (1 - \sigma_\lambda)/\tau_\lambda \qquad (6)$$

For the series of Ln(III) complexes (IV), the comparison of the Ω_λ(tot) estimates with the corresponding Ω_λ(obs) values indicates that the screening/antiscreening ratio (eqn. 6), while approximating to unity for $\lambda = 4, 6$, has a value of *ca.* 0.8 for the heavier lanthanides and decreases over the lighter lanthanides to *ca.* 0.5 for Pr(III) (Fig. 3, Table II).

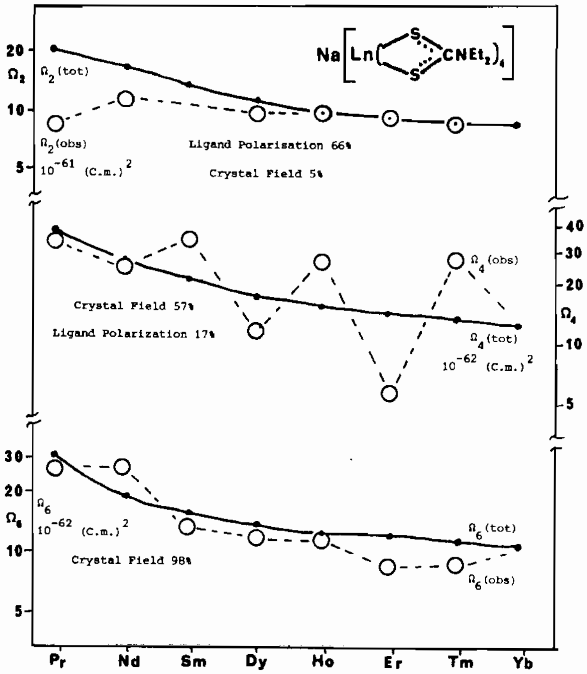


Fig. 3. The relationship across the series of lanthanide coordination compounds, Na[Ln(Et_2dtc)$_4$] (IV), between the observed, Ω_λ(obs), and the total calculated dipole strength parameter, Ω_λ(tot) (eqn. 4), with a screening/antiscreening ratio (eqn. 6) of unity for $\lambda = 4, 6$ and with the value of 0.8 for $\lambda = 2$. The calculated Ω_λ values of Table II refer to a ratio of unity throughout.

Calculated values of the screening constants σ_4 and σ_6 are small, but the values obtained for σ_2 are 0.675 for Tm^{3+} and as large as 0.825 for Pr^{3+} [66], the increase from Tm^{3+} to Pr^{3+} correlating semiquantitatively with the change in the screening/antiscreening ratio observed between the heavier and the lighter lanthanides for $\tau_2 \sim 0.4$ (Fig. 3, Table II). The extent of the reduction of the tripositive charge on a Ln(III) ion in a coordination compound, decreasing τ_2 below unity, remains as yet uncertain, but the corresponding reductions in transition metal complexes are substantial [67–69]. Direct integration of the electron density around the cobalt(III) ions in an X-ray diffraction study of the crystal $[Co(NH_3)_6][Co(CN)_6]$, indicates that the effective charge on the metal ion is +0.7 in the cation and +0.2 in the anion [67]. Analogous reductions in the effective positive charge on the metal ion are reported for $[Co(II)Cl_4]^{2-}$ [68] and $[Ni(II)(NH_3)_4]^{2+}$ [69]. Double-exponent 3d radial functions for cobalt [70] show that the expectation value of $\langle r^2 \rangle$ for a 3d electron of cobalt increases by a factor of 1.878 between the tripositive ion and the neutral atom, corresponding to $\tau_2 \sim 0.53$ in equation (6) with σ_2 negligible.

Overall the calculated dipole strength parameters (eqn. 4) show that the dynamic polarization mechanism is important mainly for the hypersensitive quadrupolar f–f transitions, as originally envisaged from the dependence of Ω_λ(LP) upon $R_L^{-2\lambda-4}$ [46, 47]. There are no major differences between the relative crystal-field and ligand-polarization contributions to the Ω_λ(tot) values across the series of Na[Ln(Et_2dtc)$_4$] complexes (IV) from Pr to Yb (Fig. 3, Table II). On an average over the series, the ligand polarization contribution to Ω_λ(tot) decreases from 66% to 17% and to 0.1% for $\lambda = 2, 4, 6$, respectively, while the corresponding crystal field contribution increases from 5% to 57% and to 98.5%, respectively. The remaining pseudoscalar cross term component, Ω_λ(CT) in eqn. (4), is significant for $\lambda = 2$ and 4, contributing the respective average of 29% and 25%, respectively [64].

Conclusion

Within the general independent-systems model, the static and the dynamic coupling mechanisms provide complementary first-order perturbation treatments of $\Delta l = 0$ electronic transitions. The multiplet-to-multiplet f–f intensities of the excitations with an electric 2^6-pole as the leading moment are governed predominantly by the crystal field mechanism in the Ln(III) complexes (IV), and probably in all lanthanide coordination compounds. The dynamic polarization mechanism has its salient applications to the probabilities of $\Delta l = 0$ transitions with an electric quadrupole or, to a lesser degree, an electric hexadecapole as the leading moment in noncentric compounds with a single set of polarizable ligands, which are symmetry-related, or approximately so. Where there are multiple sets of ligands with a small polarizability, as in the case of the Ln^{3+} guest ions in the LaF_3 host lattice, both the crystal field [24] and the ligand polarization [48, 49] treatments account individually for the observed quadrupolar f–f intensities, and the two mechanisms are not distinguished.

A possible distinction between the two mechanisms may be drawn from the restriction of the ligand-dependent crystal field parameters, B^k_m (eqn. 4), to the odd values, $k = (\lambda \pm 1)$, with $\lambda = 2, 4$ or 6, dependent upon the leading electric 2^λ-pole of the metal ion transition. The corresponding dynamic coupling ligand-dependent parameters, including the anisotropy of the ligand polarizability, $[\underset{\sim}{\alpha}^{(2)}\underset{\sim}{G}^{(\lambda+1)}]^{(k)}$ have the range of ranks, $k = \lambda$, $(\lambda \pm 1)$, [71–73], which is required group-theoretically [59]. For the electric quadrupole case, the ligand-dependent term of the isotropic polarizability approximation in eqn. (1), $[G^L_{\alpha\beta\gamma}\bar{\alpha}_L]$, is tensorially third rank $(\lambda + 1)$, but the corresponding term of the anisotropic polarizability case, $[G^L_{\alpha\beta\delta}\alpha^L_{\gamma\delta}]$ in eqn. (2), may be contracted to first or second rank additionally, λ or $(\lambda \pm 1)$. The particular additional rank of the ligand-dependent tensor of the anisotropic dynamic polarization mechanism is even, $k = \lambda$, and, for the quadrupolar $\Delta l = 0$ electronic transitions, with $\lambda = 2$, in coordination compounds with D_4 and higher dihedral symmetry, the only non-zero dynamic polarization intensity parameters are second rank [73], like those of the $\Delta M_J = \pm 1$ quadrupolar transitions in the D_3 lanthanide coordination compounds (II) and (III) [54].

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