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HYPERSENSITIVITY IN THE ELECTRONIC TRANSITIONS OF LANTHANIDE AND ACTINIDE COMPLEXES

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A. INTRODUCTION

In 1962, Judd [1] and Ofelt [2] independently developed a model for the calculation of the oscillator strengths of lanthanide $f \rightarrow f$ transitions. The model was developed by considering the mixing of excited states of parity different than f^n with states of the f^n configuration. This mixing arises from the presence of spherical harmonics Y_k^m (with k odd) in the static crystal field potential as well as in certain vibrational modes of lanthanide complexes (dynamic crystal field). The general form of the equation obtained for the oscillator strength P of an $f \rightarrow f$ transition is the same for both the static and dynamic mechanism:

$$P = \bar{\nu} \Sigma T_\lambda < l^n \psi J | U^{(\lambda)} | l^n \psi' J' >^2 ; \lambda = 2,4,6 \qquad (1)$$

where $\bar{\nu}$ is the transition energy, $\langle l^n \psi J|$ and $|l^n \psi' J'\rangle$ are the initial and final states respectively of the transition characterized by the quantum numbers

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l, J, J', ψ and ψ'. $U^{(\lambda)}$ is the sum over all the electrons of the single electron unit tensor operator $u_i^{(\lambda)}$. The T_λ are functions of the refractive index of the medium, the radial wave-functions of the initial and final states and the parameters describing the perturbing mechanism(s). The T_λ are, in principle, calculable but in practice are treated as adjustable parameters.

Since both the static and dynamic crystal field (vibronic coupling of vibrational and electronic states) yield an equation of the same form, Judd notes, "If the T_λ are treated as parameters to be adjusted to fit the experimental data, a good fit is no guarantee that the lines are purely electronic in origin" [1]. They may under certain circumstances have vibronic components. If a center of symmetry is present in the complex, the mechanism for mixing these odd parity components must, most reasonably, come from the vibronic interactions. Thus, when a static field is present which has a center of symmetry to a high degree of approximation, any experimentally observed transitions should have a substantial contribution due to a vibronically induced intensity.

Several tests of the semi-empirical Judd—Ofelt treatment have been made with satisfactory results [3—5]. For example, it has been used to extend the band assignments into the ultra-violet absorption region for several lanthanides [4].

Certain transitions, called "hypersensitive", exhibit a relatively strong sensitivity of the oscillator strength to the environment about the ion. That is, the oscillator strengths of the hypersensitive transitions exhibit a relatively greater variability than do the oscillator strengths of non-hypersensitive transitions. It is this relative variability rather than the absolute magnitude of oscillator strengths which measures how sensitive a given transition is to the environment. Judd [1] noted that these hypersensitive bands are associated with large values of the $U^{(2)}$ matrix elements of eqn. (1); thus hypersensitivity is intimately associated with the T_2 parameter of eqn. (1) [1, 6—9]. As long as the T_λ are treated as adjustable parameters, the Judd—Ofelt treatment fits even the hypersensitive transition oscillator strengths well. The T_2 parameter varies quite widely, while T_4 and T_6 are less affected. For a given ion in different environments, the relative variation in the T_2 parameter probably provides the best measure of the degree of hypersensitivity exhibited by that ion. The specific mechanism(s) responsible for hypersensitivity remains a subject of much debate, however, and the physical interpretation of the T_λ parameters is still unclear. Tables 1 and 2 are a listing of the known hypersensitive transitions of the lanthanide and actinide ions, respectively. In Fig. 1 the hypersensitivity of the ${}^5G_6 \rightarrow {}^5I_8$ transition in $\mathrm{Ho^{III}}$ (the band at 4475 Å) compared to normal transitions is illustrated by comparing the spectra of $\mathrm{Ho^{3+}_{(aq)}}$ and $\mathrm{Ho(TTA)_x^{(3-x)^+}}$ in H_2O/acetone solvent.

In this review we discuss hypersensitivity in the light of a correlation between oscillator strength and ligand basicity which has recently been reported [16,17] and reevaluate much of the published data in terms of this discussion. The literature is not covered completely here, but rather we have selected

TABLE 1

Hypersensitive transitions of lanthanides

Ion (+3)	Transition	Energy (kK)	$E_{ff} \times (E_{ct})^{-3}$ ($\times 10^4$)	$E_{ff} \times (E_{fd})^{-3}$ ($\times 10^4$)
Pr	${}^3P_2 \leftarrow {}^3H_4$	22.5	2	4
	${}^1D_2 \leftarrow {}^3H_4$	17.0	1	3
Nd	$\left.\begin{matrix}{}^4G_{7/2}\\ {}^3K_{13/2}\end{matrix}\right\} \leftarrow {}^4I_{9/2}$	19.2	2	2
	$\left.\begin{matrix}{}^4G_{5/2}\\ {}^2G_{7/2}\end{matrix}\right\} \leftarrow {}^4I_{9/2}$	17.3	2	1
Sm	$\left.\begin{matrix}{}^6P_{7/2}\\ {}^4D_{1/2}\\ {}^4F_{9/2}\end{matrix}\right\} \leftarrow {}^6H_{5/2}$	26.6	6	2
	${}^6F_{1/2} \leftarrow {}^6H_{5/2}$	6.2	1	$\frac{1}{2}$
Eu	${}^5D_2 \leftarrow {}^7F_0$	21.5	15	1
Dy	${}^6F_{11/2} \leftarrow {}^6H_{15/2}$	7.7	1	1
	$\left.\begin{matrix}{}^4G_{11/2}\\ {}^4I_{15/2}\end{matrix}\right\} \leftarrow {}^6H_{15/2}$	23.4	4	1
Ho	${}^3H_6 \leftarrow {}^5I_8$	28.0	4	1
	${}^5G_6 \leftarrow {}^5I_8$	22.2	3	1
Er	${}^4G_{11/2} \leftarrow {}^4I_{15/2}$	26.5	3	1
	${}^2H_{11/2} \leftarrow {}^4I_{15/2}$	19.2	2	1
Tm	${}^3H_4 \leftarrow {}^3H_6$	12.6	2	$\frac{1}{2}$

TABLE 2

Hypersensitive transitions of trivalent actinides

Ion (+3)	Transition	Energy (kK)	Ref.
U	${}^4F_{5/2} \leftarrow {}^4I_{9/2}$	9.5	10, 11
	${}^4G_{5/2} \leftarrow {}^4I_{9/2}$	11.1	
Np	$(J = 2) \leftarrow {}^5I_4$	7.6	10, 11
	$2 \leftarrow J = 4$	11.7	
Pu	${}^6F_{3/2} \leftarrow {}^6H_{5/2}$	6.8	10, 11
	${}^6F_{1/2} \leftarrow {}^6H_{5/2}$	7.1	
Am	${}^7F_2 \leftarrow {}^7F_0$	5.3	12
	${}^5G_2 \leftarrow {}^7F_0$	21.0	13, 14
Bk	${}^7F_5 \leftarrow {}^7F_6$	5.0	11
Cf	${}^6F_{11/2} \leftarrow {}^6H_{15/2}$	6.5	11
	${}^6H_{13/2} \leftarrow {}^6H_{15/2}$	8.0	
Es	$6 \leftarrow J = 8$	13.1	15
	$6 \leftarrow J = 8$	20.1	

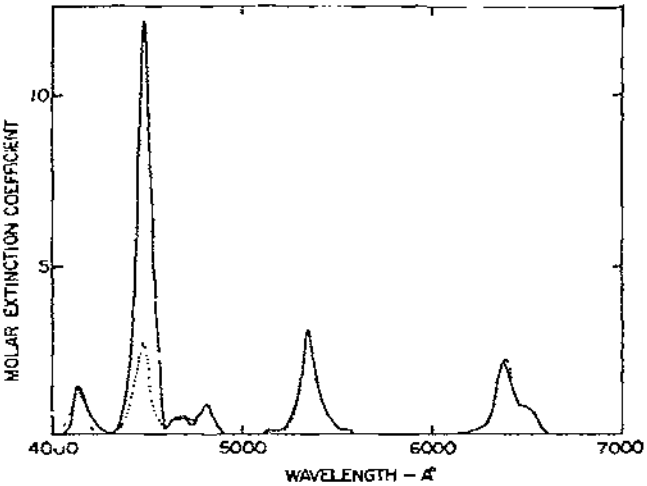


Fig. 1. Spectra of Ho^{3+} and $Ho(TTA)^{3-x}$ in water/acetone showing the effect on a hypersensitive transition and a normal one.

representative portions in order to provide an overview of the current activity in the field. A relation between the intensity data and the Judd—Ofelt theory is suggested and a theoretical model outlined to account for the observed behavior.

B. EXPERIMENTAL RELATION OF LIGAND BASICITY AND HYPERSENSITIVITY

With the discovery of a direct correlation between the oscillator strength of hypersensitive transitions of complexed lanthanides and ligand basicity as measured by the pK_a of the complexing ligand (see Fig. 2) it has become apparent that such a relationship has a much broader applicability than simply to complexes in solution. It should be noted here that there are other quantities which may be as good as or even better than pK_a for providing a quantitative measure of "basicity". The correlation with average electronegativity, ligand orbital ionization energy, Pearson softness or with many other ligand characteristics might be equally reasonable. Ligand pK_a however, is a useful and very practical quantity from our point of view since there is a relatively large number of values available. Regardless of how one chooses to measure ligand basicity, such correlations would seem to have significant implications to lanthanide and actinide bonding theory. Perhaps of even broader significance is the possibility once the significance of the correlation is understood, of using hypersensitivity to obtain structural information on the coordination chemistry of both the lanthanides and the actinides. A discussion of the published data in light of the correlation between ligand basicity and oscillator strength can serve to show the significance and application of this correlation.

Hypersensitivity has been studied in a variety of ligand systems in solids,

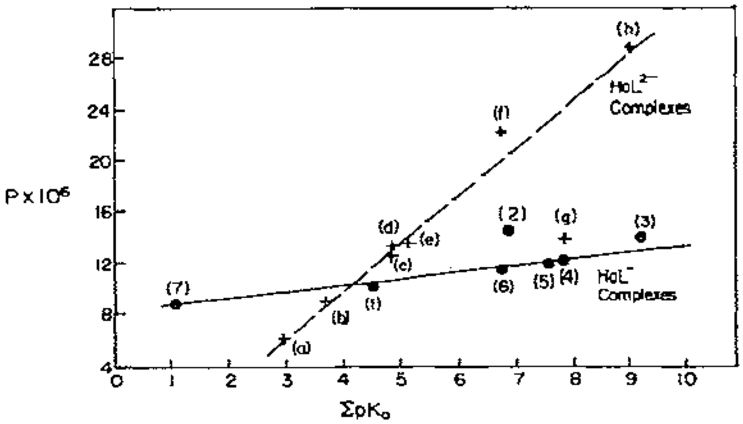


Fig. 2. Plot of the oscillator strength P of the 1:1 complexes of Ho^3 with monobasic (+) and dibasic (•) ligands vs. the ΣpK_a of the ligand acid (from refs. 16 and 17) (a) fluoride, (b) glycolate, (c) acetate, (d) propionate, (e) α-picolinate, (f) tropolonate, (g) kojate, (h) acetylacetonate, (1) IMDA, (2) dipicolinate, (3) methyl succinate, (4) malonate, (5) maleate, (6) fumarate, (7) sulfate.

melts, aqueous and non-aqueous solvents and in the vapor state. Pappalardo [18] has prepared and studied crystalline cyclopentadienide complexes of several lanthanides. The cyclopentadienide ion is undoubtedly very strongly basic although, because of its instability in water, aqueous solution pK_a values are not known. As expected from the ligand basicity correlation, large hypersensitive intensities are observed in these organometallic complexes.

The fluorescent intensities of the hypersensitive transition $^5D_0 \leftarrow {}^7F_2$ in Eu^{3+} were studied by Charles and Ohlmann for crystalline Eu(dibenzoylmethide)$_3$ and some of its adducts with Lewis base molecules [19]. The intensity increased as the base strength increased for both the oxygen containing bases and the nitrogen containing adducts. Similar results have been obtained in other studies of the fluorescent intensities of several Eu^{3+} and Tn^{3+} complexes [20,21].

Blasse [22] reported the results of some quite imaginative experiments in which Eu^{3+} was doped into crystals of $Ba_2Gd(Nb, Ta\ or\ Sb)O_6$. Since Nb^{5+}, Ta^{5+} and Sb^{5+} have virtually equivalent ionic radii, one expects little variation in lattice parameters and site symmetries in the different crystals. The Eu^{3+} enters Gd^{3+} sites so that a generalized bonding structure can be visualized as Ru—O—M. When M is Nb^{5+} or Ta^{5+} (both d^0), the Eu^{3+} hypersensitive band ($^5D_0 \leftarrow {}^7F_2$) has a much lower luminescence intensity than when M is Sb^{5+} (d^{10}). The O—M bond is more covalent when M = Nb or Ta so the electron donating ability of the oxygen (to Eu^{3+}) would be less than when M = Sb. These results again show that the intensity of hypersensitive transitions is dependent on the electron donating ability of the ligand. Blasse's work also demonstrates vividly how the second coordination sphere of the lanthanide ion can, in certain instances, markedly influence the $f \rightarrow f$ transitions.

The T_2 parameter of eqn. (1) has been directly related to hypersensitivity [1—3] and covalency (vide infra). In the study of Eu^{3+} in phosphate and germanate glasses, Reisfeld and Eckstein [23] conclude that a static covalency mechanism is consistent with the T_2 behavior while their results with Tm^{3+} and Er^{3+} in these glasses and in borate glass are more consistent with a vibronic mechanism. It is worthwhile to note here, that the T_2 parameters for Tm^{3+} and Er^{3+} increase with decreasing Ln—O bond distance [24] as might be expected for covalent interactions.

A comparison of Nd^{3+} hypersensitive band intensities in a series of yttrium—aluminum oxide phases indicates decreasing hypersensitivity in the order $Y_2O_3 > YAlO_3 > Y_3Al_5O_{12}$(YAG) [25—27]. The site symmetries of the Nd^{3+} ion in these lattices have been established as C_2 and C_{3i}, D_2 and C_{1h} respectively. One can qualitatively model these oxide phases for our purposes by first considering that these crystal matrices are various simple mixtures of Y_2O_3 and Al_2O_3. Secondly, Al^{3+} classically is a more acidic cation than Y^{3+}, therefore one can view Al_2O_3 as a more acid lattice than U_2O_3. Based upon the basicity correlation, the relative order of hypersensitivity would then be determined by the basicity of the host matrix which is $Y_2O_3 >$ $Y_2O_3 \cdot Al_2O_3$ (= $YAlO_3$) $> 3Y_2O_3 \cdot 5Al_2O_3$ (= YAG)— the experimentally observed order of hypersensitivity.

A more quantitative comparison can be made based upon expected Nd—O bond lengths (vide infra). Since Nd^{3+} substitutionally replaces Y^{3+} in these lattices, the Y—O bond distances can be assumed to be a relative measure of the Nd—O bond distances in these oxide matrices. Y^{3+} is six coordinate in Y_2O_3 with Y—O bond distances of 2.249 Å (2 bonds), 2.261 Å (2) and 2.278 Å (2) in the C_2 site (and 6 bonds at 2.261 Å in the C_{3i} site). Y^{3+} in YAG is eight coordinate and has Y—O bond distances of 2.303 Å (4) and 2.432 Å (4). The Y—O bond distances are significantly shorter in Y_2O_3 than in the YAG matrix suggesting that hypersensitivity should occur in the order $Y_2O_3 >$ YAG. The case involving $YAlO_3$ is not clear because no single crystal X-ray structural work has been done, hence explicitly defined Y—O bond distances are not known. The coordination number is known to be eight as in YAG crystals. Based upon the observed hypersensitive band intensities and relying on the hypersensitivity model to be described later in this paper, one should expect that the smallest Y—O bond distances should be somewhat shorter than those in YAG.

Krupke's [25] comparisons of the difference in the hypersensitive behavior of Nd^{3+} doped in Y_2O_3 and in LaF_3 crystals led him to propose that hypersensitivity is due to a change in symmetry. However, an alternate interpretation seems acceptable. From his work it is apparent that the non-hypersensitive transition intensities in the Y_2O_3 lattice are about twice as intense as in the LaF_3 lattice while the respective hypersensitive band intensities are over seven times greater. It would seem very probable that this larger difference can be attributed predominantly to the greater basicity of the oxide lattice. Sinha's lanthanide nephelauxetic series [28] in fact places O^{2-} as the most basic ligand studied and F^- as the least basic. EPR studies of Ln^{+3} ions in $CsNaYCl_6$ lattices also indicate greater covalency for the oxides compared to the fluorides [29].

Undoubtedly Krupke's interpretation of higher symmetries about the Nd^{3+} ion in the LaF_3 lattice is qualitatively correct. The non-hypersensitive bands are less intense in the LaF_3 lattice implying that the symmetry is quite high and probably that a center of symmetry is present. It should be noted, however, in making symmetry interpretations based only on the hypersensitive band intensities, that the effects of ligand basicity on the intensities are substantial.

A comparison of the Nd^{3+} hypersensitive band behavior in dilute aqueous perchlorate solutions, in KNO_3—$LiNO_3$ melts [3], in KCl—LiCl melts [30] in the perchlorate and chloride salts and their concentrated solutions [4] indicated increasing oscillator strengths in the order $ClO_4^- < Cl^- < NO_3^-$. This is the order expected from the pK_a values of −10, −7 and −1.4 respectively for these anions [31].

More recent studies [32] of anhydrous Nd^{3+}, Ho^{3+} and Er^{3+} chlorides in formamide and related solvents have shown that the chloride complexing is not inner sphere in these solvents. Although the authors did not so interpret the data, indications are that the hypersensitive band intensities increase as the electron donating ability of the solvent increases, i.e., in the order formamide < dimethyl formamide < diethyl formamide. When water is present in these solvents, the band intensities are somewhat increased, probably indicating inner sphere water complexation. Methyl formamide solvent exhibits inconsistent behavior with its expected position between formamide and dimethyl formamide. Intensities in this solvent are considerably less than one would expect from its relative basic character and one might speculate that the unsymmetrically substituted nitrogen is somewhat a factor in the decreased metal—solvent interaction.

Absorption spectra of several lanthanide tribromide and triiodide vapors have been determined at 1200°C. Gruen et al. [33,34] found that the hypersensitive transitions were more than ten times more intense than for the analogous aqueous solutions, and that the other transition intensities were comparable to the aqueous values. The NdI_3 hypersensitive intensities were larger than the $NdBr_3$ intensities. Covalency and orbital overlap were considered to make sizeable contributions to the hypersensitive band intensities. From oscillator strength and bond length data for gaseous, liquid and solid NdI_3: $(530 \times 10^{-6}, 2.94\ \text{Å})_{\text{gas}}$, $(210 \times 10^{-6}, ?\ \text{Å})_{\text{liquid}}$, $(170 \times 10^{-6}, 2.38\ \text{Å})_{\text{solid}}$ it was apparent that as the Nd—I bond length decreased, the oscillator strength of the hypersensitive band increased. Such an interpretation is consistent both with the expected increasingly basic character of the iodide ion compared to bromide and the increasing interaction of the metal and ligands as exemplified by the bond lengths.

The greatly diminished hypersensitive band intensity in gaseous $NdCl_3 \cdot (Al_2Cl_6)_x$ (where $x = 1.5$ and 2) [35] compared to $NdBr_3$ and NdI_3 is expected on two grounds. First, the coordinating chlorides are less basic than either Br or I. Second, in a coordinating structure of the type Nd—Cl—Al, the very acidic Al^{3+} (or $AlCl_3$, a classic Lewis acid) competes very favorably with Nd^{3+} for the available electron density in a manner directly analogous to the systems studied by Blasse [22].

An analogous effect is noted in the case of NdI_3 and $NdI_3 \cdot CsI$ vapor phase spectra [36]. The $NdI_3 \cdot CsI$ intensity is half that of the NdI_3 with symmetries of C_{2v} or C_{3v}, and D_{3h} respectively. The use of basicity arguments requires that, as in the case of $NdCl_3 \cdot Al_2Cl_6$, the CsI adduct has a smaller hypersensitive intensity than the parent NdI_3 if the interaction of Cs is with the iodine moiety of NdI_3.

The general behavior of the hexahalide complexes of the lanthanides [37—40] provides some indication as to the relative role which symmetry and covalency play in hypersensitive behavior. The absorption intensities of the non-hypersensitive $f \rightarrow f$ transitions (as measured by molar extinction coefficients) decrease in the order $LnCl_6^{3-} > LnBr_6^{3-} > LnI_6^{3-}$. Ryan and Jørgensen [37] interpret this as indicating that the iodide complex is least distorted from true octahedral symmetry. The hypersensitive transitions, on the other hand, show the opposite trend in that the intensities follow the order $LnI_6^{3-} > LnBr_6^{3-} > LnCl_6^{3-}$. This increase in intensity, which parallels that observed for the NdI_3 and $NdBr_3$ vapors by Gruen et al. [33,34], corresponds to an increasing electron donating ability of the ligands and is opposite to the trend in distortion from O_h symmetry. The oscillator strength of the hypersensitive transition of Nd^{3+} in $NdCl_6^{3-}$, in fact, is only slightly greater than the aquo ion value although it is about an order of magnitude larger than the non-hypersensitive transition oscillator strengths [39].

It appears, then, that for these nearly octahedral complexes, two major effects can be related to intensity changes in the $f \rightarrow f$ transitions; a center of symmetry which affects all transition intensities, and metal—ligand covalency which affects predominantly the hypersensitive transition intensities. These observations appear to indicate that hypersensitivity occurs independently of the presence or absence of a center of symmetry in the complex, and that its occurrence is more intimately related to the covalent bonding ability (or electron donating power) of the ligand. Hypersensitivity is also apparent in the hexacyanolanthanide complexes studied by Martin et al. [41] and the hexacoordinate TBP-aqueous solution complexes studied by Katzin and Barnett [42].

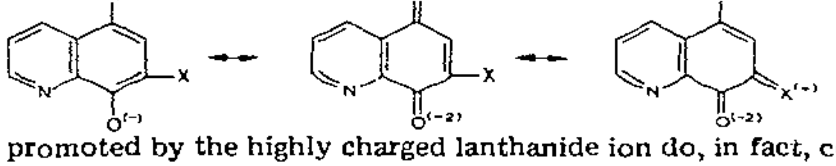
In the case of the hexacoordinate selenocyanate complexes recently prepared [43], the dominant features of the $Er(NCSe)_6^{3-}$ $f \rightarrow f$ spectrum are clearly the hypersensitive bands at ~19 and 26.5 kK. Similarly, the analogous thiocyanate complexes [44] also had enhanced hypersensitive intensities. A striking feature of the $Dy(NCS)_6^{3-}$ spectrum is the enormously enhanced intensity in the region of the $({}^4F_{9/2}, {}^4I_{15/2}, {}^4G_{11/2}) \leftarrow {}^6H_{15/2}$ manifold at 21—23.5 kK. Although not normally considered to be hypersensitive, at least two of these transitions are consistent with the experimental criterion [8] for hypersensitivity of $|\Delta J| \leqslant 2$. Assuming that the observed Dy enhancement is due to an $f \rightarrow f$ transition, this is the first hypersensitivity noted for this Dy^{3+} band.

These hexacoordinate complexes present a unique opportunity for study of hypersensitive behavior because of their essentially isomorphous character. Quantitative oscillator strength values would help demonstrate the electron donating character of the coordinating ligands in a manner which is free from coordination number and substantial symmetry changes.

Previous work involving β-diketone complexes of the lanthanides has suggested that the shapes of the hypersensitive absorption bands are characteristic of the coordination number (symmetry) about the lanthanide ion [45,46]. Few conclusions were drawn about the intensities of these same bands, however, and it seems very unlikely that changes in coordination number or symmetry would result in the relatively smooth trends in the correlation of oscillator strength and pK_a [16,17]. The series of β-diketone complexes were obtained independently by two other groups [47,48]. Taken together the three publications [46—48] provide a self-consistent series of increasing ligand basicity with increasing hypersensitivity in the order hexafluoroacetylacetone < trifluoroacetylacetone < acetylacetone < (ditertiary-butylacetylacetone), (benzoylacetylacetone < thenoyltrifluoroacetylacetone < (dibenzoylacetylacetone). Data from Mehta and Tandon [49] indicate that the relative order of benzoylacetylacetone and thenoyltrifluoroacetylacetond could possibly be reversed. It is evident that this series does not in all cases parallel the pK_a values (most notably with the conjugated or aromatic systems) but rather it reflects the ligand basicity when associated with a highly polarizing +3 ion [16,17].

Some important work has been published recently [50] in which a homologous series of 5,7-dihalogenated 8-hydroxyquinoline (oxine) derivatives was studied for its influence on the hypersensitive transitions of Nd^{3+}, Ho^{3+} and Er^{3+}. Although the increase in hypersensitive intensities was correlated with increasing mass of the coordinating ligand, alternatively, the increase can be correlated with increasing ligand basicity. Independent studies of the basicity of the 5,7-dihalogenated oxine derivatives [51,52] found that the pK_a's increase in the order 5,7-dichloro < 5-chloro, 7-iodo < 5,7-dibromo < 5,7-diiodo, the order of observed increasing hypersensitive enhancement.

The "anomalously" low oscillator strength (from the point of view of the ligand pK_a), of the unsubstituted 8-hydroxyquinoline suggests that the classical zwitterionic resonance forms of the type



promoted by the highly charged lanthanide ion do, in fact, contribute significant amounts of electron density to the lanthanide ion. The lack of such resonance forms in the unsubstituted oxine would limit its electron donating ability (decrease its relative basicity) and, therefore, decrease the intensity of the hypersensitive bands of the coordinated lanthanide ions.

The intensity-ligand basicity relationship opens a whole new range of interpretative possibilities when lanthanides are used as probes of metallic binding sites in biological materials. The basicities of the binding sites can be determined directly from the absorption spectrum of the complexed lanthanide ion. Recent studies [53] have implicitly made use of this type of relationship by relating the difference spectrum of $Nd^{3+}_{(aq)}$ and Nd^{3+}-bovine serum albumin complexes to simple acid complexes of Nd^{3+}.

The tripositive lanthanide and actinide ions have many similar properties as a result of the similar ionic radii and the similar electronic configurations involving the 4*f* and 5*f* orbitals, respectively. This would lead to the expectation that hypersensitivity should be exhibited by the actinide ions. Thus far, however, it has been clearly demonstrated only for Am^{3+}. Although the investigations of the hypersensitivity in Am^{3+} spectra are rather limited, the results again support a correlation between the spectral intensities and the ligand basicities.

As in the case of the lanthanides, $AmCp_3$ was found to have a very large intensity for the hypersensitive band [12].

An examination of Am^{3+} and Nd^{3+} spectra in molten alkali chloride salts indicates that with both ions, the relative intensity of the hypersensitive band increases when the alkali cations are changed from the more acidic Li—K pair to the more basic Na—Ca pair [13]. Comparison of Am^{3+} extinction coefficient changes in molten LiCl—KCl and those in $LiNO_3$—KNO_3 [54] indicates that the nitrate melt increases the intensity relative to the chloride melt which, again, correlates with the relative basicities of these two anions.

Relative enhancement of these bands has also been demonstrated in organic solutions of Am^{III} with chloride complexing [55], and in aqueous bromide, iodide, nitrate and carbonate solutions [14].

Hypersensitivity has been studied in crystalline $AmCl_3$, $AmBr_3$ and AmI_3 [56]. The intensity is greatest for AmI_3 but $AmBr_3$ does not exhibit the expected intermediate intensity (compared to $AmCl_3$ and AmI_3). Inasmuch as the Am^{3+} has a coordination number of 6 in AmI_3, 8 in $AmBr_3$ and 9 in $AmCl_3$, the lack of isomorphous coordination makes interpretation of the results uncertain. One might speculate that the Am—Br interaction is considerably decreased relative to the Am—I interaction either because of the smaller coordination number, the significantly longer Am—Br distance (for two of the bonds) or both. To account for the observed hypersensitivity it has also been argued that the iodide crystal structure is relatively "more compressed" than the others. The character of the bromide spectrum and the lack of apparent vibronic bands was noted as also being inconsistent with the chloride and iodide results [56] and again indicates that the tribromide spectrum is not behaving in an isomorphous manner with the trichloride and triiodide spectra.

In summary, we can interpret a broad range of experimental data on hypersensitive transitions in the lanthanides and actinides as showing a fundamental correlation between the oscillator strength of the transitions and the basicity of the ligands in the coordination sphere of the cation. In contrast to the effect of ligand basicity on the intensity of the hypersensitive transitions, the non-hypersensitive bands apparently are more sensitive to the presence of a center of symmetry in the coordination sphere of the cation. This difference is most notable in the spectra of the 6-coordinate lanthanide complexes. However, in this review our primary concern is with the hypersensitive transitions, for which we can state three useful generalizations, (everything else being equal):

(a) an increasing basic character of the coordinating ligand results in increasing absorption intensity;

(b) decreasing metal—ligand bond distances results in intensity enhancement;

(c) the greater the number of coordinated (more basic) ligands, the greater the enhancement of intensity.

With quantitative intensity data, quantitative basicity correlations can be established for the ligand. This correlation would be useful in measuring the basicity of ligands which are not amenable to other methods (due to solution instability, etc.). It seems probable that hypersensitive behavior can be developed into a very useful investigative technique to study both the structural aspects of the coordination chemistry of the lanthanides and actinides, and the basic characteristics of ligands themselves.

C. THEORIES OF HYPERSENSITIVITY

In general, attempts to develop a theoretical basis for hypersensitivity have involved either a vibronic mechanism (in which the terms of Y_m^k of odd k are involved) or a crystal field potential effect (again, when terms of odd k are present). Let us consider the latter proposal first since there is considerable evidence indicating that hypersensitivity cannot be explained using simple crystal field arguments.

Carnall et al. [3] pointed out that the crystal field model predicts the proportionality

$$T_\lambda \sim \langle r^{t+1} \rangle^2 R^{-2t-2} \qquad (2)$$

where for $\lambda = 2$, t is 1 and 3; for $\lambda = 4$, t is 3 and 5; and for $\lambda = 6$, t is 5 and 7. This leads to the expectation that the order of decreasing sensitivity of the parameters to the environment should be $T_6 > T_4 > T_2$ whereas the authors found that the reverse order is observed for solutions of lanthanide complexes. Krupke's study [5] of single crystals of Nd^{3+} in Y_2O_3 and LaF_3 lattices gave the same (reverse) order of sensitivity as do many other studies [6—8,23,24].

A further observation which indicates that crystal field symmetry arguments do not provide a general rationalization of hypersensitive behavior is the occurrence of hypersensitivity in octahedral complexes of the lanthanides [37—40] and actinides [56]. This conflicts with the fact that for O_h symmetry *no* spherical harmonics with odd values of k are permitted in the crystal field potential.

Another interesting observation pertaining to hypersensitivity was noted by Pappalardo [18] in his studies of $Nd(C_5H_5)_3$ and $Er(C_5H_5)_3$. In these complexes, the simultaneous occurrence of hypersensitivity and a large splitting of $J = \frac{3}{2}$ levels is observed. Pappalardo notes that in a crystal field model, the quantities $\langle f|r^2/a_0^2|f\rangle$ are a measure of the second order terms of the crystal field potential which are responsible for the splitting of the $J = \frac{3}{2}$ levels, moreover, it is quantities of this type which also occur in the theoretical expression of the oscillator strengths of quadrupolar transitions. However, this contribution to the oscillator strength was found to be too small to account for the phenomenon of hypersensitivity [8].

Jørgensen and Judd [8] concluded from their investigation of possible mechanisms for the occurrence of hypersensitivity that an ion imbedded in an inhomogeneous dielectric would exhibit hypersensitive behavior since the (normally weak) electric quadrupole transitions would most probably be enhanced under these circumstances. They termed hypersensitive transitions occurring via this mechanism "pseudoquadrupole" transitions. Later, Judd [9] proposed that hypersensitivity can occur in symmetries where spherical harmonics, Y_m^k, with $k = 1$ transform as the totally symmetric representation, thus permitting their inclusion in the crystal field potential.

Both of these proposals (i.e., the pseudoquadrupole mechanism and Judd's symmetry argument) are apparently at odds with the experimental results of Gruen and DeKock [34] that gaseous NdI_3 indicated D_{3h} symmetry in which spherical harmonics with $k = 1$ do not transform as the totally symmetric representation; thus, Judd's symmetry argument does not hold for this case. Also, the gas phase molecules are in a relatively homogeneous dielectric, indicating that the pseudoquadrupole mechanism should be inoperative. However, it should be noted that, while one may regard gaseous NdI_3 molecules as being in a homogeneous dielectric; from the point of view of the Nd^{3+} ion (where most of the *f*-electron density resides) the environment is provided by the ligand (I^-) electrons which do not provide a homogeneous dielectric for the *f*-electrons. Thus, one may envisage that the pseudoquadrupole mechanism would still be operative in some form. By utilizing an order-of-magnitude calculation of contributions to the oscillator strength, Gruen and DeKock were able to argue that a vibronic mechanism, including covalency, could best explain their observations for gas phase molecules. Of general interest in this connection is their observation that increases in hypersensitive oscillator strengths generally follow the expected increase in the degree of covalency of the metal—ligand bonding.

For a series of Nd^{3+} complexes, Henrie and Choppin [57] found an approximately linear correlation between hypersensitive oscillator strength and a parameter which included estimated covalency (using the nephelauxetic

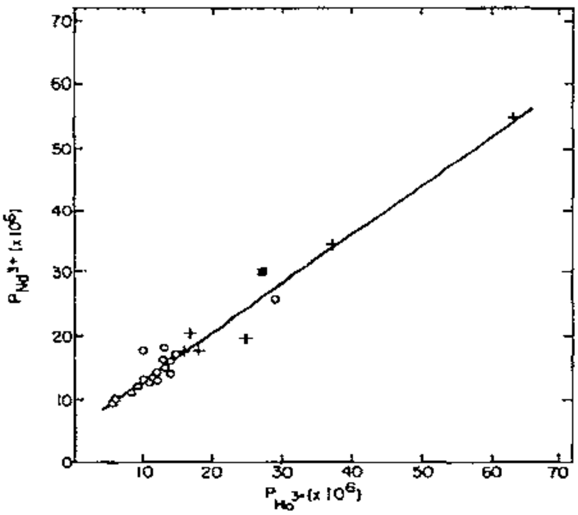


Fig. 3. Graph of the oscillator strength of the hypersensitive $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition of Nd^3 plotted against the oscillator strength of the hypersensitive $^5G_6$, $^5F_1 \leftarrow {}^5I_8$ transition of Ho^3. The data is from refs. 16 and 17 except that of $Ln(NO_3)_3$ in TBP (designated by ■) which is from ref. 39. The data for 1:1 complexes are designated by ○ and that for 1:2 by +.

effect) [58]. They rationalized their results via a vibronic mechanism. Peacock [59], however, did not find a similar relationship for some Ho^{3+} complexes. Data from refs. 16 and 17 are shown in Fig. 3 as a plot of $P_{Nd^{3+}}$ vs. $P_{Ho^{3+}}$. A slope of 0.8 would seem to indicate a greater degree of hypersensitivity for Ho^{3+} than for Nd^{3+}, contrary to what one expects from considering the relative nephelauxetic shifts [60]. This seems to argue against a general correlation between the oscillator strength and nephelauxetic effect for all hypersensitive transitions. By contrast, the linearity in Fig. 3 as well as that evidenced in similar plots in refs. 50, 61 and 62 supports a similar intensity mechanism for the hypersensitive transitions of Nd^{3+} and Ho^{3+} with the same numbers and kinds of ligands. The observation that the correlation of P and pK_a holds for one of the light lanthanides (Nd^{3+}) as well as for a member of the heavy part of the series (Ho^{3+}) indicates that this correlation may be of more general applicability than the previously reported correlation with "covalency" as estimated via the nephelauxetic effect. However, both the nephelauxetic and pK_a correlations indicate that we should attempt to formulate a model which explicitly includes covalency. If we assume that hypersensitive transition oscillator strengths are related in some manner to covalency, it is reasonable that the correlation with ligand basicity be more generally applicable than a correlation with covalency estimated from the nephelauxetic effect. For the lanthanides in solution, nephelauxetic shifts are especially difficult to determine for several reasons. The shifts are of the order of 1 to 2%, a full order of magnitude smaller than observed for transition metal complexes. It is also difficult to determine the value of the shift because there are often present a multiplicity of closely spaced absorption lines with varying intensities and shifts. The situation is further complicated by the crystal field splitting of the levels which may be of the order of kT at room temperature, so that changing the ligand changes both the splitting and the populations of the ground state components. In fact, with the same ligand, different absorption bands of the same lanthanide may be observed to shift in different directions. Since the f—f transitions are extremely weak, a degree of mixing with an allowed transition too small to result in a pronounced shift in the energy of the f—f transition can produce marked increases in the oscillator strength. One might expect that ligand basicity which is a measure of the electron donating power of the ligand would provide good qualitative indication of the ability of a ligand to bond covalently with a metal ion. Hence, the relation of hypersensitivity to ligand basicity can be regarded as an extension of the covalency arguments of Gruen and DeKock [34] and Henrie and Choppin [57].

In the formulation of a model which explicitly includes covalency we should keep in mind that although the semi-empirical crystal field model works well for calculation of the lanthanide energy levels, theoretical calculations of these crystal field parameters do not fare so well. In fact, Jørgensen et al. [63] suggested that the "crystal field parameters", $A_n^m\langle r^n\rangle$, have no real meaning other than to keep track of the different f-orbital energies which arise from covalent interactions. The empirical values of $A_2^0\langle r^2\rangle$ are smaller than those of $A_6^0\langle r^6\rangle$ and $A_6^6\langle r^6\rangle$. Also, the theoretically calculated values of $A_2^0\langle r^2\rangle$ are five times too large while those of $A_6^0\langle r^6\rangle$ are ten times too small. This apparently contradicts the electrostatic model which requires that $\langle r^2\rangle$ be much smaller than R^2. These authors have utilized the so-called Angular Overlap Model to interpret the energy level structure with satisfying results. Subsequently, Ellis and Newman [64] performed rigorous calculations and demonstrated the essential correctness of this interpretation. The approaches in refs. 63 and 64 explicitly include covalency involving the f-orbitals. Also of interest is a paper by Lowther and Hagston which discusses relationships between static and dynamic "crystal field parameters" when overlap and covalency are important [65]. It is likely that similar considerations are necessary for the interpretation of the T_λ parameters of the Judd—Ofelt theory.

Before proceeding with an outline of the development of our "covalent" model, let us first summarize the general observations with respect to hypersensitivity which such a model must attempt to explain:

(i) the observed order of sensitivity of the parameters to the environment is $T_2 > T_4 > T_6$ [5,57].

(ii) the general trend of the (hypersensitive) oscillator strength increases with "estimated" covalency [34,57].

(iii) the observation of hypersensitivity in octahedral complexes [37—40, 56].

(iv) the simultaneous occurrence of hypersensitivity and large splittings of $J = \frac{3}{2}$ levels [18].

(v) the correlation between (hypersensitive) oscillator strength and ligand basicity [16,17].

D. COVALENCY MODEL OF HYPERSENSITIVITY

In order to account for hypersensitive behavior (assuming that the transitions are electric dipolar in nature) a perturbation is necessary which mixes states of parity different from f^n with the states of the f^n configuration. The discussion to this point has indicated that covalency is also an important consideration. The speculative model we now propose is based on the observation of charge transfer transitions in lanthanide complexes. The energies and oscillator strengths of the charge transfer transitions are extremely sensitive to the type of ligand and to the metal ion. The $4f$ to $5d$ transitions are, on the other hand, relatively insensitive to the ligand when compared with the charge transfer transitions. Thus, if the hypersensitive transitions gain some charge transfer character, the sensitivity to the environment is, in a sense, built into the model by the nature of the charge transfer transition itself.

In addition to the intensification which would be expected from partial charge transfer character, two other types of observations would tend to support this type of model. Barnes and Pincott [66] have shown that not only are the energies of the lanthanide charge transfer transitions dependent on the coordinating ligand but also they are incremented in a stepwise manner with stepwise ligand additions. In a recent publication, Poluéktov et al. [62] demonstrated for a series of phenol-like derivatives of Nd^{3+}, Ho^{3+} and Er^{3+} that the hypersensitive bands also increase in intensity with increasing numbers of coordinated ligands. This is consistent both with the observations which have been made with a broader range of ligands [16,17] and the inclusion of charge transfer character in the hypersensitive transitions.

The rigorous derivation of a theoretical model is beyond the scope of the present work, but some suggestions as to the derivation procedure are in order. Basically the procedure would be analogous to that of Judd [1] and Ofelt [2], however we modify the model to include charge transfer states in addition to $f^{n-1}5d^1$ and $f^{n-1}5g^1$ as the excited stated to be mixed with f^n. The charge transfer states which we consider arise from one electron transfers from ligand orbitals to the f orbitals on the metal. The problem becomes one of sufficiently describing the excited charge transfer states so that an approximate equation of the form of eqn. (1) results. Let ϕ represent the appropriate ligand wave functions and m represent the number of ligand electrons. We represent the states of f^n as

$$\sum_M a_M(\phi^m f^n \psi JM| \tag{3}$$

and the charge transfer states as

$$\sum_{M''} b_{M''}(\phi^{m-1} f^{n+1} \psi'' M''| \tag{4}$$

A perturbation (odd molecular field components or odd vibrational modes) of the form

$$V = \sum_{t,p} [4\pi/(2t+1)]^{1/2} Y_{tp}(\phi_i,\theta_i) F_{tp}(r_i) \tag{5}$$

will mix states of the f^n configuration with charge transfer states of differing parity. We obtain the following result for the contribution of the charge transfer states (eqn. 4) to the electric dipole matrix element $(B|D_q^{(1)}|B)$ (analogous to eqn. 4 of Judd [1]).

$$\begin{aligned}(B|D_q^{(1)}|B^1) = {} & \Sigma a_m a[4\pi/3]^{1/2}[4\pi/(2t+1)]^{1/2} \\ & \times [(\phi^m f^n \psi JM|F_{1p}(\theta_i,\phi_i)|\phi^{m-1} f^{n+1} \psi'' J'' M'') \\ & \times (\phi^{m-1} f^{n+1} \psi'' J'' M|F_{tp}(r_i) Y_{tp}(\theta_i \phi_i)|\phi^m f^n \psi' J' M) \\ & \times [E(\psi' J') - E(\phi, \psi'' J'')]^{-1} \\ & + (\phi^m f^n \psi JM|F_{tp}(r_i) Y_{tp}(\theta_i \phi_i)|\phi^{m-1} f^{n+1} \psi'' J'' M'') \\ & \times (\phi^{m-1} f^{n+1} \psi'' J'' M'' F|p(r_i) Y|_p(\theta_i \phi_i)|\phi^{m-1} f^{n+1} \psi' J' M')] \\ & \times [E(\psi J) - E(\phi_1 \psi' J'')]^{-1}\end{aligned} \tag{6}$$

the sum being taken over M, M', t, p, ψ'', J'' and M''. By appropriate approximation techniques, it should be possible to simplify the form of eqn. (6) and obtain a result for the oscillator strengths which is of the same form as the Judd—Ofelt eqn. (1). By our analogy to the results of Judd, the T_λ's are proportional to ΔE^{-2} where ΔE is the energy difference $E(\phi^{m-1} f^{n+1}) - E(\phi^m f^n)$. We can relate this ΔE via Jørgensen's work [67] on ligand-to-4f charge transfer transitions to the (optical) electronegativity difference between the ligand and metal, viz.

$$E = 30(X_M^{\text{opt}} - X_{\text{Ligand}}^{\text{opt}}) + c^1(n)E^1 + C^3(n)E^3 + C^2(n)\zeta_{nf} \tag{7}$$

where X_M^{opt} and $X_{\text{Ligand}}^{\text{opt}}$ are the optical electronegativities of metal and ligand respectively, E^1 and E^3 are Racah's parameters of interelectron repulsion, ζ_{nf} is the spin orbit coupling constant and $C^1(n)$, $C^2(n)$, and $C^3(n)$ are coefficients which can be found in ref. 67. The ligand optical electronegativity is expected to be related quantitatively to the ligand pK_a, thus a theoretical basis for the correlation of P with pK_a would be established. The relation of P and optical electronegativity $(X)_{\text{Ligand}}^{\text{opt}}$ is semiquantitatively confirmed in Fig. 4 which is a plot of P vs. $X_{\text{Ligand}}^{\text{opt}}$ for Nd^{3+} and Ho^{3+} with the several ligands for which data are available [67,68]. A much better correlation would be expected if both parameters were determined from exactly the same complexes.

The mixing of charge transfer character into f^n configurations can rationalize other phenomena in addition to a P vs. pK_a correlation. By considering electron transfer states of the same parity as f^n (e.g. $f^{n+1}\phi^{m-1}$) (with ϕ and f transforming as the same irreducible representations) being mixed with f^n via the Coulomb interaction (configuration interaction) the correlation of a red shift of $f \to f$ transitions with increasing degree of covalency can be ex-

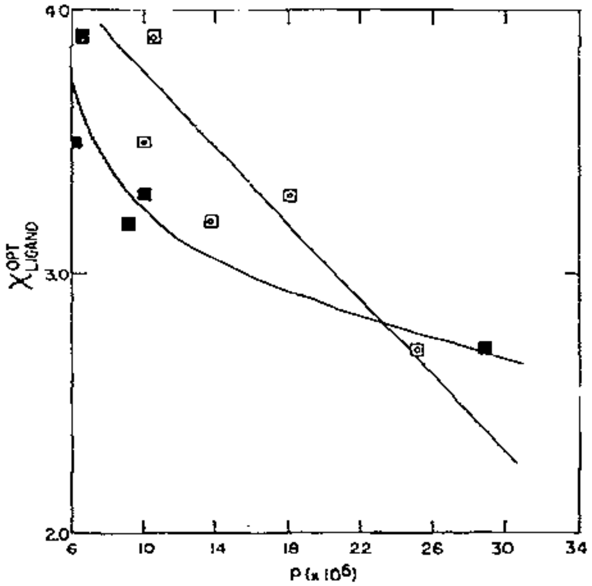


Fig. 4. Plot of Optical Electronegativities [67,68] ($X^{\mathrm{opt}}_{\mathrm{Ligand}}$) vs. hypersensitive band oscillator strengths for Nd^{3+} (▣) and Ho^{3+} (■) complexes with various complexing ligands. The oscillator strengths are values for 1:1 complexes [16,17] while the $X^{\mathrm{opt}}_{\mathrm{Ligand}}$ are for varying degrees of ligand complexation.

plained since the $f^{n+1}\phi^{m-1}$ levels lie lower for more covalent ligands. Using this model we can also reply to a question asked in ref. 63 as to why the triplet levels of Pr^{3+} show a greater nephelauxetic shift than the singlet levels from compound to compound. The excited states arising from charge transfers from ligand to metal give rise to (for Pr^{3+}) singlets with a baricenter higher than the triplets. Thus the triplet states arising from electron transfer shift the triplets of f^2 to a greater extent than the singlets. Finally, the same model can be used to interpret variations in the nephelauxetic effect as a function of Z for lanthanides and actinides.

The T_λ parameters of the Judd—Ofelt theory can be associated with some specific patterns of behavior in the lanthanide complexes. In order to compare the T_λ values for different lanthanides, Carnall et al. [4] have removed the dependence of T_λ on the ground state multiplicity $(2J+1)$ and defined a new set of parameters, τ_λ given by the following eqn.;

$$\tau_\lambda = T_\lambda(2J+1)^c \qquad (8)$$

Values of τ_2 have been calculated using the oscillator strengths given in refs. 16 and 17 by the method of Gruen et al. [7] and Peacock [59]. These τ_2 values are presented in Tables 3 and 4. The τ_4 and τ_6 parameters were assumed to be constant and equal to the aqueous values for all the complexes studied. The τ_2 parameter is consequently assumed to be directly proportional to the

TABLE 3

τ_2 values ($\times 10^{-9}$) for 1:1 Nd^{3+} complexes in aqueous solution [a]. These values were calculated from the hypersensitive band ($^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$) oscillator strengths.

	DTPA	DCTA	EDTA	HEDTA	NTA	IMDA
ML	4.8	4.2	6.6	6.1	3.4	3.3
ML_2					5.4	5.9

	Dipicolinate	Methyl Succinate	Malonate	Maleate	Fumarate	Sulfate
ML	4.2	4.8	4.5	5.4	5.4	3.8
ML_2	9.5	9.8				

	Fluoride	Glycolate	α-Picolinate	Acetate $\mu = 0.1$	Acetate $\mu = 2.0$	Propionate $\mu = 0.1$
ML	1.4	2.4	6.5	3.8	3.5	4.6
ML_2		6.3	8.1	6.4	7.3	7.2
ML_3		6.1	11.6			

	Propionate $\mu = 2.0$	Tropolonate	Kojate	Acetylacetonate	NTA-Malonate	HEDTA-OH
ML	3.8	17.1	5.6	11.7	3.3	6.2
ML_2	7.5		16.9	29.9		
MLL′					4.5	7.2

[a] Oscillator strengths were taken from ref. 16, 17 and calculations were made according to eqn. 1 with $\nu_{^4G_{5/2}} = 17300$, $\nu_{^2G_{7/2}} = 17460$, $\tau_4 = 6.44 \times 10^{-9}$, and $\tau_6 = 10^{-9}$. $U^{(\lambda)}$ values from ref. 4. τ_2 for $Nd^{3+}_{(aq)} = 1.2 \times 10^{-9}$.

oscillator strength of the hypersensitive band. Although not rigorously correct, this method serves to give a semiquantitative picture of the τ_2 behavior because τ_4 and τ_6 have been demonstrated to be much less variable [6,7,59]. Figures 5 and 6 show a linear correlation between ligand pK_a and τ_2 for Nd^{3+} and Ho^{3+} which suggests that the τ_2 parameter is affected predominately by the covalency in the metal—ligand bonding.

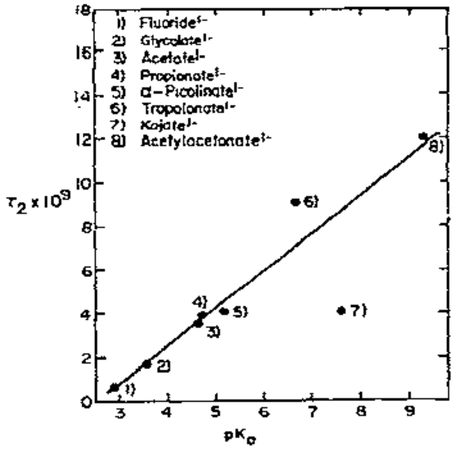
The effect of symmetry on the overall spectral intensity has some significant implications. Nearly all of the experimentally observed $f \rightarrow f$ transitions have either $U^{(4)}$ or $U^{(6)}$ matrix elements [4] and consequently are influenced by the τ_4 and τ_6 parameters. The τ_4 and/or τ_6 parameters would then be expected to reflect the symmetry of the lanthanide environment. The fact that nearly all hypersensitive transitions also have $U^{(4)}$ and $U^{(6)}$ matrix elements means that they also will be influenced by symmetry in the metal—ligand complex, but hypersensitivity per se cannot be classified as being due to a symmetry phenomenon.

TABLE 4

τ_2 values (× 10^{-9}) for 1:1 Ho^{3+} complexes in aqueous solution. These values[a] were calculated from the hypersensitive band ($^5G_6$, $^5F_1 \leftarrow {}^5I_8$) oscillator strengths.

	DTPA	DCTA	EDTA	HEDTA	NTA	IMDA
ML	3.8	2.1	2.4	4.7	3.0	2.6
ML_2					3.3	5.0
	Dipicolinate	Methyl Succinate	Malonate	Maleate	Fumarate	Sulfate
ML	4.6	4.4	3.4	3.4	3.1	1.9
ML_2		7.7	6.7	7.8	3.1	1.9
	Fluoride	Glycolate	α-Picolinate	Acetate $\mu = 0.1$	Acetate $\mu = 2.0$	Propionate $\mu = 0.1$
ML	0.6	1.6	4.0	3.5	3.1	3.9
ML_2		5.7	6.0	6.6	8.1	9.1
ML_3		6.1	3.9			
	Propionate $\mu = 2.0$	Tropolonate	Kojate	Acetyl-acetonate	NTA-Malonate	HEDTA-OH
ML	3.7	9.0	3.9	11.9	3.0	4.4
ML_2	10.0		16.3	29.5		
MLL′					4.6	3.0

[a] Oscillator strengths were taken from ref. 16, 17 and calculations were made according to eqn. 1 with $U(\lambda)$'s from ref. 4, $\tau_4 = 4.05 \times 10^{-9}$, $\tau_6 = 3.96 \times 10^{-9}$, and $\nu = 22100$. τ_2 for $Ho_{(aq)} = 0.5 \times 10^{-9}$.



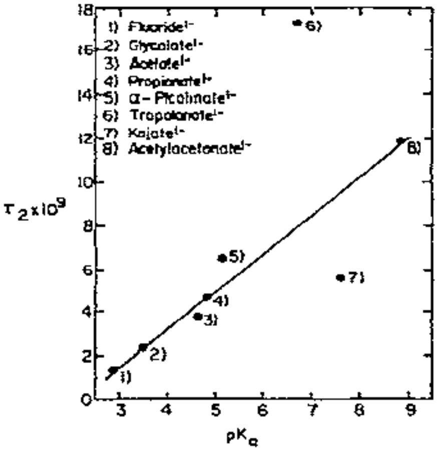


Fig. 5. τ_2 vs. ligand pK_a values for NdL^{2+} complexes.

Fig. 6. τ_2 vs. ligand pK_a values for HoL^{2+} complexes.

The hypersensitivity of some of the transitions listed in Tables 1 and 2 cannot readily be accounted for by the usual form of the Judd—Ofelt theory inasmuch as they have either vanishing or very small matrix elements of $U^{(2)}$. Peacock [59,69] discussed this problem for the $^3P_2 \leftarrow {}^3H_4$ and $^1D_2 \leftarrow {}^3H_4$ transitions of Pr^{3+}. Henrie and Smyser [70], in a recent study of oscillator strengths and T_λ parameters for some $Ln(NO_3)_3$ salts in TBP, noted that in some instances, normal transitions which have vanishing $U^{(2)}$ matrix elements exhibit relative oscillator strength variations which are comparable to the changes shown by some "hypersensitive" transitions. However, the observation of significant variability in oscillator strengths of "non-hypersensitive" transitions need not be interpreted to mean that the Judd—Ofelt theory is incorrect but, rather, such variations may indicate that significant changes in the symmetry about the ion have occurred (as evidenced by variations in the T_4 and T_6 parameters.) This is very evident in the oscillator strengths of $NdCl_6^{3-}$ reported in ref. 39.

In much of the work on hypersensitivity, workers have come to use the oscillator strengths of hypersensitive transitions as proportional to the T_2 parameter of the Judd—Ofelt theory. This is likely to be a reasonably good assumption in aqueous systems. However, certain hypersensitive transitions have $U^{(4)}$ and/or $U^{(6)}$ matrix elements which are significant relative to the magnitude of $U^{(2)}$. Caution should be used when considering absolute oscillator strength values alone, since symmetry effects may cause substantial contributions to the intensity of both hypersensitive and non-hypersensitive transitions. Hypersensitive transitions which should be viewed with caution in this context are those for which contributions from $U^{(2)}$ and either or both of $U^{(4)}$ and $U^{(6)}$ are of comparable magnitudes.

An interesting general observation is that the $^7F_0 \leftarrow {}^5D_2$ hypersensitive transition of Eu^{3+} when compared with Nd^{3+} seems to exhibit a greater sensitivity to the environment than the hypersensitive transitions of any other tripositive lanthanide. A striking example of this behavior is the effect of Cl^- concentration on the hypersensitive bands of Eu^{3+} when compared with Nd^{3+}. Nd^{3+} shows essentially no effect until about 6 M HCl, whereas Eu^{3+} exhibits spectral changes at concentrations below 1M. This greater sensitivity for Eu^{3+} is accounted for by considering the following simplified model for the mixing of electron transfer character into the hypersensitive transition. The oscillator strength of an allowed electron transfer transition is given [71] by

$$P_{CT} = kE_{CT}\langle\psi_0|\gamma|\psi_{ct}\rangle^2$$

where k is a constant, E_{CT} is the energy of the charge transfer transition, and ψ_0 and ψ_{ct} are the ground and excited state wave functions respectively. If an $f \rightarrow f$ transition "borrows" some intensity from the charge transfer transition, the contribution to the $f \rightarrow f$ oscillator strength is of the form

$$P_{ff} = a^2 E_{ff}(E_{CT})^{-3} P_{CT}$$

where P is the oscillator strength, the subscripts ff and CT refer to the $f \rightarrow f$ or charge transfer transitions respectively and a represents matrix elements of asymmetrical vibrations or odd terms in the molecular field which mix the charge transfer level with the f^n level. Thus, the oscillator strength should be extremely sensitive to the charge transfer transition energy, which varies greatly depending on the ligand. The quantity $E_{ff} \times (E_{CT})^{-3}$ is given in Table 1, where E_{CT} was taken from the $LnBr_6$ data [3—72]. In cases where E_{CT} was not observed, it was calculated using Jørgensen's method [73]. Extrapolation of these $E_{ff} \times (E_{CT})^{-3}$ values to other complexes is not strictly correct because of changes in E_{CT} but for the present purpose, semiquantitative comparisons are sufficient. We note from Table 1 that this quantity is significantly larger for Eu^{3+} than for the other lanthanides; thus a change in the charge transfer energy should result in a greater relative effect for Eu^{3+}. This can be regarded as due to the relatively low charge transfer energy of Eu^{3+} combined with the relatively high value for the hypersensitive transition energy, and is in agreement with the general observation that Eu^{3+} is more sensitive to the environment. We also note that the same arguments indicate a significantly greater sensitivity for Ho^{3+} than Nd^{3+} in agreement with the experimental behavior previously discussed. Similarly, for f—d and f—g mixing, an inverse third power dependence of the oscillator strength on the $f \rightarrow d$ or $f \rightarrow g$ transition energy exists. Ce^{3+}, Pr^{3+} and Tb^{3+} have the lowest $f \rightarrow d$ transition energies of the tripositive lanthanides, and, as expected, $f \rightarrow d$ transitions have been observed for the hexabromo complexes of these ions. We, therefore, expect that these ions may show the largest effects due to variations in $f \rightarrow d$ energies. The observed and calculated $f \rightarrow d$ energies from ref. 72 have been used to calculate the quantity $E_{ff} \times (E_{fd})^{-3}$ for the $LnBr_6^{3-}$ complexes (see Table 1). This quantity shows a smaller variation with atomic number than the corresponding quantity for charge transfer energies, and its maximum value occurs for Pr^{3+}. Peacock's observation of hypersensitivity in some complexes of Pr^{3+}, apparently unexplained by the Judd—Ofelt theory, is probably due to variations in f—d energies invalidating some of the approximations made in the theory [1,2]. For different ligands, the f—d energy varies much less than does the charge transfer energy, hence the contribution to hypersensitivity from f—d mixing is expected to be much smaller for most systems. Our explanation, involving variations in charge transfer energies, is also consistent with Peacock's observation [74] that T_2 values are different for different transitions in the same ion. It seems, then, that most hypersensitive behavior can be rationalized by the mixing of electron transfer character into the hypersensitive transition.

A rationalization of hypersensitivity has recently been proposed by Mason et al. [75]. Their "dynamic coupling" proposal is similar to the pseudoquadrupolar explanation [8] and ascribes the intensities of the hypersensitive f-electron transitions as arising from the Coulombic correlation of induced electric dipoles in the ligands by the transition quadrupole moment of the metal ion. Their theory should not be confused with the "dynamic" contributions mentioned above by us, although as pointed out in ref. 75, a dynamic (vibronic) version of the Mason et al. mechanism is possible. Their theory gives quantitative values for the observed intensities of the $^4G_{5/2} \leftarrow ^4I_{9/2}$ transition of gaseous $NdBr_3$ and $NdIr_3$. The intensities of 6 coordinate compounds may be explained by this proposal if there is a slight distortion from octahedral symmetry present [76]. We note that the Mason et al. mechanism, the pseudoquadrupole mechanism, and our suggestion involving charge transfer states are all conceptually consistent with a correlation between oscillator strength and ligand basicity. All these proposals are similar in that they involve a ligand polarization, charge transfer being thought of as an extreme type of ligand polarization. Of course, further experimental work will help ascertain the correctness of any theoretical explanation of hypersensitivity.

Our proposal of explaining hypersensitivity by including covalent effects in the Judd—Ofelt approach via charge transfer states allows utilization of either vibronic or static perturbations (or both) as the mechanism(s) for mixing of states. Unfortunately, the data are often less than definitive. For example, the intensities of the octahedral complexes and gaseous complexes indicate that hypersensitivity is not strongly dependent on the symmetry of the complex. This appears to argue for a dynamic field (vibronic mechanism) as the major contributing perturbation for hypersensitive transitions. For $NdCl_6^{3-}$ the relative intensities have been observed to be temperature invariant from room temperature to 77 K [40]. The observed effect of temperature on the oscillator strength is usually considered to give a good indication of the nature of the perturbing mechanism; temperature invariance of P indicates a static mechanism, temperature variance suggests a vibronic mechanism. Thus the $NdCl_6^{3-}$ system leads to conflicting interpretations of the mechanism of mixing since the symmetry would suggest a vibronic mechanism while the temperature effects would indicate a static mechanism. In cases like this it has been suggested that data at still lower temperatures are generally necessary to definitely rule out a vibronic mechanism [77]. The tricyclopentadienides, in fact, do exhibit a rather large temperature variation of the oscillator strengths [18] when cooled to liquid He temperature (indicating significant vibronic contributions are present, although the possibility of low temperature structural changes cannot be ruled out). Peacock [78] has shown in another case that an observed temperature dependence of the hypersensitive transition oscillator strength can be rationalized via a static mechanism by considering variations in the populations of low lying electronic levels as a function of temperature. It appears, then, that the question of temperature effects on oscillator strengths (and thus their value as a test of static vs. dynamic mechanisms) requires further experimental and theoretical study.

The techniques of Magnetic Circular Dichroism (MCD) and Circular Dichroism (CD), applied to optically active complexes, may yield measurements which can be interpreted in terms of the relative contributions of static and dynamic mechanisms to the observed oscillator strengths. The oscillator strength for a transition is proportional to the second power of the electric dipole moment of the transition;

$P\alpha(\mu_e)^2$.

The rotatory strength is the scalar product of the electric (μ_e) and magnetic (μ_m) dipole moments:

$R = \mu_m \cdot \mu_e$.

Moffit [79] pointed out that the rotatory strength involves only the static contributions to μ_e while, as we have discussed, P can include both static and dynamic contributions. The magnitude of the magnetic dipole moment is expected to be relatively independent of the environment. Thus, it should be possible to obtain an estimate of the magnitude of the static contribution from the measured rotary strengths, which, when combined with the observed oscillator strengths, will yield an estimate of the dynamic contribution.

Katzin et al. [80—83] conducted a number of studies of ORD-CD spectra for solutions of lanthanide complexes with optically active ligands. Misumi et al. [84—86] have looked at some similar systems and reported that for most absorption bands the CD intensities parallel the absorption intensities. Certain bands, which they call "CD-sensitive", exhibit much greater CD intensities than expected from the absorption intensities. These bands are ones which have relatively large values for the magnetic dipole moment. Unfortunately, there is little quantitative CD data available for the hypersensitive transitions at present.

A recent MCD study [87] reported no apparent correlation between MCD intensities and other properties, e.g. whether a transition is magnetic dipole allowed or not. Caldwell et al. [88] have noted a general trend in the ORD spectra of D-(—)-1,2-propylenediaminetetraacetato complexes of the trivalent lanthanides. These authors proposed an explanation for this general trend based upon the effect of the ionic potential on far-ultraviolet charge transfer bands of these systems. Much work, both experimental and theoretical, is needed and it appears that ORD, CD and MCD should provide a rich field for future investigations. Our proposed model facilitates the inclusion of covalent effects on P (and R) via both static and dynamic mechanisms.

Of the five general observations with respect to hypersensitivity listed previously (ii), (iii) and (v) seem to be qualitatively explained by our proposed model. (i) and (iv) involve for their qualitative explanation the realization that the f-orbitals lose their "pure" $l = 3$ character and gain some $l = 1$ angular dependence through configuration interaction involving excited charge transfer states of the same parity as f^n (this explains (iv)). When these modified states are perturbed by vibrations with Y_m^k of odd k and/or odd k molecular field components, the resultant behavior of T_λ (observation) is rationalized, as previously discussed by Henrie and Choppin [57]. We feel, therefore, that the correlation of P with pK_a can be justified theoretically and that our speculative model is in general accord with other experimental results as well. A more rigorous development of this model is currently underway.

E. SUMMARY

In summary, the linear correlation of ligand basicity with oscillator strength of the lanthanide hypersensitive transitions has been shown to be of general utility and can be applied to lanthanide spectra of compounds in vapor, liquid solution or crystalline phases. A mechanism for hypersensitivity involving metal—ligand covalency via charge transfer levels is suggested. Physical interpretations of the τ_λ parameters in the Judd—Ofelt theory have been presented based on covalency and symmetry arguments. The τ_2 parameters are apparently directly related to metal—ligand covalency while the τ_4 and/or τ_6 parameters seem to be primarily a function of the degree of symmetry in the coordinated complexes.

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NOTE ADDED IN PROOF

A single crystal X-ray structure of $YAlO_3$ has recently been reported [89] and is directly pertinent to the discussion involving the behavior of the Nd^{3+} spectra when Nd^{3+} is doped into mixed yttrium aluminum oxides. In $YAlO_3$, the Y^{3+} ions are situated in a very distorted twelve-coordinate polyhedron of O^{2-} ions. The Y—O bond distances are 2.237 Å (1 bond), 2.283 Å (2), 2.306 Å (1), 2.480 Å (2), 2.570 Å (2), 3.010 Å (1), 3.119 Å (1), and 3.262 Å (2).

The four shortest Y—O bond distances in $YAlO_3$ are at least as small as the smallest $Y_3Al_5O_{12}$ (YAG) Y—O bond distances (2.303 Å (4) and 2.432 Å (4)) but they are longer than those in Y_2O_3 (2 bonds each at 2.249 Å, 2.261 Å and 2.278 Å). Based upon these bond lengths, the relative order of $Y^{3+}—O^{2-}$ interaction in these crystals is $Y_2O_3 > YAlO_3 > Y_3Al_5O_{12}$ i.e. the observed order of hypersensitive behavior. The bond distances which are observed in $YAlO_3$ confirm the structural predictions which were made previously (vide supra) based solely on the behavior of the Nd^{3+} hypersensitive band.

REFERENCES

1 B.R. Judd, Phys. Rev., 127 (1962) 750.
2 G.S. Ofelt, J. Chem. Phys., 37 (1962) 511.
3 W.T. Carnall, P.R. Fields and B.G. Wybourne, J. Chem. Phys., 42 (1965) 3797.
4 W.T. Carnall, P.R. Fields and K. Rajnak, Argonne National Laboratory Report ANL 7358-1967. See also J. Chem. Phys., 49 (1968) 4412, and the following papers.

5 W.F. Krupke, Phys. Rev., 145 (1966) 325.

6 K. Bukietynska and G.R. Choppin, J. Chem. Phys., 52 (1970) 2875.

7 D.M. Gruen, C.W. DeKock and R.L. McBeth, Advan. Chem., 71 (1967) 102.

8 C.K. Jørgensen and B.R. Judd, Mol. Phys., 8 (1964) 281.

9 B.R. Judd, J. Chem. Phys., 44 (1966) 839.

10 Potentially hypersensitive but has not yet been experimentally demonstrated.

11 W.T. Carnall, personal communication, October 1973.

12 R.G. Pappalardo, W.T. Carnall and P.R. Fields, J. Chem. Phys., 51 (1969) 842.

13 Yu.A. Barbanel, V.P. Kotlin and V.R. Klokman, Radiokhimiya, 15 (1973) 366.

14 M. Shiloh, M. Givon and Y. Marcus, J. Inorg. Nucl. Chem., 31 (1969) 1807.

15 R.L. Fellows, J.R. Peterson, M. Noe, J.P. Young and R.G. Haire, to be published.

16 G.R. Choppin and R.L. Fellows, J. Coord. Chem., 3 (1973) 209.

17 R.L. Fellows and G.R. Choppin, J. Coord. Chem., 4 (1974) 79.

18 R. Pappalardo, J. Chem. Phys., 49 (1968) 1545.

19 R.G. Charles and R.C. Ohlmann, J. Inorg. Nucl. Chem., 27 (1965) 119 and references therein.

20 N. Filipescu and N. McAvoy, J. Inorg. Nucl. Chem., 28 (1966) 253 and references therein.

21 S.P. Sinha, J. Inorg. Nucl. Chem., 28 (1966) 189 and references therein.

22 G. Blasse, Chem. Phys. Lett., 20 (1966) 189.

23 R. Reisfeld and Y. Eckstein, Solid State Commun., 13 (1973) 265.

24 R. Reisfeld, Struct. Bonding (Berlin), 13 (1973) 53.

25 W.F. Krupke, Phys. Rev., 145 (1966) 325.

26 M.J. Weber, T.E. Varitimos and B.H. Matsinger, Phys. Rev. B, 8 (1973) 47.

27 W.F. Krupke, IEEE J. Quantum Electron. QE-7, (1971) 153.

28 S.P. Sinha, Complexes of the Rare Earths, Pergamon Press, Oxford, 1966, p. 106.

29 R.W. Schwartz and N.J. Hill, J. Chem. Soc. Faraday II, (1974) 124.

30 C.V. Banks, M.R. Heusinkveld and J.W. O'Laughlin, Anal. Chem., 33 (1961) 1235.

31 M.C. Day, Jr. and J. Selbin, Theoretical Inorganic Chemistry, Reinhold Book Corporation, New York, (1969) pp. 365 ff.

32 J. Legendziewicz, K. Bukietynska and B. Jezowska-Trzebiatowska, Act. Phys. Acad. Sci. Hung., 35 (1974) 167.

33 D.M. Gruen, C.W. DeKock and R.L. McBeth, Advan. Chem., 71 (1967) 102.

34 D.M. Gruen and C.W. DeKock, J. Chem. Phys., 45 (1966) 455.

35 H.A. Øye and D.M. Gruen, J. Amer. Chem. Soc., 91 (1969) 2229.

36 C.S. Liu and R.J. Zollweg, J. Chem. Phys., 60 (1974) 2384.

37 J.L. Ryan and C.K. Jørgensen, J. Phys. Chem., 70 (1966) 2845.

38 J.L. Ryan, Inorg. Chem., 8 (1969) 2053.

39 D.E. Henrie and B.K. Henrie, J. Inorg. Nucl. Chem., 36 (1974) 2125.

40 J.B. Gruber, E.R. Menzel and J.L. Ryan, J. Chem. Phys., 51 (1969) 3816.

41 J.L. Martin, L.C. Thompson, L.J. Radonovich and M.D. Glick, J. Amer. Chem. Soc., 90 (1968) 4493.

42 L.I. Katzin and M.L. Barnett, J. Phys. Chem., 68 (1964) 3779.

43 J.L. Burmeister and E.A. Deardorff, Inorg. Chim. Acta, 4 (1970) 97.

44 J.L. Burmeister, S.D. Patterson and E.A. Deardorff, Inorg. Chim. Acta, 3 (1969) 105.

45 G.R. Choppin, D.E. Henrie and K. Buijs, Inorg. Chem., 5 (1966) 1743.

46 D.G. Karraker, Inorg. Chem., 6 (1967) 1863.

47 L.I. Kononenko, M.A. Tishchenko and U.N. Drobyazko, Zh. Anal. Khim., 26 (1971) 729.

48 T. Isobe and S. Misumi, Bull. Chem. Soc Jap., 47 (1974) 281.

49 P.C. Mehta and S.P. Tandon, J. Chem. Phys., 53 (1973) 414.

50 N.S. Poluéktov, V.T. Mishchenko, R.S. Lauer and E.A. Zhikhareva, Dokl. Akad. Nauk. SSSR (Phys. Chem.), 211 (1973) 646.

51 R.D. Gupta, G.S. Manku, A.N. Bhat and B.D. Jain, Z. Anorg. Allg. Chem., 379 (1970) 312.
52 M.P. Bratzel, J.J. Aaron, J.D. Winefordner, S.G. Schulman and H. Gershon, Anal. Chem., 44 (1972) 1240.
53 E.R. Birnbaum, J.E. Gomez and D.W. Darnall, J. Amer. Chem. Soc., 92 (1970) 5287.
54 W.T. Carnall and P.R. Fields, Develop. Appl. Spectrosc., 1 (1962) 233.
55 Y. Marcus and M. Shiloh, Isr. J. Chem., 7 (1969) 31.
56 R.G. Pappalardo, W.T. Carnall and P.R. Fields, J. Chem. Phys., 51 (1969) 1182.
57 D.E. Henrie and G.R. Choppin, J. Chem. Phys., 49 (1968) 477.
58 It is important to note that estimating covalency by using the nephelauxetic effect gives only qualitative information useful for correlation of data. The numbers should be related to actual "covalency" with caution. (See D.E. Henrie, Mol. Phys., 28 (1974) 415; D.J. Newman, Advan. Phys., 20 (1971) 197).
59 R.D. Peacock, J. Chem. Soc. (A), (1971) 2028.
60 The relative nephelauxetic effects for Nd^{3+} and Ho^{3+} can be seen from values of *d* given in Table VIII of ref. 37 and of Table 3 of R.D. Peacock and T.J.R. Weakly, J. Chem. Soc. (A), (1971) 1937.
61 N.S. Poluéktov, M.A. Tishchenko and G.E. Gerasimenko, Dokl. Akad. Nauk. SSSR, 213 (1973) 1334.
62 N.S. Poluéktov, L.A. Alakaeva and M.A. Tishchenko, Zh. Prikl. Spektrosk., 17 (1972) 819.
63 C.K. Jørgensen, R. Pappalardo and H.H. Schmidtke, J. Chem. Phys., 39 (1963) 1422.
64 M.M. Ellis and D.J. Newman, J. Chem. Phys., 49 (1968) 4037.
65 J.E. Lowther and W.E. Hagston, Physica (Utrecht), 70 (1973) 27.
66 J.C. Barnes and H. Pincott, J. Chem. Soc. (A), (1966) 842.
67 C.K. Jørgensen, Modern Aspects of Ligand Field Theory, American Elsevier, 1971, Ch. 6 and 28, and references therein.
68 C.K. Jørgensen, Inorganic Complexes, Academic Press, London, (1963) p. 117.
69 R.D. Peacock, Chem. Phys. Lett., 7 (1970) 187.
70 D.E. Henrie and C.E. Smyser, to be published.
71 C.J. Ballhausen, Introduction to Ligand Field Theory, McGraw Hill, 1962, p. 188.
72 L.J. Nugent, R.D. Baybarz, J.L. Burnett and J.L. Ryan, J. Phys. Chem., 77 (1973) 1582.
73 L.J. Nugent, R.D. Baybarz, J.L. Burnett and J.L. Ryan, J. Inorg. Nucl. Chem., 33 (1971) 2503.
74 R.D. Peacock, Mol. Phys., 25 (1973) 817.
75 S.F. Mason, R.D. Peacock and B. Stewart, Chem. Phys. Lett., 29 (1974) 149.
76 R.D. Peacock, private communication.
77 W.T. Carnall, private communication to R.L.F., April 1973.
78 R.D. Peacock, Chem. Phys. Lett., 10 (1971) 134.
79 W. Moffitt, J. Chem. Phys., 25 (1956) 1189.
80 L.I. Katzin, Inorg. Chem., 7 (1968) 1183.
81 L.I. Katzin, Inorg. Chem., 8 (1969) 1649.
82 L.I. Katzin and E. Gulyas, J. Amer. Chem. Soc., 92 (1970) 1211.
83 L.I. Katzin, Inorg. Chem., 12 (1973) 1951.
84 S. Misumi, S. Kida, T. Isobe, Y. Nishida and H. Furuta, Bull. Chem. Soc. Jap., 42 (1969) 3433.
85 S. Kida, T. Isobe and S. Misumi, Bull. Chem. Soc. Jap., 39 (1966) 2768.
86 S. Misumi, S. Kida and T. Isobe, Spectrochim. Acta Part A, 24 (1968) 291.
87 J.P. Sipe, III and R.B. Martin, J. Inorg. Nucl. Chem., 36 (1974) 2122.
88 D.L. Caldwell, P.E. Reinbold and K.H. Pearson, J. Amer. Chem. Soc., 92 (1970) 4554.
89 R. Diehl and G. Brandt, Mater. Res. Bull., 10 (1975) 85.