MASTER**OPTICAL SPECTROSCOPY OF f-ELEMENT COMPOUNDS**

by

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I. INTRODUCTION

The energies and intensities of transitions observed in the optical spectra of lanthanide (Ln) and actinide (An) compounds can typically be measured with a high degree of accuracy. The observed transitions can then be directly represented as upper state energy levels where the structure is induced by the environment. We discuss here the systematic theoretical interpretation of these transitions both in terms of energy level structure and transition probability. Particularly for the trivalent lanthanides and actinides, the detail to which the interpretation can be carried is unique in the periodic table. Although we will emphasize the electronic structure of organometallic lanthanides and actinides in the present discussion, it will be clear that this type of ligand does not present any unique interpretive problems. The basic framework of the interpretation is not dependent upon the specific ionic environment. On the other hand, organometallic compounds represent a particularly interesting group in which to study excited state relaxation.

As lanthanide and actinide metal atoms are progressively ionized, the observed energy level structure undergoes profound changes. We are able to make accurate general statements about this structure because systematic trends have been deduced from an existing large but still incomplete reservoir of data from atomic spectroscopy. Our interest will normally center on the one or two lowest-energy electronic configurations at any given state of ionization. The energy region for optical spectroscopy will be taken to extend to $\sim 50000 \text{ cm}^{-1}$ or $\sim 6 \text{ eV}$, the beginning of the vacuum ultraviolet range. In the lanthanide series, the

Fig. 1. Absorption Spectra of NdCp_3 and NdCl_3 (MeOH-EtOH)
at $\sim 4^\circ\text{K}$

electronic structure consists of the Xe-core with outer 5d and/or 6s electrons. The $4f^N$ -shell is located interior to and shielded by the filled $5s^2 5p^6$ shells. A similar situation occurs in the actinide series which is built on the Rn-core. The characteristic lack of sensitivity of the f^N -series to the environment compared to, for example, members of the d^N -transition series, is ascribed to the inner (shielded) character of the f-electron shell.

Normally the singly ionized states of the f-elements are of lesser interest to chemists because of the difficulty of stabilizing them in compounds. However, all the valence states from +2 through +7 have been characterized in one or another actinide or lanthanide compound. In several instances unusual oxidation states have been stabilized in organometallic compounds. Although our principal purpose is to examine the nature of the electronic structure revealed in optical spectra, and to show how this is related to transition probability theory, insights into bonding character will also be mentioned.

II. NATURE OF THE TRANSITIONS OBSERVED IN ACTINIDE AND LANTHANIDE ABSORPTION SPECTRA

In order to interpret the various features observed in the spectra of f-element organometallics, we need to be aware of the types of transitions that can occur. Consider first the basic electronic structure associated with atoms as they are progressively ionized. Two types of electronic transitions may be distinguished: those transitions that occur between different configurations of electrons and those that occur between states within a particular configuration.

Taking Eu^{2+} as an example, the lowest energy configuration is $4f^7$, with the next higher energy configurations being $4f^6 5d$ and $4f^6 6s$, respectively, Brewer (1971). Thus with the ground state of $4f^7(^8S_{7/2})$ as the reference energy, promotion of an f-electron to a d shell ($4f^7 \rightarrow 4f^6 5d$) requires ~ 4.3 eV (34500 cm^{-1}), and the intensity of the absorption band observed as a result of this process would be representative of a normal "allowed" electric dipole transition. Electronic transitions can in principle also occur at $< 34500 \text{ cm}^{-1}$ in Eu^{2+} , but the corresponding absorption bands, characterized as due to parity forbidden transitions between states within the $4f^7$ -configuration ($4f^7 \rightarrow 4f^7$), would be $\sim 10^6$ -fold weaker than the f $\rightarrow$ d bands. Typical sharply defined absorption bands ($f^3 \rightarrow f^3$) in neodymium tricyclopentadienide, (NdCp_3), observed at $\sim 4^\circ \text{K}$ are shown in Fig. 1, Pappalardo (1965a), where they are compared to the same group in NdCl_3 (dissolved in $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}$ and cooled to form a glass).

Fig. 2. Diffuse Transmission Spectra (77°K) of LaCp_3 and GdCp_3

Examination of the structure in the region of an $f \rightarrow f$ transition frequently reveals the presence of weak sharp bands that cannot be correlated with the $f \rightarrow f$ electronic transitions. These extra lines are usually interpreted as vibronic (lattice) states coupled to the actual $f \rightarrow f$ states, and have been observed, for example, strongly coupled to the 3F_3 and 3F_2 states of $TmCp_3$, Pappalardo (1969). In some cases detailed analysis in terms of characteristic vibrations have been made, Cohen and Moos (1967).

In addition to the foregoing, both charge transfer transitions and spectra solely characteristic of the ligands ($\pi \rightarrow \pi^*$) are observed in the systems of interest here. The process of charge (electron) transfer, usually from filled molecular orbitals principally concentrated on the ligands, to the partly filled f -shell gives rise to relatively intense broad bands. Energy correlations with the redox potential of the trivalent f -elements have been made, Jørgensen (1969), Nugent (1975). Since Eu^{3+} is the most oxidizing of the trivalent lanthanides, the electron transfer bands would be expected to occur at the lowest wave number. Pappalardo and Jørgensen (1967) pointed out the surprising result that intense bands characterized as resulting from charge transfer transitions were identified in $YbCp_3$ at a slightly lower energy than in $EuCp_3$. The broad absorption bands in $ThCp_3$ at ~ 18000 and 25000 cm^{-1} , Kanellakopulos, et al. (1974), are somewhat reminiscent of the spectrum of $YbCp_3$ in the same energy range.

Since attention will focus on the $LnCp_3$ compounds, the optical properties associated with the Cp -ligand are important to recognize. In both $LaCp_3$ and $GdCp_3$ the transmission spectrum of a thin film, Fig. 2, reveals strong ultraviolet absorption associated with the Cp ligand, Pappalardo and Losi (1965). Excitation at 27300 cm^{-1} yielded strong fluorescence near 20000 cm^{-1} which could be interpreted as a transition from essentially triplet states of the C_5H_5 to a singlet ground state. Strong absorption in the ultraviolet range is an expected characteristic of organolanthanide and actinide compounds and will, in general, severely limit the range in which f -electron transitions can be observed. In $(\eta^5-C_5H_7)U$ the cut-off is already observed near 14000 cm^{-1} , Goffart and Duyckaerts (1978); and the same problem occurs in Ln^{3+} complexes with the cyclooctatetraene dianion, Hodgson et al. (1973)

III. INTERPRETATION OF THE ENERGY LEVEL STRUCTURE OBSERVED IN THE OPTICAL SPECTRA OF THE TRIVALENT LANTHANIDES AND ACTINIDES

The purpose of this section is to briefly summarize the extensive theoretical model presently being used to interpret f -electron spectra and to show some examples of the correlation between theory and experiment. The examples will be taken from

trivalent systems where the most extensive experimental work is available. There is an intrinsic interest in developing insights into the electronic structure of actinides and lanthanides in different environments; however, for present purposes our interest centers on obtaining the best available description of the electronic states (eigenvectors) in a particular environment for use in intensity calculations to be discussed later. It will be shown that there is considerable similarity between the well characterized energy level schemes for f-elements in certain crystal hosts and what can be established of the level schemes in particular organometallic compounds. The similarity in part justifies the use of the eigenvectors derived for better characterized systems in connection with calculations involving the organometallic compounds. Of particular relevance to this discussion is the availability of published spectra recorded at low temperature and moderately high resolution for practically all of the LnCp_3 and the corresponding AnCp_3 from Th^{3+} through Cf^{3+} .

III.1. Energy level analysis

Extensive analysis of trivalent lanthanide and actinide spectra has been possible because the crystal or ligand-field splitting of states is small compared to the principal electrostatic and magnetic interactions which determine the structure of the f^N -configuration. As a consequence many electronic states are relatively isolated in energy and selection rules governing transitions can be related in detail to the experimental data. The similarities in the energies of states in LnCp_3 and LnX_3 , where X is a halide, has led to the characterization of the cyclopentadienides as highly ionic in their bonding, Nugent et al. (1971), Hayes and Thomas (1971). Interpretation of cyclopentadienide spectra is however, limited by the strong ultraviolet absorption already discussed, Fig. 2, which restricts the energy range over which $f \rightarrow f$ transitions can be observed.

The model interactions that make up the total Hamiltonian or representation of the energy of the system are treated in detail in the literature, Judd (1963), Wybourne (1965), Dieke (1968), and Carnall et al. (1977). As shown in the lecture on electronic structure, the basic single configuration model for interactions within the f^N -configuration can be written:

$$E = E_F + E_{CF} \quad (3.1)$$

$$\text{where } E_F = \sum_{k=0}^6 F^k(nf, nf) f_k + \zeta_f A_{so} \quad (k \text{ even}). \quad (3.2)$$

Thus the energy of any state is the sum of atomic (free-ion) interactions (E_f) and those characteristic of the crystal (ligand) field (E_{CF}). $F^K(nf,nf)$ and ζ_f represent the radial parts of the electrostatic and spin-orbit interactions between the f-electrons, respectively; f_K and A_{SO} are the corresponding angular interactions whose matrix elements can be computed.

In proceeding with the energy level analysis of an ion such as $Nd^{3+}:LaF_3$, the problem is to evaluate radial integrals such as those in (3.2). In practice this is done by a data fitting process in which the integrals are treated as parameters; however, the values which these parameters may assume and still retain physical significance is limited. Extensive Hartree-Fock (HF) calculations of the F^K and ζ , (3.2), have been carried out, but the resulting HF-integrals are larger than those determined by a fit to experimental data. This discrepancy simply indicates that the ab initio results do not include the effects of "configuration interaction"; they assume as does (3.2) that the ground configuration is purely f^N in character. In practice, the f^N -electrons can be thought of as spending some time in higher-lying configurations where they move in larger orbits and thus interact less than in the f^N -configuration. The fitted parameters reflect these effects of other configurations. On the other hand, the ratios of F^4/F^2 and F^6/F^2 found in the ab initio calculations, while typically somewhat smaller than those deduced from experiment, serve as a useful first approximation.

It has been known for many years that analysis of experimental data for the trivalent f^N -spectra based solely on (3.2), results in large deviations between observed and computed energy levels, Rajnak and Wybourne (1963). In response to this deficiency, additional effective operators have been added to the Hamiltonian in order to take explicit account of the effects of configuration mixing. To the extent that such a procedure is successful, it should result in a lesser distortion of the purely f^N -character of the F^K and ζ obtained from fitting experimental data.

The effects of the environment on the electronic orbitals of Ln^{3+} or An^{3+} are significant, but as noted earlier, $E_f \gg E_{CF}$. Consequently, efforts have concentrated on an expansion of the atomic Hamiltonian to permit the accurate description of observed groupings of crystal-field levels. The crystal-field interaction itself, (3.1), appears at present to be adequately described in terms of the single particle model

$$E_{CF} = \sum_{k,q,i} B_q^k(C_q^k)_i \quad (3.3)$$

discussed in the companion lecture.

Rajnak and Wybourne (1963) showed that both two and three-body terms must be considered in correcting E_F for the effects of configuration mixing. The interacting configurations will be those of the same parity as f^N . Opposite parity configurations interact with f^N via the crystal-field. Although the configurations of interest can be classified as weakly coupled to f^N by the Coulomb field, their inclusion in the model was essential to recent developments in energy level analysis.

In second-order perturbation theory, there are 2 two-body scalar terms required to describe the two-electron excitations in the f^N -configuration, i.e., for f^N there are three terms. The interactions in question for f^3 would include, for example, $4f^3$ with $4f5d^2$, $4f5f^2$, or $4f6p^2$. In the development by Rajnak and Wybourne (1963) the additional terms are of the form

$$\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) \quad (3.4)$$

where α , β , and γ are parameters. The eigenvalues of $G(G_2)$ and $G(R_7)$ have been tabulated, Wybourne (1965).

The overt effects of (3.4) on the terms of a configuration are not simple to describe, but clearly the $L(L+1)$ coefficient of α provides for a shift in energy of the higher with respect to the lower orbital angular momentum terms. There is some similarity in the effects of α and β on a configuration since both are functions of L . They should be varied together where this can be justified by the data base, or one should be assigned an approximate fixed value while the other is varied. One effect of γ is to provide for a shift in terms of differing multiplicity. However, $G(R_7)$ has very large matrix elements for those few states of different seniority number than the N -value of the f^N -configuration being studied. Thus γ can move a single state several hundred cm^{-1} with respect to the rest of the configuration. The importance of this effect has been well documented.

Perturbations of a pure f^N -configuration with $N > 2$ are also described by three-body operators, Rajnak (1965), Judd (1966a). Typical interactions of f^3 with the class of same parity configurations differing from it in the quantum numbers of one electron and described by three-body operators would be $4f^2nf$ (i.e., $4f^25f$), $4f^2np$, or $n'p^64f^3 \leftrightarrow n'p^54f^4$. We have used Judd's formulation which results in six new terms added to the Hamiltonian, T^1_i ($i = 2, 3, 4, 6, 7, 8$) where T^1_i are the integrals treated as parameters. As a very rough estimate for $4f^N$, the two-body operators represent an approximate 4% contribution to the Hamiltonian, while the three-body terms give a ~1% contribution.

In addition to the above, there are small corrections to the spin-orbit interaction (spin-spin and spin-other-orbit) which have

been included in recent work, Judd et al. (1968). Ab initio calculations of all of the corrections to the basic model have been made, and the values of the computed terms are in good agreement with those determined by fitting experimental data, Morrison and Rajnak (1971), Balasubramanian et al. (1975). For the small corrections to ζ , ab initio results are often used directly and not varied.

Significant improvements in the fits to experimental data by incorporating the two-body terms in the model were first demonstrated by Rajnak (1965) in the analysis of PrIII ($4f^3$). The deviation in fitting 38 (of the 41) free-ion states dropped from 500 cm^{-1} using (3.2) to 149 cm^{-1} by adding the terms of (3.4). Further improvement to 29 cm^{-1} was obtained by the addition of three-particle terms. Computations have also been made using data for $\text{Nd}^{3+}:\text{LaF}_3$ where 147 of the 182 crystal-field levels in the $4f^3$ -configuration representing 39 of the 41 free-ion states have been assigned. Important new insights were gained when the data were fit first with the free-ion parameters only, and then with the addition of (3.3). Fits made to the pseudo free-ion levels in LaF_3 , i.e., the centers of gravity of the observed crystal-field components of each state, showed deviations between theory and experiment that were similar to those reported by Rajnak for the same number of parameters. It should be emphasized that the four-parameter model (3.2) did not provide useful correlation with the experimental data except at low energy, and values of F^4 and F^6 particularly were distorted compared to those obtained with the inclusion of (3.4) and the three-body corrections.

The data for PrIII ($4f^3$) fit by Rajnak (1965) were derived from actual free-ion spectra, whereas the centers of gravity of crystal-field components of states in $\text{Nd}^{3+}:\text{LaF}_3$ are, in fact, perturbed from their true free-ion energies by the effects of the environment. In addition, it is important to recognize that there are interactions between neighboring crystal-field states that can only be accommodated by ceasing to use J as a valid means of describing a state and resorting to eigenvectors based on crystal-field states (J -mixing). Use of this new description of states requires the simultaneous diagonalization of the atomic and crystal-field interactions. For the f^3 -configuration the computation is readily accommodated by available computers since the largest matrix involved is 62×62 (for D_{3h} -symmetry).

The results of including the crystal-field interaction in computing the energy level parameters for $\text{Nd}^{3+}:\text{LaF}_3$ starting with the four free-ion parameters (3.2) and progressively adding the two and three-body correction terms, parallel those for the free-ion case. When the model was restricted to E_{CF} and the atomic interactions in (3.2), the deviation was 350 cm^{-1} . Examination of the data shows that the lowest-energy states are fit best and

that it is clearly the inability to account for the free-ion structure that produces very large deviations at higher energies. Thus the addition of the crystal-field parameters to the model does not automatically improve the fit to the experimental data. The new parameters are constrained by their angular dependence in the type of interactions that they can reproduce. The complete present model reproduced the 147 observed crystal-field transition energies with a deviation of 16 cm^{-1} , Carnall et al. (1977).

There are, of course, higher order interactions that could be introduced. However, with use of the present model including two and three-body electrostatic corrections and the indicated magnetic corrections there no longer appear to be a limited number of large "effects" that would further significantly reduce the error.

III.2. Typical results for several organometallic lanthanides and actinides

Since the values of the radial integrals in the theoretical model are established by a fit to experimental data, the data base must be large enough to justify an extensive parametrization. In the early stages of this type of analysis, severe restrictions were placed on the bounds within which the parameters could vary and second order effects were not all included. Only the lower energy range of the spectra could be interpreted. As indicated in the previous section, a poor correlation with experiment results when the parametrization is limited. Analyses of data have now been carried out for lanthanide ions doped into single crystal LaCl_3 or LaF_3 which establish the systematic variation of parameters across the series in both cases, Crosswhite (1977). Similar results for actinides in LaCl_3 are presently being obtained. Thus even though the region in which the LnCp_3 and AnCp_3 optical spectra can be observed is limited, the groups can be compared in energy to those observed in the halide crystals. Where similar energy structures are indicated, it can confidently be assumed that the model parameters are similar. Detailed spectroscopic studies are necessarily carried out in host lattices. Dilution of the ion of interest in a suitable host minimizes ion-ion interactions and the intensities of the vibronically coupled bands which tend to broaden the spectral lines even at low temperatures. Corresponding host dilution studies of the cyclopentadienides have not been conducted. All the reported structure is of the pure compounds.

If we compare the reported band energies of several groups in NdCp_3 , Pappalardo (1965a) or ErCp_3 , Pappalardo (1968), with the corresponding data for $\text{Ln}^{3+}:\text{LaCl}_3$, Dieke (1968) or $\text{Ln}^{3+}:\text{LaF}_3$, Carnall et al. (1977), we see the clear parallel in the energy

level structures, Table 1. The absence of any large shifts in the f^N -structure is also apparent in the solution spectra of PrCp_3 and ErCp_3 in THF, Birmingham and Wilkinson (1956). While the crystal-field splitting of the ground state in NdCp_3 , for example, is greater than that in $\text{Nd}^{3+}:\text{LaCl}_3$, it is quite comparable to that in the highly ionic lattice LaF_3 . A similarity in structure is also revealed in comparing data for the actinide cyclopentadienides with the halides, Kanellakopulos et al. (1970), Carnall et al. (1968a), Pappalardo et al. (1969), as shown in Fig. 3, although, for the actinides, larger crystal-field splitting is observed. The interpretation of the data is therefore more complex, particularly in the light half of the series where the free-ion states are not as isolated in energy as they are at lower energies in the heavier actinides.

We conclude that even though an extensive analysis of the spectrum of an organometallic lanthanide or actinide may not be possible, the energy level parameters may be approximated by reference to available extensive single crystal free-ion analyses.

IV. CALCULATION OF TRANSITION PROBABILITIES FROM THE ABSORPTION SPECTRA OF TRIVALENT f-ELEMENTS

Reference has already been made to the great differences in transition probabilities (band intensities) observed when comparing the (electric dipole forbidden) $f \rightarrow f$ bands with those corresponding to $f \rightarrow d$ transitions or to charge transfer processes. We now turn to the theory of $f \rightarrow f$ transition probabilities. Our purpose is to explore the extent to which the current model can reproduce observed absorption spectra, then use the model to compute the rates of relaxation of the longer-lived fluorescing states.

We approach the problem of intensity correlation in the Ln^{3+} and An^{3+} ions with the realization that for many systems of potential interest we have no adequate model for the effect of the environment on the central atom. The purely electrostatic model which treats the nearest neighbor atoms as point charges in an array defined by the crystal structure does not provide the basis for a good approximation of crystal-field parameters. We therefore, discuss here only the free-ion approximation which relates to the actual spectra observed at 25°C. Since $E_{\text{CF}} \ll E_{\text{f}}$, many distinct bands corresponding to the collective intensities of the crystal-field components of individual free-ion states are observed. Based on the discussion in III, we bring to the intensity calculation a reliable set of eigenvectors for these states.

TABLE 1. Comparison of Crystal-field Levels of Nd^{3+} Observed at 4°K in Different Environments

State	$\text{Nd}^{3+}:\text{LaCl}_3^{\text{a}}$ (cm^{-1})	$\text{Nd}^{3+}:\text{LaF}_3^{\text{b}}$ (cm^{-1})	NdCp_3^{c} (cm^{-1})
$4\text{I}_{9/2}$	0	0	0
	115	45	70
	123	136	310
	244	296	570
	249	500	670
$4\text{F}_{7/2} + 4\text{S}_{3/2}$	13396	13514	13245
	400	590	394
	474	671	485
	488	676	555
	527	711	611
	531	715	721
$4\text{G}_{5/2} + 4\text{G}_{7/2}$	17095	17306	16778
	(114)	316	818
	165	363	958
	228	511	17062
	(254)	518	197
	(294)	571	247
	297	605	370

^a Dieke (1968).

^b Carnall et al. (1977).

^c Pappalardo (1965a).

Fig. 3 Absorption Spectra of PuI_3 , PuCl_3 , and PuCp_3

IV.1. Induced electric-dipole and magnetic-dipole transitions

The quantitative treatment of the intensities of trivalent f-element absorption bands relates an experimentally determined quantity, a normalized band envelope, P_{EXPT} , to a theoretical model based on the mechanisms by which radiation is absorbed. The terms oscillator strength or transition probability are applied interchangeably to the symbol P . There is some magnetic dipole character in a few transitions ($P_{\text{M.D.}}$), but an induced electric-dipole mechanism ($P_{\text{E.D.}}$) accounts for the intensities of most absorption bands. The term induced or forced electric dipole is used to emphasize that true electric dipole transitions require the initial and final states to be of different parity. In contrast, magnetic dipole transitions within a configuration are (parity) allowed. The existence of some intensity in intra- f^N transitions is usually ascribed to a small amount of the character of higher-lying opposite-parity configurations mixed into the f^N states via the odd terms in the potential due to the ligand field, Wybourne (1965). We neglect higher multipole mechanisms (electric quadrupole, etc), and write

$$P_{\text{EXPT}} = P_{\text{E.D.}} + P_{\text{M.D.}} \quad (4.1)$$

The appropriate expression for P_{EXPT} , which represents the number of classical oscillators in one ion, Hoogschagen (1946), is

$$P_{\text{EXPT}} = \frac{2303 \text{ mc}^2}{N\pi e^2} \int \epsilon_i(\sigma) d\sigma = 4.32 \times 10^{-9} \int \epsilon_i(\sigma) d\sigma \quad (4.2)$$

where ϵ_i is the molar absorptivity of a band at $\sigma_i(\text{cm}^{-1})$, N is the Avogadro constant and the other symbols have their usual meaning. P is a dimensionless quantity. The molar absorptivity at a given energy is computed from the Beer-Lambert law, $\epsilon \ell = \log I_0/I$, where ℓ is the concentration of the lanthanide ion in moles/1000 cm^3 , ℓ is the light path in the sample (cm), and $\log I_0/I$ is the absorptivity.

Since both absorption and fluorescence processes are to be considered, the basic relationship is given by the Einstein coefficient which expresses the transition probability due to dipole radiation

$$A(i, f) = \frac{64\pi^4 \sigma^3}{3h} |\langle i | D | f \rangle|^2 \quad (4.3)$$

where i and f signify the initial and final states, A is the (spontaneous) transition probability per unit time, $\sigma(\text{cm}^{-1})$ is the energy difference between the states, and D is the dipole

operator, Condon and Shortley (1957). Following Broer et al. (1945), we transform (4.3) via the substitution $P = mcA(i,f)/8\pi^2\sigma^2e^2$ to give the computed oscillator strength, P_{CALC} , of a band

$$P_{\text{CALC}} = \frac{8\pi^2 m c \sigma}{3 h e^2 (2J+1)} \left[\chi \bar{F}^2 + n \bar{M}^2 \right] \quad (4.4)$$

where $\bar{F}^2$ and $\bar{M}^2$ represent the matrix elements of the electric dipole and magnetic dipole operators, respectively, joining an initial state J to the final state J' , $\chi = (n^2+2)^2/9n$, and n is the refractive index of the medium.

Judd (1962), and Ofelt (1962), independently derived expressions for the oscillator strength of induced electric dipole transitions between free-ion states within the f^N -configuration. However, Judd's expression (4.5), was cast in a form that could be directly related to oscillator strengths derived from lanthanide absorption spectra

$$P_{\text{E.D.}} = \sum_{\lambda=2,4,6} T_{\lambda} \nu(\psi J \| U^{(\lambda)} \| \psi' J')^2 \quad (4.5)$$

where $\nu(\text{sec}^{-1})$ is the mean frequency of the transition $\psi J \rightarrow \psi' J'$, $U^{(\lambda)}$ is a unit tensor operator of rank λ , the sum running over the three values $\lambda = 2, 4, 6$, and the T_{λ} are three parameters which can be evaluated from experimental data. These parameters involve the radial parts of the $4f^N$ wave functions, the wave functions of perturbing configurations such as $4f^{N-1}5d$, and the interaction between the central ion and the immediate environment. Axe (1963) showed that (4.5) could be rewritten in the form

$$\bar{F}^2 = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} (\psi J \| U^{(\lambda)} \| \psi' J')^2 \quad (4.6)$$

where Ω_{λ} is related by a constant to Judd's T_{λ} parameter. The matrix elements of $U^{(\lambda)}$, (4.6), for transitions between various excited states as well as between the ground and excited states of the whole series of lanthanide ions using the energy level parameters obtained from a systematic treatment of the $\text{Ln}^{3+}:\text{LaF}_3$ series have been tabulated, Carnall et al. (1977).

Following Condon and Shortley (1957), the magnetic dipole operator is given as $M = -e(L + 2S)/2mc$. The matrix elements of the operator $\bar{M}^2$ in (4.4) can then be written,

$$\bar{M}^2 = e^2 (\psi J \| L + 2S \| \psi' J')^2 / 4m^2 c^2 \quad (4.7)$$

TABLE 2. Oscillator Strengths for Er^{3+} (25°C)

Spectral Range ^a (cm ⁻¹)	S'L'J'	$P \times 10^6$			
		$\text{Er}^{3+}(\text{HClO}_4\text{-DClO}_4)$		$\text{ErCp}_3(\text{MeTHF})$	
		Expt	Calc ^b	Expt	Calc ^b
6200-7000	$4I_{13/2}$	2.19	$\begin{cases} 0.41^c \\ 1.98 \end{cases}$	-	-
9400-10800	$4I_{11/2}$	0.84	0.66	1.47	3.73
12000-12900	$4I_{9/2}$	0.29	0.35	1.05	0.39
14800-15800	$4F_{9/2}$	2.25	2.36	4.80	4.96
18000-18700	$4S_{3/2}$	0.66	0.62	2.55	2.17
18700-19800	$2H_{11/2}$	2.89	3.26	68.5	75.0
20000-21100	$4F_{7/2}$	2.27	2.43	6.50	7.26
21800-23000	$4F_{5/2}$	1.25	1.20	1.80	2.62
	$4F_{3/2}$			0.77	1.52
24100-25100	$(2G, 4F, 2H)_{9/2}$	0.80	0.92	7.25	3.01
25800-27100	$4G_{11/2}$	5.92	5.76	136	132
27100-27700	$4G_{9/2}$	1.75	1.56		
27700-28400	$2K_{15/2}$	0.91	0.05 ^c		
	$2G_{7/2}$		0.99		
31300-31900	$(2P, 2D, 4F)_{3/2}$	0.091	0.083		
32700-33600	$2K_{13/2}$	0.12	0.12		
	$4G_{5/2}$				
	$2P_{1/2}$				

^a Range encompassing observed band(s).^b The parameters used to obtain these values were:

$$\frac{\text{Er}^{3+}(\text{HClO}_4\text{-DClO}_4)}{\Omega_2 = 1.59 \times 10^{-20} \text{ (cm}^2\text{)}}$$

$$\Omega_4 = 1.95$$

$$\Omega_6 = 1.90$$

$$\frac{\text{ErCp}_3(\text{MeTHF})}{\Omega_2 = 64.1 \times 10^{-20} \text{ (cm}^2\text{)}}$$

$$\Omega_4 = 1.76$$

$$\Omega_6 = 6.34$$

^c Calculated magnetic dipole oscillator strength.

The non-zero matrix elements will be those diagonal in the quantum numbers α , S , and L . The selection rule on J , $\Delta J = \pm 0, 1$, restricts consideration to three cases, $J' = J$, $J' = J-1$, and $J' = J+1$. In each instance (4.7) reduces to a quantity that can be computed exactly. The matrix elements of (4.7) have been tabulated, Carnall et al. (1968b).

IV.2. Comparison with experiment

While intensity correlations in the actinides and lanthanides have been explored extensively in all phases, detailed analysis with organometallic compounds does not appear to have been pursued. Thus, to provide some basis for judging the extent to which correlation is possible, results for $\text{Er}^{3+}(\text{aq})$, Carnall et al. (1968b) and ErCp_3 in 2-methyl tetrahydrofuran (MeTHF), Pappalardo (1968), are compared in Table 2. The data for $\text{Er}^{3+}(\text{aq})$ were chosen because the numerous isolated absorption bands are both well characterized in terms of the transitions involved and occur over an extensive energy range. The excellent correlation between observed and calculated intensities consequently demonstrates the power of the theory.

The results for ErCp_3 in MeTHF were computed from data given by Pappalardo (1968). While it is apparent that the fit of the $\text{Er}^{3+}(\text{aq})$ data is much better than that of the ErCp_3 , it is the change in intensity pattern that is particularly striking. The interpretation of the increase in intensities of the $^4\text{I}_{15/2} \rightarrow ^4\text{H}_{11/2} (\sim 19000 \text{ cm}^{-1})$ and $^4\text{G}_{11/2} (\sim 26000 \text{ cm}^{-1})$ transitions in ErCp_3 relative to $\text{Er}^{3+}(\text{aq})$ is discussed in the next section.

IV.3. Hypersensitive transitions

A comparison of the spectra of the 3+ lanthanides and actinides in many different environments reveals that the intensities associated with most absorption bands for a given f-element corrected to unit concentration are remarkably invariant. In contrast, the intensities of one or two transitions in each element can change significantly as a function of the environment. With the advent of the Judd-Ofelt Theory these "hypersensitive" transitions, Jørgensen and Judd (1964), were systematized. They were shown to follow electric quadrupole selection rules, $\Delta J \leq \pm 2$, and to be identified with large matrix elements of $U^{(2)}$. A particularly dramatic change in intensity was noted in (IV.2.) comparing data for $\text{Er}^{3+}(\text{aq})$ to that for ErCp_3 (MeTHF).

Intense hypersensitive bands have also been identified in other LnCp_3 and clearly established in AmCp_3 as well, Pappalardo et al. (1969). Our interest for present purposes stems in part

from what these transitions reveal about bonding conditions, and in part because they represent a possible avenue for pumping energy into the f^N -configurations in connection with potential lasing experiments.

Since we have already recognized the relative insensitivity of the energy of transitions in trivalent f-electron systems to the immediate environment, considerable interest derives in possible correlations between bonding type and band intensity. Judd (1962) showed that the values of Ω_λ (4.6) computed from an approximate model of $\text{Ln}^{3+}(\text{aquo})$ were consistent with those derived by a fit to experimental data, and that, to a good approximation only the value of Ω_2 was sensitive to changes in the environment. Mechanisms for increased intensity that would uniquely influence the value of Ω_2 were examined by Jørgensen and Judd (1964), but subsequently Judd (1966b) pointed out that, without reference to any detailed mechanism, symmetry arguments could be used as a basis for classification. In effect, only a limited number of point groups would permit Ω_2 to vary independently of Ω_4 and Ω_6 within the context of the original Judd theory. Most of these groups, C_s , C_n ($n=1-4,6$), C_{nv} ($n=2-4,6$) represent low site symmetries, but a unique assignment to one of these symmetries would not appear to be possible.

More recently, a dynamic coupling mechanism relating the polarizability of the ligands to the intensity of the hypersensitive transitions has been advanced by Mason et al. (1975), Peacock (1975). This represents a refinement to and extension of the Judd theory, since it assumes that the intensities of most transitions are correctly described by (4.4) and deals only with the increase of intensity in the hypersensitive transitions. According to this model, there is a Coulombic correlation between transient induced electric dipoles in the ligands and the f-electron quadrupole moments of Ln^{3+} (or An^{3+}). The transient charge distribution at the metal site is induced by the $f \rightarrow f$ transition. The dynamically induced oscillator strength for trivalent f-elements is given by

$$P_{\text{DYN}} = \frac{8\pi^2 m c \sigma}{3h(2J+1)} \times \Omega_{\text{DYN}} (f^N \psi_J \| U^{(2)} \| f^N \psi'_{J'})^2$$

$$\Omega_{\text{DYN}} = \frac{28}{5} \langle 4f | r^2 | 4f \rangle^2 \sum_{m=0}^3 (2-\delta_{m,0}) \sum_L |R_L^{-4} \bar{\alpha}(L) C_m^{(3)}(L)|^2$$

$\bar{\alpha}(L)$ is the average polarizability of the ligand, R_L is the metal-ligand bond distance, and $C_m^{(3)}(L)$ describes the orientation of each ligand with respect to the central metal atom. Since R_L occurs to a high power, R^{-12} and R^{-16} for Ω_4 and Ω_6 , respectively, it is obvious why Ω_4 and Ω_6 do not contribute to P_{DYN} .

The values of Ω_λ computed for Er^{3+} in a number of different environments are listed in Table 3. Only a limited number of calculations of PDYN have been reported, but the results for $\text{ErI}_3(\text{g})$, $\text{ErBr}_3(\text{g})$, and $\text{Er}^{3+}:\text{LaF}_3$ are reported to be in agreement with the values of Ω_2 derived from experiment. This suggests that the large Ω_2 in ErCp_3 may also be reproduced with a judicious interpretation of α and R_L for the Cp ligands. This continues to be an active area of investigation, and new insights into bonding may be forthcoming.

V. LUMINESCENCE SPECTRA OF 3+ LANTHANIDES AND ACTINIDES

Interest in the luminescence properties of the 3+ lanthanides was at a peak in the mid 1960's as the laser potential of various systems including solutions of lanthanide chelates was explored, Lempicki and Samelson (1966), Crosby (1966), Lempicki (1971). The basis for the interest in chelates was the discovery by Weissman (1942), that they could absorb energy in the ultraviolet range and in certain cases transfer this energy "intramolecularly" to the lanthanide ion. The transfer of energy in Eu^{3+} resulted in emission characteristic of f-f transitions in the visible region. The process is indicated in Fig. 4. The potential efficiency of this mechanism in populating f-electron states is suggested by the much greater intensity of the bands characteristic of the ligands compared to those of the weak f-f transitions.

There are several reasons for continued basic interest in the luminescence properties of chelates and organometallic compounds of the f-elements. The Judd-Ofelt theory now makes it possible to compute the radiative component of the lifetimes of fluorescing states based on measurements of absorption spectra. This provides a means of developing new insights into the fundamental nature of relaxation processes and energy transfer. There have also been important advances in the ability to obtain relevant experimental data. Micro to nanosecond lifetimes are measured routinely, and tunable dye lasers provide a means, not available earlier, of pulsed excitation at selected energies throughout a wide range of the spectrum. Interestingly, little attention has been given to the study of the luminescent properties of f-elements in the vapor phase, yet the volatility of many organometallics is one of the unique properties of this class of compounds.

V.1. Mechanisms of relaxation of excited states and the computation of radiative emission rates

The forced-electric and magnetic dipole processes discussed relative to the absorption of radiation are also primarily responsible for the radiative decay of excited f^N -states. Non-radiative

TABLE 3. Values of Ω_λ for Er^{3+} in Various Systems

System	Phase	T °C	$\times 10^{20} \text{ cm}^2$			Ref.
			Ω_2	Ω_4	Ω_6	
$\text{Er}^{3+}(\text{aq})$	Liquid	25	1.59	1.95	1.90	a
$\text{ErCp}_3(\text{MeTHF})$	Liquid	25	64.1	1.76	6.34	b
$\text{Er}^{3+}:\text{LaF}_3$	Solid	25	0.74	0.19	0.44	c
$\text{Er}^{3+}:\text{YAlO}_3$	Solid	25	1.06	2.63	0.78	c
$\text{Er}^{3+}:\text{Li-KNO}_3$	Liquid	160	15.8	1.84	1.39	d
$\text{Er}(\text{thd})_3$	Vapor	288	46	2.70	3.70	e
$\text{ErCl}_3(\text{AlCl}_3)_x$	Vapor	~400	25.8	2.70	2.01	f
ErI_3	Vapor	993	97.7	5.90	-1.47	e
ErBr_3	Vapor	1105	60	1.47	1.66	e

^a Carnall et al. (1968b).

^b Pappalardo (1968).

^c Riseberg and Weber (1976).

^d Carnall et al. (1978a).

^e Gruen et al. (1967).

^f Carnall et al. (1978b).

Fig. 4. SCHEMATIC ENERGY TRANSFER
CYCLE IN LANTHANIDE-ACTINIDE

$\times 10^3 \text{ cm}^{-1}$ ORGANOMETALLIC COMPOUNDS

mechanisms compete strongly with the radiative mode and usually control the relaxation rate.

From (4.3) and (4.4), the radiative relaxation rate of an excited state (ψJ) to a particular final state ($\psi' J'$) is

$$A(\psi J, \psi' J') = \frac{64\pi^4 \sigma^3}{3h(2J+1)} [\chi' \bar{F}^2 + n^3 \bar{M}^2] \quad (5.1)$$

where $\sigma(\text{cm}^{-1})$ represents the energy gap between states (ψJ) and ($\psi' J'$), $\chi' = n(n^2 + 2)^2/9$, and n is the refractive index of the medium. As in the absorption process, there is an implicit assumption that all crystal-field components of the initial state are equally populated. In principal, if fluorescence can be detected, the lifetime of the state is long compared to the rate at which it is populated in the excitation process, so thermal equilibrium at the temperature of the system can be achieved prior to emission.

The matrix elements of the electric and magnetic dipole operators, $\bar{F}^2$ and $\bar{M}^2$, are identical to those of (4.6) and (4.7), respectively. However, the form of the refractive index correction is not the same as for the absorption process. Equation (5.1) can thus be evaluated using parameters Ω_λ established from measurement of the absorption spectrum of the lanthanide ion for a system identical to that studied in fluorescence.

Since excited state relaxation generally involves transitions to several lower-lying states, we define a total radiative relaxation rate, $A_T(\psi J)$

$$A_T(\psi J) = \sum_{\psi' J'} A(\psi J, \psi' J') \quad (5.2)$$

where the sum runs over all states lower in energy than the fluorescing state. It is also useful to define the radiative branching ratio, β_R , from the relaxing state (ψJ) to a particular final state ($\psi' J'$)

$$\beta_R(\psi J, \psi' J') = \frac{A(\psi J, \psi' J')}{A_T(\psi J)} \quad (5.3)$$

and the radiative lifetime of a state

$$\tau_R(\psi J) = [A_T(\psi J)]^{-1} \quad (5.4)$$

While the relaxation of an excited state may occur via a purely radiative process, this must be recognized as the exception

rather than the rule. Detailed studies of the fluorescence spectra of f-elements in various compounds reveal that only a few excited states can be observed to fluoresce. Most are rapidly relaxed by non-radiative processes even at low temperatures. Typically, several different non-radiative mechanisms may operate simultaneously.

Formally, we can express the total fluorescence lifetime of a state as

$$(\tau_T)^{-1} = A_T(\psi J) + W(\psi J) \quad (5.5)$$

where A_T is the total radiative rate and $W(\psi J)$ is the sum of the rates of the various non-radiative processes.

V.2. Comparison of experimental and computed excited state lifetimes

While fluorescence from excited states of f-elements in crystals, solution and in the vapor phase has been observed, actual lifetime measurements have been made on relatively few systems. A great deal of interest has been manifest in the spectra of solid phases because of laser applications. As an example of the use of the theory outlined, the following results were obtained in single crystal $\text{Er}^{3+}:\text{LaF}_3$, Weber (1967):

Transition	Calculated $\tau_R(\text{msec})$	Observed $\tau_T(\text{msec})$
$^4I_{13/2} \rightarrow ^4I_{15/2}$	10.9	13
$^4I_{11/2} \rightarrow ^4I_{15/2}$	11.6	11
$^2P_{3/2} \rightarrow ^4I_{15/2}$	0.43	0.29

It was recognized experimentally before any quantitative theories were developed that the fluorescence lifetime of an excited level in a crystal host was related to the energy gap to the next lower-lying state. For example, fluorescence in $\text{Ln}^{3+}:\text{LaCl}_3$ was not observed at 25°C if the energy gap was $<10000\text{ cm}^{-1}$, Barasch and Dieke (1965). The principal mechanism identified in this case was a multiphonon process involving transfer of energy to the lattice, and it has been treated phenomenologically by assuming that the appropriate phonon energy corresponds to the cut-off in phonon states or $\sim 350\text{ cm}^{-1}$, in LaF_3 , Moos (1970), Riseberg and Weber (1976). The corresponding expression for $W(\psi J)$ as a function of temperature is:

$$W(\psi J) = Ce^{\alpha \Delta E} [1 - e^{-\hbar \omega_i / kT}]^{-\Delta E / \hbar \omega_i} .$$

where $\hbar \omega_i$ is the maximum phonon energy, ΔE is the energy gap, α and C are parameters characteristic of the host. For example, the radiative lifetime of the $^4I_{9/2}$ state of $Er^{3+}:LaF_3$ at $\sim 12000 \text{ cm}^{-1}$ is computed to be 20.7 msec but observed to be ~ 0.15 msec, Weber (1967). Since ΔE is $\sim 2000 \text{ cm}^{-1}$ we compute $W(\psi J) = \sim 10^4 \text{ sec}^{-1}$ at 25°C . Thus the non-radiative lifetime of ~ 0.1 msec is rate determining.

As indicated earlier, Pappalardo and Losi (1965) observed band emission in both $GdCp_3$ and $LaCp_3$ near 20000 cm^{-1} upon excitation further in the ultraviolet, while line fluorescence was reported in undiluted sublimates of $TbCp_3$, $SmCp_3$ and $DyCp_3$, Pappalardo (1965b). The $f \rightarrow f$ states in $GdCp_3$ are encompassed by the broad absorption characteristic of C_5H_5 . In contrast, there exist f^N -states at lower energies for the ions where line fluorescence was observed. Thus intramolecular energy transfer in the latter appears to be well established. The band emission corresponds to a triplet-singlet transition characteristic of the Cp-ligand. Similar broad band fluorescence of lanthanide acetylacetonate chelates due to $\pi \rightarrow \pi^*$ ($T \rightarrow S$) relaxation has been reported by Crosby et al. (1971).

In $CmCp_3$, several sharp bands were observed near 15600 cm^{-1} upon excitation in the ultraviolet range, Laubereau and Burns (1970). These correspond well to expected $^5D_{7/2} \rightarrow ^8S$ transitions in Cm^{3+} . Since the ground state is not split, the observed structure is due to fluorescence from several crystal-field levels of $^5D_{7/2}$ which are populated at the temperature of the measurement, 25°C . It should be emphasized that fluorescence in $LnCp_3$ and $AnCp_3$ has to date been studied in pure samples where concentration quenching can be an important relaxation mechanism. In the future studies using dilution techniques will need to be emphasized.

V.3. Energy transfer and emission in the vapor phase

One of the unique properties of organometallic f-elements as a class is their volatility. Just as renewed interest is being focussed on the fundamental mechanisms of energy transfer in solids and solutions as a result of increased experimental capabilities and theoretical insights, there is much to be learned about fluorescence properties in the gas phase. Indeed a number of limitations presently imposed on the generation of high power densities in solid state lasers would not exist in a circulating gas phase system.

Although the lifetimes associated with the fluorescing 5D_4 state of Tb^{3+} in vapor phase $Tb(thd)_3^*$ at elevated temperatures were predictably reduced compared to those observed in the liquid and solid at lower temperatures, pulsed excitation and fast detection techniques made it possible to investigate some aspects of the energy transfer process, Jacobs et al. (1975). The chelate ligands were pumped with the direct 29670 cm^{-1} pulse from a N_2 -laser, and transient fluorescence from $Tb(thd)_3$ was observed at right angles to the exciting light. Emission characteristic of fluorescence from the 5D_4 state to several components of the 7F ground multiplet was observed but no emission from the 5D_3 state was detected. This suggests that the lowest triplet state in the chelate may lie at an energy intermediate between the 5D_3 and 5D_4 states. The absorption spectra of a number of the $Ln(thd)_3$ compounds in the gas phase were reported by Gruen et al. (1967), and in each case intense hypersensitive transitions were observed.

The transfer of energy is typically rapid in the $Tb(thd)_3$ vapor since the observed risetime of the 5D_4 fluorescence was $>$ the pump pulse duration. This indicates a transfer time [singlet $\rightarrow$ triplet $\rightarrow$ 5D_4] on the nanosecond time scale. Similar experiments with organometallic lanthanide and actinides could lead to valuable insights into the nature of the bonding and the types of relaxation mechanisms that are important.

*2,2,6,6-tetramethyl-3,5,heptanedione

REFERENCES

- AXE, J. D. (1963), J. Chem. Phys. 39, 1154.
 BALASUBRAMANIAN, G., M. M. ISLAM and D. J. NEWMAN (1975), J. Phys. B. 8, 2601.
 BARASCH, G. E., and G. H. DIEKE (1965), J. Chem. Phys. 43, 988.
 BIRMINGHAM, J. M., and G. WILKINSON (1956), J. Am. Chem. Soc. 78, 42.
 BREWER, L. (1971), J. Opt. Soc. Am. 61, 1011, 1666.
 BROER, L. L. F., C. J. GORTER, and J. HOOGSCHAGEN (1945), Physica 11, 231.
 CARNALL, W. T., P. R. FIELDS, and R. G. PAPPALARDO (1968a), Proc. 11th Intern. Conf. Coord. Chem. Haifa.
 CARNALL, W. T., P. R. FIELDS, and K. RAJNAK (1968b), J. Chem. Phys. 49, 4412.
 CARNALL, W. T., H. M. CROSSWHITE and H. CROSSWHITE (1977), "Energy level structure and transition probabilities in spectra of the trivalent lanthanides in LaF_3 ," Chemistry Division Report, Argonne National Laboratory.
 CARNALL, W. T., JAN P. HESSLER, and F. WAGNER, JR. (1978a), J. Phys. Chem., in press.
 CARNALL, W. T., JAN P. HESSLER, H. R. HOEKSTRA, and C. W. WILLIAMS (1978b), J. Chem. Phys. 68, 4304.

- COHEN, E., and H. W. MOOS (1967), Phys. Rev. 161, 258, 268.
- CONDON, E. U., and G. H. SHORTLEY (1957), "The Theory of Atomic Spectra", Cambridge University Press, London, pp. 91-109.
- CROSBY, G. A. (1966), Molecular Crystals 1, 37.
- CROSBY, G. A., R. J. WATTS, and S. J. WESTLAKE (1971), J. Chem. Phys. 55, 4663.
- CROSSWHITE, H. M. (1977), Colloques Internationaux C.N.R.S., Paris, No. 255, p. 65.
- DIEKE, G. H. (1968), "Spectra and Energy Levels of Rare Earth Ions in Crystals", H. M. Crosswhite and H. Crosswhite, eds., Wiley, New York.
- GOFFART, J., and G. DUYCKAERTS (1978), Inorg. Nucl. Chem. Lett. 14, 15.
- GRUEN, D. M., C. W. DE KOCK, and R. L. MC BETH (1967), Adv. Chem. Series 71, 102.
- HAYES, R. G., and J. L. THOMAS (1971), Organomet. Chem. Rev. A, 7, 1.
- HODGSON, K. D., F. MARES, D. F. STARKS, and A. STREITWEISER, JR. (1973), J. Am. Chem. Soc. 95, 8650.
- HOOGSCHAGEN, J. (1946), Physica 11, 513.
- JACOBS, R. R., M. J. WEBER, and R. K. PEARSON (1975), Chem. Phys. Lett. 34, 80.
- JØRGENSEN, C. K., and B. R. JUDD (1964), Mol. Phys. 8, 218.
- JØRGENSEN, C. K. (1969), "Oxidation Numbers and Oxidation States," Springer Verlag, Berlin.
- JUDD, B. R. (1962), Phys. Rev. 127, 750.
- JUDD, B. R. (1963), "Operator Techniques in Atomic Spectroscopy," McGraw-Hill, New York.
- JUDD, B. R. (1966a), Phys. Rev. 141, 4.
- JUDD, B. R. (1966b), J. Chem. Phys. 44, 839.
- JUDD, B. R., H. M. CROSSWHITE and H. CROSSWHITE (1968), Phys. Rev. 169, 130.
- KANELLAKOPOULOS, B., R. D. FISCHER, E. DORNBERGER and F. BAUMGÄRTNER (1970), J. Organometall. Chem. 24, 507.
- KANELLAKOPOULOS, B., E. DORNBERGER and F. BAUMGÄRTNER (1974), Inorg. Nucl. Chem. Lett. 10, 155.
- LAUBEREAU, P. G., and J. H. BURNS (1970), Inorg. Nucl. Chem. Lett. 6, 59.
- LEMPICKI, A., and H. SAMELSON (1966), "Organic Laser Systems", in A. K. Levine, ed., Lasers 1, 181, Marcel Dekker, N. Y.
- LEMPICKI, A. (1971), "Rare Earth Liquid Lasers," R. J. Pressley, ed., Handbook of Lasers, p. 355, Chemical Rubber Pub. Co.
- MASON, S. F., R. D. PEACOCK and B. STEWART (1975), Mol. Phys. 30, 1829.
- MOOS, H. W. (1970), J. Luminescence 1, 106.
- MORRISON, J. C., and K. RAJNAK (1971), Phys. Rev. A4, 536.
- NUGENT, L. J., P. G. LAUBEREAU, G. K. WERNER and G. K. VANDER SLUIS (1971), J. Organomet. Chem. 27, 365.

- NUGENT, L. J. (1975), "Chemical Oxidation States of the Lanthanides and Actinides", K. W. Bagnall, ed., International Review of Science, Inorganic Chemistry Series Two, 7, (University Park Press, Baltimore), Chapter 6.
- OFELT, G. S. (1962), J. Chem. Phys. 37, 511.
- PAPPALARDO, R. (1965a), Helv. Phys. Acta 38, 178.
- PAPPALARDO, R. (1965b), Proc. Fifth Rare Earth Conference, Ames, Iowa, p. 87.
- PAPPALARDO, R., and S. LOSI (1965), J. Inorg. Nucl. Chem. 27, 733.
- PAPPALARDO, R., and C. K. JØRGENSEN (1967), J. Chem. Phys. 46, 632.
- PAPPALARDO, R. (1968), J. Chem. Phys. 49, 1545.
- PAPPALARDO, R. (1969), J. Mol. Spectr. 29, 13.
- PAPPALARDO, R. G., W. T. CARNALL and P. R. FIELDS (1969), J. Chem. Phys. 51, 842.
- PEACOCK, R. D. (1975), Struct. Bonding 22, 83.
- RAJNAK, K., and B. G. WYBOURNE (1963), Phys. Rev. 132, 280.
- RAJNAK, K. (1965), J. Opt. Soc. Am. 55, 126.
- RISEBERG, L. A., and M. J. WEBER (1976), Prog. Optics 14, 89.
- WEBER, M. J. (1967), Phys. Rev. 157, 262.
- WEISSMAN, S. I. (1942), J. Chem. Phys. 10, 214.
- WYBOURNE, B. G. (1965), "Spectroscopic Properties of Rare Earths," Wiley, N. Y.