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**ELECTRONIC AND MAGNETIC HYPERSENSITIVITY
IN THE MCD SPECTRA OF
LANTHANIDE COMPLEXES**

by

PAMELA A. WOLFF, B.Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Master of Science
Department of Chemistry

Carleton University
Ottawa, Ontario
April, 1990

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The undersigned recommend to the Faculty of Graduate Studies
and Research acceptance of the thesis

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submitted by Pamela A. Wolff, B.Sc.
in partial fulfilment of the requirements for
the degree of Master of Science

Thesis Supervisor

Chair, Department of Chemistry

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April, 1990

ABSTRACT:

Complexes of the rare earth ions have been widely studied using U.V./visible spectroscopy, with the main focus of interest being the transitions having a change in total angular momentum of $\Delta J = 2$, which show much greater intensity variation upon changing the nature of the complexing ligand than do any of the other transitions. Many different models have been proposed to account for this phenomenon, known as hypersensitivity.

A study of rare earth complexes using MCD spectroscopy has revealed a new phenomenon; a hypersensitivity analogous to the $\Delta J = 2$, but involving those transitions having $\Delta J = 1$. This magnetic hypersensitivity is not observed in the absorption spectra of these complexes. An experimental correlation between this magnetic hypersensitivity and the optical electronegativity of the complexing ligand is observed. Several mechanisms are considered to explain the effect, and a vibronic mechanism is chosen as the model which best describes the observations.

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I. INTRODUCTION:

The rare earth elements are probably the least known elements on the periodic table. They are shown, together with the actinide elements, below the "regular" elements, and they have never been treated as an integral part of any introduction to the elements. Their chemistry is generally ignored or touched upon in a very cursory manner in introductory chemistry courses.

They do, however, have a great deal to contribute to the base of chemical knowledge on a very fundamental level. They exhibit strong spin-orbit coupling, and so provide a framework in which fully coupled systems can be studied. They also show only a weak interaction with their surroundings, and so allow the study of their metal ions in solution, without the complications of ligand field effects. In fact, the solution spectra approximate the gas phase spectra, removing the necessity for complex and costly gas-phase equipment.

The spectra of the rare earth ions are rather poorly understood, and many questions about them remain unanswered.

The electronic transitions of the trivalent rare earth ions in the UV/visible wavelengths are internal $f \rightarrow f$ transitions, which are parity forbidden. It is necessary to invoke some mechanism by which the parity restriction may be lifted to account for the observed intensities of the spectra.

In addition to the requirement for some mechanism to explain the presence of intensity in the spectra of the rare earth elements, it is also necessary to explain the

manner in which they do interact with the ligands to which they are bound, to give observable changes in the spectra of their complexes. The most notable manifestation of their interaction with the environment is the effect known as hypersensitivity. A small number of electronic transitions show marked intensity changes on changing the ligand, while the rest of the bands in the spectrum show no change. Although this effect has been known for almost 40 years, there has so far been no consensus as to its mechanism. Three mechanisms have been prominent in the literature as possible explanations of the effect; these are a pseudoquadrupole mechanism, where the ligands cause an inhomogeneous dielectric about the metal ion, a static mechanism, where configurations above the 4f, such as the 5s, 5p, 6s, and 5f interact with the states of the 4f configuration, and a vibronic mechanism, where vibrational modes couple with the electric transitions, enhancing some, while leaving the intensities of others insensitive to the nature of the ligand.

Magnetic circular dichroism (MCD) spectroscopy should be a useful tool for examining the nature of the rare earth complexes. It is a magnetic phenomenon, and responds to changes in the magnetic dipole, which is equivalent to the electric quadrupole. While absorption spectroscopy responds to dipolar events, therefore, MCD is particularly sensitive to quadrupolar events. MCD intensities should yield additional information on the nature of the electronic transitions of the rare earth complexes in general, and the hypersensitive transitions in particular.

MCD spectroscopy itself is a truly three dimensional experiment. The circularly polarized light has associated with it a phase, a sense of rotation, and a chirality. Current theoretical treatments of spectroscopy do not allow for the inclusion of all of this information, and there are no theories which allow the *a priori* calculation of

the sign for a given MCD transition. Theoretical treatments ignore the tensorial information by assuming that the roots of all expressions will be real and positive. They then reintroduce signs by multiplying the results by $(-1)^n$. A fully vectorial treatment of the theory is beyond the scope of this thesis, but the implications of the neglect of the tensorial information will be considered.

Finally, there is no evidence in the literature of any attempts to correlate observable hypersensitivity in rare earth complexes with a physically measurable ligand parameter. Such an experimental correlation will be sought during the course of this study, using the degree of hypersensitivity in the MCD spectra as the dependent parameter, and the ligand electronegativity as the independent parameter.

II. THE RARE EARTH ELEMENTS:

II.1 Introduction:

Over the past 40 years, researchers have been examining the optical spectra of complexes of the rare-earth elements. These did not attract the attention given to the d-block transition elements, partly due to difficulties in purifying the elements, and partly to their strong thermodynamic tendencies to form oxides or complexes with oxy ligands. The advent of preparatory scale ion-exchange chromatography has eliminated the first of these technical difficulties. but in comparison with the other blocks of the periodic table there is still only a small knowledge base on the bonding and spectroscopy of the lanthanides. Recently, the organometallic chemistry of the rare earths has been discovered, and several new classes of complexes synthesized.

The advent of the solid state laser¹ opened up the field of solid state R.E. spectroscopy, as the R.E. elements doped in glasses make excellent lasers. Nd³⁺ in particular has been widely studied in various hosts.^{2,3,4} Rare earth sesquisulfides

¹ T. H. Maiman, Nature 187, 493, 1960

² L. F. Johnson, J. Appl. Phys. 34, 897, 1962

³ R. E. Hoskins and B. H. Soffer, Appl. Phys. Lett. 4, 22, 1964

⁴ U. Deserno, D. Röss and G. Zeidler, Phys. Lett. 28A, 422, 1968

have also been studied recently for their application to semiconductor technology.^{5,6}

II.2 Observable Electronic Structure of Atoms and Ions:

Any study on the nature and properties of rare earth complexes must begin with an understanding of the properties of the atom, and of the free ion. Thus, the spectral energies, intensities and selection rules for atomic and ionic systems must be known in detail before any significant changes can be recognized in the complexes and correlated to ligand properties.

The neutral atoms of the rare earth elements differ from the atoms of the other periodic blocks in that their outermost subshell, the 5p, is entirely filled, while an inner subshell, the 4f, is only partially filled. Thus, the incomplete shell is shielded from external fields by the spherically symmetric filled outer shell, and so it responds only weakly to its surroundings. Figure 1a is an energy plot of subshell energies as a function of the atomic number, with the rare earth elements falling in the range from $Z = 58$ to $Z = 70$. When the square of the radial wavefunction for the orbitals involved in the chemistry of the rare earth elements is plotted against the radius, the distribution in space is given by figure 1b.

⁵ G. H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals, 1968, (John Wiley and sons, Inc, New York.)

⁶ J. R. Henderson, M. Muramoto, T. M. Henderson, and J. B. Gruber, J. Chem. Phys., 47, 5097, 1967

Figure II.1a: Variation of orbital energies with Z for values of Z from 1 to 100. The energies are given as the square root of the absolute energy to allow for the large range of values to be placed on one graph.

Figure II.1b: Square of the radial wavefunction vs. the radius for the 4f, 5s, 5p, and 6s electrons. The plot was derived for Gd^{3+} , but holds true for the Ln(III) ions, except that these will have smaller values overall for r , due to the higher effective nuclear charge.⁷

⁷ A. J. Freeman and R. E. Watson, *Phys. Rev.*, **127**, 2058, 1962

II.2.i. Radii:

The radii of the lanthanides and of their ions decrease sharply across the period. This decrease is much more pronounced than the one that occurs for the d block elements, but occurs for the same reason: The shielding of an f electron by the other f electrons is almost negligible, while the charge on the nucleus increases by one for each successive atom or ion. The electrons experience an increased effective nuclear charge at each successive element across the period, and the radii decrease, as shown in figure II.2.

Figure II.2. The ionic radii of the Ln(III) ions going across the period.⁸

This implies that not only are the f electrons well shielded from the outside environment, but that this shielding becomes more pronounced on going across the period. Even the filled d subshell becomes less accessible as the radius shrinks. The decreasing size of the ions on the right of the group also dictates changes in the

⁸ D. H. Templeton and C. H. Dauben J. Amer. Chem. Soc., 76, 5237, 1954

geometry of any complexes which they form, since the radius ratio rule⁹ predicts that they will be surrounded by a decreasing number of ligands.

II.2.ii. Configurations:

Using the Aufbau principle, the electronic configuration of the neutral atoms of these elements is given by:

where n is the number of 4f electrons in the atomic ground state. At the beginning of the series, $4f^{n-1} 5d^1$ is also observed, giving the elements in this configuration behavior similar in some ways to that of the d-block. The stability of a half filled shell is also apparent from the formation of $6s^2 4f^7 5d^1$ for Gd, as well as the formation of Gd^{2+} , with the electronic configuration $4f^7 5d$, and the formation of Tb^{4+} , having the configuration $4f^{710}$.

The rare earth elements are most commonly found in complexes in their trivalent oxidation state. This is formed by loss of the least stable electrons, so that the electronic configuration of these ions is generally:

or

where $N = n - 1$

⁹ A. Magnus, Z. Anorg. Allgem. Chem., **124**, 288, 1922

¹⁰ F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed. 1972, (Interscience, New York).

Historically, the rare earth elements are defined as those elements which, in their trivalent state, have a partially filled 4f subshell¹⁰. This definition encompasses the elements from Cerium to Ytterbium.

element:	N =	element:	N =
Ce	1	Tb	8
Pr	2	Dy	9
Nd	3	Ho	10
Pm†	4	Er	11
Sm	5	Tm	12
Eu	6	Yb	13
Gd	7		

† No natural occurrence; radioactive.

Table II.1. The number of f electrons in the Ln(III) ions.

II.2.iii Electronic States:

Atoms or ions with partly filled shells can always exist in more than one "state", or identifiable arrangement of electrons in the open shell characterized by specific values of angular momenta¹⁰. The rare earth elements in their +3 states all have relatively large spin-orbit coupling constants ($\approx 1000 \text{ cm}^{-1}$), with specific values given in table II.2, and therefore have ground states which can be identified by single, well defined values of J, the total angular momentum. This are comparable

to the spin-orbit coupling constants of the ions of the third row of the d-block,, which have spin-orbit coupling constants of several thousand ($\lambda \text{ Os}^{\text{IV}} \approx 3\,600\text{cm}^{-1}$), and therefore also require a J description, and contrasted with those of the lighter d-block ions, which may have spin-orbit coupling constants of less than 100 ($\lambda \text{ Cr}^{\text{II}} \approx 90\text{ cm}^{-1}$) and therefore have states characterized by the quantum numbers L and S¹⁰.

element:	λ	element:	λ
Ce ¹¹	625	Tb	1709
Pr	758	Dy	1932
Nd	884	Ho	2141
Pm	1000	Er	2380
Sm	1157	Tm	2628
Eu	1326	Yb ¹²	2870
Gd	1450		

Table II.2. Spin-orbit coupling constants for the Ln(III) ions.¹³

The rare earth spin-orbit coupling constants are large enough that the first excited state is well separated from the ground state, and is generally not populated at room temperature. Only samarium and europium have first excited states which are at energies comparable to kT at room temperature. The ground states for +3 states

¹¹ K.Hellwege, E.Orlich, and J Schaak, Phys.Kondens Mater 4, 196, 1965

¹² R.A. Buchanan, et al, Phys. Rev. 159, 245, 1967

¹³ W.T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. 49, 4412, 1968

are shown in Table II.3. These may be determined by Hund's rule for values up to the half filled shell, and then by the "holes for particles" model.

element:	Ground State	deg.	element:	Ground State	deg.
Ce	$^2F_{5/2}$	2(3)	Tb	7F_6	13
Pr	3H_4	9	Dy	$^6H_{15/2}$	2(8)
Nd	$^4I_{9/2}$	2(5)	Ho	5I_8	17
Pm†	5I_4	9	Er	$^4I_{15/2}$	2(8)
Sm	$^6H_{5/2}$	2(3)	Tm	3H_6	13
Eu	6F_0	1	Yb	$^2F_{7/2}$	2(4)
Gd	$^8S_{7/2}$	2(4)			

Table II.3.: Ground states and ground state degeneracies of the Ln(III) ions.

The configurations of higher energy than the $4f^N$, involving promotion of electrons to higher orbitals such as the $4f^{N-1}5d$, have been found experimentally to be well separated from the $4f^{14}$; only Ce^{3+} has the $4f^05d^1$ within the range of the near UV, at approximately $50\,000\text{ cm}^{-1}$. At Yb^{3+} , the separation has increased to nearly $100\,000\text{ cm}^{-1}$. These separations are given in figure II.4. The $4f^N \rightarrow 4f^{N-1}5d$ transitions are very intense, however, as they are allowed under the parity selection rules.

† S. Hufner, Optical Spectra of Transparent Rare Earth Compounds, Acad. Press, New York, 1978

Figure II.3: Approximate relative positions of the $4f^N$ and excited configurations of the Ln(III) ions.¹⁴

The degeneracies of these states are given by the value of the term $(2J + 1)$, though in the case of the half-integer J values, a final degeneracy of 2 is not lifted by the conditions of these experiments. It is therefore more instructive to consider the degeneracy as being given by $2(J + 1/2)$. The lifting of these degeneracies by a magnetic field frequently causes the bands for each term to overlap, making unambiguous assignments difficult.

II.2.iv. Electronic Transitions:

Trivalent rare-earth complexes have been found to have transition oscillator strengths of 10^{-8} or smaller in the UV/visible region, while those of typical d-block elements approach 1.⁵ This characteristically low intensity in the UV/visible region relative to the d-block elements has led to the conclusion that, unlike the majority of the d-block complex transitions, these transitions are not fully allowed, and points to them being strictly $f \rightarrow f$ in nature, and therefore Laporte (parity) forbidden^{5,14}. The mechanism which permits these transitions to be observed at all has been the subject of much speculation, and as early as 1937, van Vleck¹⁵ suggested that in condensed phases, the interaction with the crystal field could mix in states of opposite parity, such as the metal d or ligand p, to give the transitions some allowedness.

This explanation still does not explain the presence of intensity in the spectra of free ions, however, or in the spectra of complexes having states for which interaction with the surroundings is symmetrically forbidden. It is evident therefore that the mechanism proposed by van Vleck is not sufficient to explain the nature of intensity in the lanthanide spectra, and that other mechanisms must be considered in light of the existing data, and also in light of new data available from the MCD spectra of these complexes.

¹⁵ J.H. van Vleck, J. Phys. Chem 41 67,1937

II.3: Electromagnetic Structure of the Ln(III) Ions:

II.3.i: The Hamiltonian:

The first step in describing the electromagnetic structure of the states of the $4f^N$ configurations is the calculation of state energies, to allow the sequence of states to be identified. Once it is accepted that all levels below the $4f$ orbital are filled, and therefore spherically symmetric, the Hamiltonian of states of $4f$ is generally written as:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i - \sum_{i=1}^N \frac{Z^* e^2}{r_i} + \sum_{i < j}^N \frac{e^2}{r_{ij}} + \sum_{i=1}^N \zeta(r_i) \mathbf{s}_i \cdot \mathbf{l}_i + \sum_i \sum_l \frac{Z_l e^2}{r_{le}} \quad (\text{II.3.1})$$

The first and second terms are spherically symmetric one-electron contributions, and so shift the baricenter, or average energy, of the f orbitals, but cannot affect the splitting of the f levels from one another. The first describes the kinetic energy of the electron, and the second describes the coulombic attraction of the electron for the nucleus. The effective nuclear charge Z^* is calculated from the shielding of the absolute nuclear charge Z , using such approximations as the Slater shielding constants, and allows for the neglect of the inner shells.¹⁴

The third term describes the mutual 2-electron coulombic repulsion of the bound electrons for each other. It is denoted H_e . The fourth term describes the one electron spin-orbit interaction, and is denoted H_{so} . The function $\zeta(r_i)$ is the spin-orbit coupling function, and is given by the definition:

$$\zeta(r_i) = \frac{\hbar^2}{2m^2 c^2 r_i} \frac{dU(r_i)}{dr_i}$$

where $U(r_i)$ is the potential in which the i^{th} electron is moving.

These third and fourth terms are responsible for the internal energy level structure of the f orbitals.

The fifth term is the ligand field term. It also affects the splitting of the f levels, but in the case of the rare-earth elements, it is much smaller than the coulombic and spin-orbit terms.

For light elements, the coulombic term H_c is observed to be much greater than the spin-orbit interaction term H_{so} . This defines the limit of Russell – Saunders coupling. At the other limit is J – J coupling, defined by the opposite inequality, $H_{so} \gg H_c$. This occurs for the heavy elements. The rare earth elements, having intermediate atomic numbers, tend to have $H_{so} \approx H_c$, however. This situation is known as intermediate coupling, and it prevents the one-step solution of the Hamiltonian. Solution is generally accomplished by starting with one extreme or the other, and approaching intermediate coupling by iteration.

Traditionally, the solutions are approached as a one-electron problem, and the many-electron effects are considered last, as perturbations on the one electron

solution; in other words starting with the Russell – Saunders case.¹⁶ The spin – orbit coupling then has the effect of mixing states of the same J value, but with different L and S values; in other words, $\mathcal{H}$ is diagonalized in J. Such an approach has led to errors in the predicted positions of the various bands, but has generally given usable results, and so has been the method of choice. Where several bands are closely spaced, however, assignments may be unreliable. These errors increase with increasing spin – orbit coupling constants.

The ligand field term, which is a significant part of the hamiltonian of the d – block ions, is often neglected completely for the f – block. Because the f orbitals are so contracted, the ligand orbitals do not cause a significant perturbation in the energies of the states of the lanthanides, and the ligand field term is smaller than the errors involved in the solution of the other terms.¹⁷

Solution of the Hamiltonian of the rare earth ions is generally carried out in the following manner¹⁴:

Initially, the closed shells are assumed not to interfere with the 4f shell. This is not strictly true, since the open shell (the 4f) can distort the spherical symmetry of the closed shells, which can then interact with it. This perturbation is neglected,

¹⁶ S. Hufner, Optical Spectra of Transparent Rare Earth Compounds, Acad. Press, New York, 1978

¹⁷ J. S. Griffith, The Theory of Transition Metal Ions, Cambridge University Press, (Cambridge, U.K.) 1961.

however, since its effect is small, and to include it would require a full configuration interaction analysis of the problem.

The Schrödinger equation of this specific Hamiltonian is solved by imposing a separation of variables into two parts, angular and radial, expressed in spherical polar coordinates. The angular portion can be solved exactly if the symmetry is known. For spherical atoms or free ions, the separation constants become quantum numbers which are simultaneously the representations and the components of the three-dimensional group O(3). This allows the exact determination of the number of energy levels to be determined, gives their relative ordering in terms of J, and allows for the elucidation of the selection rules for various types of radiation. The radial portion is much more difficult to solve, as it requires an exact knowledge of the scalar gradient of the wave function. As a result, *ab initio* calculations are rare. Instead, a semi-empirical model is used, and the radial contributions are usually treated as empirical parameters and adjusted to fit the observed data.

II.3.ii Prediction of Electronic Spectra:

For the purpose of finding the eigenvalues of the Schrödinger equation to predict f-f spectra, the spherically symmetric terms are omitted because they shift only the baricenter of the configuration. The terms which lift the degeneracy of a configuration into states are the inter-electron repulsion and spin-orbit coupling contributions to the Hamiltonian defined by:

$$\mathcal{H}' = H_C + H_{SO}$$

Assuming $j-j$ coupling, $\mathcal{H}'$ is diagonal in J , and therefore the total matrix of all states can be split into submatrices of the same J . These will be degenerate in M_J , constructed from the different combinations of L and S which couple to give the same value of J . The degeneracy in M_J will subsequently be split by the two-electron terms.

II.3.iii: Matrix Elements of Tensor Operators:

In the general case, for the matrix element between two states of momentum j and j' , with z projections m_j and $m_{j'}$, the matrix element can be evaluated according to the expression:¹⁶

$$\langle j m_j | T_{kq} | j' m_{j'} \rangle = (-1)^{j-m_j} (\gamma_j || T_k || \gamma_{j'}) \begin{bmatrix} j & k & j' \\ -m_j & q & m_{j'} \end{bmatrix} \quad (\text{II.3.2})$$

The first term is a phase factor. The second, the $(|| ||)$ term is called a reduced matrix element, and is a degeneracy term, representing the number of times a particular matrix element appears. The third term is a 3- j symbol, and is used to describe the transformation of the state $j m_j$, via the operator T_{kq} , into the state

$j' m_j'$. The reduced matrix elements and the 3-j symbols have been tabulated,^{18,19} and so it is no longer necessary to evaluate them each time.

All of the evaluation of the 3-j symbols and the reduced matrix elements are done taking all square roots to be real and positive as they arise. This has the result of removing all meaningful signs from the calculations. The phase factor is an attempt to re-introduce these signs. Condon and Shortley²⁰, and later Judd²¹, have recognized the limitations placed on the system by the removal of the sign. Judd makes several specific references to the problem: "...the vector coupling coefficients may be rapidly calculated *to within a phase factor*..."²¹; "The *conventional choice* of phase is made."²²; "Making an *arbitrary choice* of phase..."²³. He also points out,²⁴ that the choice imposes an inevitable asymmetry on the phase choice which simply must be accommodated.

¹⁸ C. W. Nielson, and G. F. Koster, Spectroscopic Coefficients for p^n , d^n , and f^n Configurations, MIT Press, Cambridge, Mass., 1964.

¹⁹ M. Rotenberg, R. Bivins, N. Metropolis, and J. Wooten, The 3-j and 6-j Symbols, MIT Press, Cambridge, Mass., 1959.

²⁰ E. U. Condon & G. H. Shortley, The Theory of Atomic Spectra, University Press, Cambridge, England, 1963

²¹ B. R. Judd, Operator Techniques in Atomic Spectroscopy, McGraw-Hill, N.Y., 1963, p.10

²² B. R. Judd, *ibid*, p.11

²³ B. R. Judd, *ibid*, p.14

²⁴ B. R. Judd, Diatomics, McGraw-Hill, N.Y., 1976.

II.3.iii.a: The Coulombic Matrix Elements:

Coulombic interaction between pairs of electrons affects only the orbital portion of the wave function, and does not act on the spin at all. The interactions are therefore calculated on the $l m_l$ basis functions, and so the description in J, M_J must first be uncoupled into an SM_S, LM_L description, and then the state description must be uncoupled to give sm_s, lm_l descriptions.

The coulomb matrix element initially written:

$$\langle \gamma S' L' J' M_J' | (e^2/r_{ij}) | \gamma S L J M_J \rangle$$

The state description is fully coupled, and must be uncoupled so that the operator can act on the orbital portion only, in a one electron description. This is achieved in two steps.

- 1) S and L must be uncoupled (the J coupling broken)
- 2) The states must be uncoupled to give a one electron (s,l) description.

The first step is achieved following the Wigner-Eckart formula:

$$|SLJM_J\rangle = \sum_{LSM_L M_S} (-1)^{S-L+M_J} (2J+1)^{1/2} \begin{bmatrix} S & L & J \\ M_S & M_L & -M_J \end{bmatrix} |SM_S LM_L\rangle \quad (\text{II.3.3})$$

this is then transformed into a one-electron description in an analogous manner:

$$\begin{aligned}
|SLM_S M\rangle = & \sum_{\substack{s_1 s_2 \\ m_{s_1} m_{s_2}}} (-1)^{s_1-s_2+M_S} (2S+1)^{1/2} \begin{bmatrix} s_1 & s_2 & S \\ m_{s_1} & m_{s_2} & M_S \end{bmatrix} |s_1 m_{s_1} l_1 m_{l_1}\rangle \\
& \times \sum_{\substack{l_1 l_2 \\ m_{l_1} m_{l_2}}} (-1)^{l_1-l_2+M_L} (2L+1)^{1/2} \begin{bmatrix} l_1 & l_2 & L \\ m_{l_1} & m_{l_2} & M_L \end{bmatrix} |s_2 m_{s_2} l_2 m_{l_2}\rangle
\end{aligned}
\tag{II.3.4}$$

The operator is also not initially in a form which can be applied directly. The term r_{ij} describes the separation between a pair of electrons in any general positions, while the axes used to describe the states are nucleus centered. The coordinates of the operator must therefore also be projected to the origin.

The initial form of the matrix elements, in mixed notation, is:

$$(\gamma s' m'_s l' m'_l | (e^2/r_{ij}) | \gamma s m_s l m_l)$$

where γ represents all of the quantum numbers not affected by the operator.

The term $1/r_{12}$, can be expanded in Legendre Polynomials about the origin to provide the desired projection:

$$1/r_{12} = \sum_k \left[\frac{r_{<}^k}{r_{>}^{k+1}} \right] P_k(\cos \omega_{12}) \tag{II.3.5}$$

The $1/r_{12}$ term expansion puts the term in the form of an infinite power series in which each term is a product of a radial and an angular contribution.

The radial portion describes the distortion of a perfectly symmetrical potential by the presence of electrons located away from the center of the sphere. This radial term is described by the ratio of the distance of the nearer electron to the center to the distance of the further electron, raised to one higher power. This ratio is found to effectively describe the perturbation of the spherically symmetrical potential.

The angular portion of the expression is described by the associated Legendre functions, which in turn are the projections of the spherical harmonics in the x - y plane. These describe the angular perturbations in terms of angular nodes which again distort the perfect sphere. The specific distortion is selected by selecting the appropriate contribution to the power series by applying the operations of the spherical symmetry group. These symmetry conditions are formally expressed in the selection rules used to construct the Wigner 3- j symbols.²¹

This expression converts the term r_{12} from a non-nucleus centered term which defines the separation between the general positions 1 and 2, to a nucleus centered projection, where $r_{<}$ is the vector joining the nearer of the electrons to the nucleus, $r_{>}$ is the vector joining the further one to the nucleus, and ω is the angle separating the two.

Figure II.4. Transformation to nucleus centered coordinates.

The expression is usually stated in spherical co-ordinates. This shows the full separation of the radial and angular portions of the term, with r fully uncoupled from from (θ, ϕ) . ψ_r contains radial information only, and therefore carries with it no quantum numbers. It is simply a fitting factor, and is generally treated empirically.

$\psi_{\theta\phi}$ contains all of the angular information about the system, and so contains the quantum numbers s, m_s and l, m_l .

When the angular portion $P_k(\cos \omega_{12})$ is expanded into spherical co-ordinates, the two-electron interaction can be modeled as a scalar product of one-electron behaviors. This is stated in terms of spherical harmonics $Y_{kq}(\theta_i, \phi_i)$ so that the full expansion is:¹⁴

$$P_k(\cos \omega_{12}) = \frac{4\pi}{2k+1} \sum_{kq} Y_{kq}^*(\theta_1, \phi_1) Y_{kq}(\theta_2, \phi_2) \quad (\text{II.3.6})$$

A "rationalized" form of this spherical harmonic can then be defined which normalizes the degeneracies in 3 dimensions:²⁵

$$C_{kq} = \left[\frac{4\pi}{2k+1} \right]^{1/2} Y_{kq} \quad (\text{II.3.7})$$

The phase associated with the two possible square roots to be taken is not defined by the conditions of scalar normalization, leaving the sign choice apparently arbitrary and ambiguous.

The full expansion of the inter-electron repulsion contribution to the Hamiltonian, $P_k(\cos \omega_{12})$, can then be written:

$$P_k(\cos \omega_{12}) = \sum_{kq} (-1)^q \left[C_{k-q}(1) \cdot C_{kq}(2) \right] \quad (\text{II.3.8})$$

The $(-1)^q$ term is an attempt to reintroduce the sign which was left out of the square root term.²⁵

It is important to note that this term is not expressed fully in Dirac operator form. The full Dirac form is derived using the Wigner-Eckart techniques for the uncoupling of two angular momenta:

²⁵ B. R. Judd, Operator Techniques in Atomic Spectroscopy, (McGraw-Hill, N.Y.,) 1963

$$P_K(\cos \omega_{12}) = \sum_{\substack{k_1 k_1 \\ q_2 q_2}} (-1)^q \left[\sum_{KQ} (-1)^{k_1 - k_2} q \begin{bmatrix} k_1 k_2 K \\ q_1 q_2 -Q \end{bmatrix} |k_1 k_2 K Q| \right] \quad (\text{II.3.9})$$

This collapses to the simplified form by arbitrarily setting $q_1 = -q_2$ and $Q = 0$

Knowing the behavior of q_1 and q_2 , the coulomb matrix element can then be written:

$$\delta_{q_1 q_2} \left\langle \gamma s' m'_s l' m'_l \left| \left[e^2 \frac{r_{<}^k}{r_{>}^{k+1}} \right] k_1 \cdot k_2 \right| \gamma s m_s l m_l \right\rangle \quad (\text{II.3.10})$$

The term in $r_{>} r_{<}$ can be taken to the front of the term, as it is a constant for each pair of electrons. This gives:

$$\left[e^2 \frac{r_{<}^k}{r_{>}^{k+1}} \right] \delta_{q_1 q_2} \left\langle \gamma s' m'_s l' m'_l | k_1 \cdot k_2 | \gamma s m_s l m_l \right\rangle \quad (\text{II.3.11})$$

The final modification to the term arises because the coulombic interaction is a two-electron effect. Each side of the bracket is shown as a one-electron term. The full matrix element must be written:

$$\delta_{q_1 q_2} \left\langle \gamma s'_1 m'_{s_1} l'_1 m'_{l_1} s'_2 m'_{s_2} l'_2 m'_{l_2} | k_1 \cdot k_2 | \gamma s_1 m_{s_1} l_1 m_{l_1} s_2 m_{s_2} l_2 m_{l_2} \right\rangle \quad (\text{II.3.12})$$

Uncoupling this element so that the two electrons can be treated separately would appear to require a 9-j symbol, which is analogous to the 3-j symbol, except that it is used to couple or uncouple terms having four angular momenta, rather than the two that the 3-j symbol is used for. The 9-j symbol is not necessary here, however, since the wavefunctions were initially normalized, and when the 9-j symbols for all of the matrix elements are combined, they are identical to one. Since the product of k_1 and k_2 is a dot product, the separation can be made directly, and the matrix elements for the coulombic interaction between two electrons, (1) and (2), becomes:

$$\delta_{q_1 q_2} \left\langle \gamma s'_1 m'_{s_1} l'_1 m'_{l_1} | k_1 | \gamma s_1 m_{s_1} l_1 m_{l_1} \right\rangle \cdot \left\langle \gamma s'_2 m'_{s_2} l'_2 m'_{l_2} | k_2 | \gamma s_2 m_{s_2} l_2 m_{l_2} \right\rangle \quad (\text{II.3.13})$$

A further simplification is possible by recalling that the coulombic operator acts only on the orbital portion, and leaves the spin unchanged. Since it is unaffected, the spin can be removed from the matrix element, and expressed as a Kroniker delta, whose value is one if $s = s'$ and $m_s = m'_s$, and zero otherwise. The expression can then be written:¹⁴

$$\delta_{q_1 q_2} \delta_{s'_1 s_1} \delta_{m'_{s_1} m_{s_1}} \delta_{s'_2 s_2} \delta_{m'_{s_2} m_{s_2}} \left\langle \gamma l'_1 m'_{l_1} | k_1 | \gamma l_1 m_{l_1} \right\rangle \cdot \left\langle \gamma l'_2 m'_{l_2} | k_2 | \gamma l_2 m_{l_2} \right\rangle \quad (\text{II.3.14})$$

These can be solved by applying the Wigner-Eckart factorization of (II.3.2).

Alternatively, tables of values for " $\langle |C_k| \rangle$ " have been provided by Rotenberg¹⁹ or Nielson and Koster¹⁸. These are used for the mixed format such as in eqn.(II.3.8), where " $\delta_{q_1 q_2} \langle k_1 \rangle \langle k_2 \rangle$ " is denoted " $\langle |C_k(1) \rangle \cdot \langle |C_k(2) \rangle$ ", and have made it unnecessary to do the calculation each time.

II.3.iii.b: The Spin-Orbit Coupling Matrix Elements:

The spin-orbit coupling matrix elements are simpler than those for coulombic interaction, because they represent one-electron effects. The spin-orbit Hamiltonian has the form:¹⁴

$$\mathcal{H} = \sum_i \zeta(r_i) s_i m_{s_i} \cdot l_i m_{l_i} \quad (\text{II.3.15})$$

The coulombic term was simplified by setting $q_1 = -q_2$, or $\delta_{q_1 q_2} = -1$. This is not possible here, but $\delta_{M_{S_i} M_{L_i}}$ is set equal to $|J|$, and the spin orbit coupling constant, $\zeta(r_i)$, which is generally treated as a constant for a given subshell and determined empirically, is given the sign of J . It is therefore only pseudoscalar. This leaves each matrix element in the form:

$$\delta_{M_{S_i} M_{L_i}} \langle \gamma S' L' J' M_J' | s_i \cdot l_i | \gamma S L J M_J \rangle \quad (\text{II.3.16})$$

Since the spin-orbit coupling must be calculated on the fully decoupled, one electron description, the uncoupling process is done in the same manner as was done for the coulombic matrix elements, to give:

$$\delta_{m_{s_i} m_{l_i}} \langle \gamma s' l' m_s' m_l' | s_i \cdot l_i | \gamma s l m_s m_l \rangle \quad (\text{II.3.17})$$

Again in a manner analogous to the coulombic terms, the dot product can be broken to give:

$$\langle \gamma s' m_s' | s_i | \gamma s m_s \rangle \cdot \langle \gamma l' m_l' | l_i | \gamma l m_l \rangle \quad (\text{II.3.18})$$

$$= (-1)^{s-m_s} (s \| \hat{s} \| s') \begin{bmatrix} s & \hat{s} & s' \\ m_s & \hat{m}_s & m_s' \end{bmatrix} \cdot (-1)^{l-m_l} (l \| \hat{l} \| l') \begin{bmatrix} l & \hat{l} & l' \\ m_l & \hat{m}_l & m_l' \end{bmatrix} \quad (\text{II.3.19})$$

Again, tabulated values for the reduced matrix elements and the 3-j symbols are available.^{18,19}

Judd²⁵ gives an example of the matrix for the $J = 4$ manifold of Pr^{3+} , an f^2 system.

$$\begin{bmatrix} W_c(^3H) - 3\zeta & -\sqrt{10/3}\zeta & 0 \\ -\sqrt{10/3}\zeta & W_c(^1G) & \sqrt{11/3}\zeta \\ 0 & \sqrt{11/3}\zeta & W_c(^3F) + 3/2\zeta \end{bmatrix}$$

Using the values $F_2 = 310 \text{ cm}^{-1}$ ²⁵ and $\zeta = 750 \text{ cm}^{-1}$ ²⁶, the calculation yields:

$$W_c(^3H_4) = 0 \text{ cm}^{-1} \text{ (arbitrarily set to zero)}$$

$$W_c(^3H_5) = 2127 \text{ cm}^{-1} \text{ (experimental value } 2152 \text{ cm}^{-1})$$

$$W_c(^3H_6) = 4355 \text{ cm}^{-1} \text{ (experimental value } 4389 \text{ cm}^{-1})$$

The deviation from theoretical values is approximately 1 per cent, but this would be expected to be larger for systems having increasing numbers of electrons.

Although these calculations allow for the determination of the splitting of the f level, and permit the assignment of band manifolds when they are well separated from each other, they have not proven precise enough to allow positive assignments when bands are closely spaced.⁵ When this is the case, knowledge of the selection rules and intensities must be used to complement the energies in assigning the spectral bands.

²⁶ A. Abragam and B. Blainey, Electron Paramagnetic Resonance of Transition Ions, (Oxford Press, London) 1970

II.4 Radial Parameters and Calculation of Energy Levels:

In 1942, Giulio Racah published his first paper on the energy levels of transition metals²⁷, in which he proposed a system of classification for the internal transitions of the atoms and free ions. In effect, his proposal concerned specific groupings in the sums of the coulombic and spin orbit coupling terms of their hamiltonians. By this system, the energy separations between states of the same spin could be classified by a one parameter fit, and those between states of different spin could all be classified by a three parameter fit. This rearrangement of contributions greatly simplified the description of the energies of electronic states of metals and their complexes, and allowed for the simplest possible comparison between different species, and for the same species synthesized at different times or by different groups.

This grouping of terms, while greatly simplifying the description of the d systems, do not contribute any simplicity to the description of the f systems. In 1949 therefore, Racah published a classification system adapted for the f electrons. In the same manner that the previous system provided a one parameter fit for spin allowed transitions in the d systems, this system provides a one parameter fit for spin allowed transitions of the f systems²⁸. While these parameters could be calculated a priori from a knowledge of the scalar gradients of the hamiltonians, they are generally treated as empirical variables, and are adjusted to fit the spectrum of the system under study.

²⁷ G. Racah, Phys. Rev. 62, 438, 1942

²⁸ G. Racah, Phys. Rev. 76, 1352, 1949

To describe the d systems, Racah chose three parameters labelled empirically A , B , and C . The first, A , is spherically symmetric, and applies to the baricenter of the configuration d^n . It has no effect on the separation of states. The B term is the most commonly used, since it is the only term required to describe the splitting of states of the same spin. Since the selection rule for spin is $\Delta S = 0$, the B term describes the energy of the spin allowed transitions. For example, for the system d^2 , the only spin allowed transition is ${}^3F \leftarrow {}^3P$. The energy of this transition can be shown to be $15B$.

The third term, C , is required in conjunction with B to describe the separation of states with different spin. Since these transitions are spin forbidden, and consequently much less intense on the actual spectrum, they are often not reported, and so in practice, the term is used much less often. In practice, although B and C are independent, there is an empirically narrow range of values for the ratio $C/B \approx 4$. While there is no theoretical explanation for this, it makes spectral assignment relatively simple.

The description of the f systems requires four parameters, and Racah chose these parameters as E^0 , E^1 , E^2 , and E^3 . In similar manner to the d system classification, the first term, E^0 , acts equally on all states, affecting only the baricenter of the configuration, and so does not affect the separations. It is E^3 in this case which describes the separation of states of the same spin. Both E^1 and E^2 are necessary, in addition to E^3 to describe the separation of the states of different spin. In his 1949 paper²⁸, Racah published the terms for the states of the f^2 system. Recall that the

ground state is 3H , followed, in order of increasing energy, by 3F , 1G , 1D , 3P , 1I , and 1S .

$$^3H \quad E^0 - 9E^3$$

$$^3F \quad E^0$$

$$^1G \quad E^0 + 2E^1 + 260E^2 - 4E^3$$

$$^1D \quad E^0 + 2E^1 + 286E^2 - 11E^3$$

$$^3P \quad E^0 + 33E^3$$

$$^1I \quad E^0 + 2E^1 + 70E^2 + 7E^3$$

$$^1S \quad E^0 + 9E^1$$

In some publications, the older Slater–Condon convention of using F_k terms is maintained, although this does not give a one parameter fit for the spin allowed transitions. Racah gives the necessary information for conversion, and the results are:

$$E^0 = F_0 - 10F_2 - 33F_4 - 286F_6$$

$$E^1 = 70/9 F_2 + 231/9 F_4 + 2002/9 F_6$$

$$E^2 = 1/9 F_2 - 3/9 F_4 + 7/9 F_6$$

$$E^3 = 5/3 F_2 + 2F_4 - 91/3 F_6$$

or alternately:

$$F_0 = E^0 + 9/7 E^1$$

$$F_2 = 1/707 (33E^1 + 6218E^2 + 121\,430/18 E^3)$$

$$F_4 = 18/1111 E^1 - 885/707 E^2 - 59/707 E^3$$

$$F_6 = 1/101 (-3/11 E^1 - 15 E^2 + E^3)$$

It is evident that E^3 , which gives a one parameter fit, is present in three of the F_k terms, and so a one parameter fit is not possible with this convention.

These parameters, whichever set is used, provide a compact language for quoting spectral information without reproducing an entire spectrum. If all three terms are quoted, the energy separations can be calculated for each transition in the spectrum.

These terms do not give any information about transition intensities, however, and do not contain any of the information necessary to reproduce the sign of the transition in the case of MCD spectroscopy.

II.5 Intensities:

The intensity information of a given spectral line is usually quoted in terms of the positive oscillator strength of the transition. This is given by the equation:

$$P = \sum_{\lambda = 2,4,6} \nu T_{\lambda} (\Psi'_{\lambda} \| U^{\lambda} \| \Psi_{\lambda})^2 (A(\Psi' \Psi)) \quad (\text{II.5.1})$$

where: ν = the frequency of the transition
 U^{λ} = a unit tensor operator, whose
 single-particle components have
 amplitudes given by: $\langle f \| U^{\lambda} \| f \rangle = 1$
 T_{λ} = an empirical fitting parameter for each λ
 $A(\Psi' \Psi)$ = a factor describing the coupling of the states

The mixing potential given by u^{λ} may be a static one, arising from odd parity terms, or a dynamic one arising from non-symmetric vibrations. These both fit the mechanism, as the T_{λ} terms are determined empirically from the spectral data.

In the limit of Russell–Saunders coupling, the dependence of J and J' on U^λ is given by:

$$A(J, J') = \delta(S, S')(2J + 1)(2J' + 1) \left\{ \begin{matrix} L & L' & 2 \\ J & J & S \end{matrix} \right\}^2 \quad (\text{II.5.2})$$

The 6- j symbol can be found from the tables of Rotenberg *et al.*¹⁹ This model can be used to show that the T_2 term acts most strongly on the transitions where $J' = (J-2)$, and so a variation in the T_2 term should appear as an intensity variation in the $J \rightarrow (J-2)$ transitions of the series on complexes. The effect on the other transitions would be too small to observe.

This model only specifies the angular allowedness of transitions, and cannot relate the intensity to any fundamental characteristics of the atoms or ions under study, since it only effects the unambiguous separation of angle and radial behaviors. The radial T_λ parameters are generally treated as empirical parameters, and are fitted to the data. A good fit of the energies observed to the predicted sequence and relative separations does establish the likelihood that the correct configuration f^n was chosen for the assignment, however, as Judd cautions, it does not serve to identify a physically meaningful model²⁰. The magnitudes of the fitting parameters T_λ establish the scalar gradients for different orders of influence λ , which indicate any changes in electron delocalization compared to the free ion control. These gradients can be related to changes in the scalar effective charge Z^* , brought about by changes in ligand softness, or optical electronegativity χ_L .

²⁰ B. R. Judd, Phys. Rev. 127, 750, 1962

II.6 Complexes of the Rare Earth Elements:

II.6.i Chemistry:

The rare earth elements were long thought to have no interesting chemistry. They are hard, or non polarizable metals, and were believed to interact with other elements on a strictly electrostatic basis. Although this was known not to be the case by the 1950's, information on the structures, stabilities and reactions of the complexes of the rare earths has been slow to appear.¹⁰

II.6.ii Hydrates:

The rare earth elements have a very strong affinity for water, and in neutral solution, their preferred configuration is an environment of 8 to 12 water molecules. The thermodynamics of hydration have been studied³⁰, and the heats of formation of the $\text{Ln(III)}_{\text{aq}}$ ion has been found to be extremely favorable. These are shown in table II.5.

³⁰ S. Bratsch and J. Lagowski, J.Phys Chem. 89, 3317, 1985

element: Ln(III)	$\Delta G_f^\circ(\text{aq})$ KJmol ⁻¹	element: Ln(III)	$\Delta G_f^\circ(\text{aq})$ KJmol ⁻¹
Ce	-677	Yb	-627
Pr	-677	Tm	-675
Nd	-672	Er	-676
Pm†	-667	Ho	-675
Sm	-665	Dy	-672
Eu	-567	Tb	-659
Gd	-662		

Table II.5: Free energy of formation of the Ln(III)_{aq} complexes in neutral solution.³⁰

The data were interpreted as showing that the coordination was nine for Ce(III) to Nd(III), changing to eight for the smaller ions further along the period.

II.6.iii Halides:

The trivalent rare earths will form complexes with the halides readily in acidic solution, showing a preference for the harder halides. The iodide complex has not been reported, while the bromide is difficult to make. As expected, the chloride and fluoride are very stable.¹⁰

In aqueous acid, the species formed is the hydrated trihalide $\text{LnX}_3 \cdot x\text{H}_2\text{O}$. The degree of hydration in solution is not well known, and has been assigned anywhere from 5 to 9, for a total coordination of 8 to 12.

Non aqueous halides of the rare earths can also be prepared. In aprotic solvents, the LnX_6^{3-} complexes are reported to be stable.³¹ Evidence suggested that these complexes may be eight coordinate and nearly cubic.

In the gas phase, LnX_3 complexes can be synthesized. There is no consensus on whether these gas phase ions are trigonal pyramidal or triangular. They have been found to be non-polar.³²

II.6.iv Other Hard Ligand Complexes:

Other complexes with hard ligands form in a manner analogous to the halides. Nitrates are extremely stable in acid solution, as are acetates.¹⁰ Borohydrates, $\text{Ln}(\text{BH}_4)$, have been reported,³³ as have thiocyanate complexes,³⁴ while the cyanates and selenocyanates are reported to be much less stable.

³¹ J. L. Ryan and C. K. Jorgensen, J. Phys. Chem. 70(9), 2845, 1966

³² R. G. Hayes and J. L. Thomas, Organometal. Chem. Rev. A, 7, 1, 1971

³³ T. Marks and J. Kolb, Chem. Rev. 77, 263, 1977

³⁴ J. L. Burmeister, S. D. Patterson, and E. A. Deardorff, Inorg. Chim. Acta, 3:1, 105, 1969

II.6.v Organometallic Complexes:

Under rigorously anhydrous conditions, it has been found that organometallic complexes of the rare earth ions can be synthesized. Cyclopentadienyl complexes have been reported for a range of rare earth ions³², and are prepared by the following reaction:

These complexes have been reported for Ln = Ce, Pr, Sm, Gd, Dy, Er, and Yb. The complexes can be sublimed, and no solvent is reported to be bound. They are reported to be trigonal pyramidal. Their spectra are reported to be very similar to those of the simple salts, evidence that the nephelauxetic effect is very small for these complexes.

Single bonds between the rare earth ions and ligand carbon atoms have also been reported³⁵. the reaction was given as:

and was carried out with Tb, Er, and Yb.

³⁵ J. L. Atwood *et al*, J. Chem. Soc. Comm., 1978, 140

A review of lanthanide organometallic chemistry was given by Marks, and gives reference for the reactions being carried out as of 1978.³⁶

II.7 Coordination and Geometry:

The trend in coordination numbers of the rare earth complexes follows the "lanthanide contraction", and decreases across the period. This can be accounted for by the decreasing ionic radii of the metals. Increasing the availability of the charge by changing the electronegativity of the ligand does not appear to change the coordination number. For a given metal, all of the vapor phase halides: F^- , Cl^- , and Br^- , yield three coordinate MX_3 species³², despite the changing electronegativities of the halide ligands. The same is observed with the MX_6^{3-} species in aprotic solvents³¹. It appears therefore that the radius of the metal ion is controlling the geometry and the coordination number of the complex, in observance of the Pauling Radius Ratio rules governing the geometry of complexes.

II.8 Nephelauxetic and Electronegativity Effects:

II.8.i Introduction:

The most immediately notable feature of the spectra of the rare earth complexes is the degree to which they resemble the spectra of the free ions. This is due to the

³⁶ T. Marks, Prog. Inorg. Chem., 24, 51, 1978

"atomic" nature of the f orbital electrons; as suggested by the radii of the 4f orbitals (Fig 1a), they are in inner orbitals, and so are not significantly split by the ligand field. Beyond this initial similarity, however, it is the ways in which the spectra of the complexes do differ from those of the free ions which give rise to the most interesting questions in the field of rare earth spectroscopy.

II.8.ii Electronegativity and the Principle of Electroneutrality:

Mulliken^{37,38} attempted to quantify the concept of electronegativity as early as 1934, by pointing out that the average of the first ionization potential (I.P.) and the electron affinity (E.A.) of an atom should be a measure of its electronegativity. This definition appears to correlate the electronegativity of an element in oxidation state zero with its ability to resist oxidation itself, but promote the oxidation of neighboring atoms, also in an oxidation state of zero. In molecules, however, most atoms are assigned formal oxidation numbers far from zero, and so the applicability of the Mulliken definition in these cases is not immediately obvious.

Pauling³⁹ defined electronegativity χ_M as the ability of an atom in a molecule to attract electrons to itself. He derived his original scale based on the difference in energy of a bond A—B, and the energy expected if this bond were completely

³⁷ R. S. Mulliken, J. Chem. Phys. 2, 782, 1934;

³⁸ R. S. Mulliken, J. Chem. Phys., 3, 573, 1935

³⁹ L. Pauling, The Nature of the Chemical Bond, 2nd ed., 1940 (Cornell Press)

covalent, which would be the arithmetic mean of the bond energies A—A and B—B. He denoted this energy difference $\Delta(A-B)$, or simply Δ , and it had energy units, generally electron volts. He then found that if the square root of these delta values was considered, an internally consistent electronegativity scale could be derived. By choosing one reference element, and assigning it an arbitrary electronegativity value, the other elements could be measured, directly or indirectly, against this scale, and assigned electronegativity values with units of $\sqrt{\text{eV}}$. Pauling then added 2.05 to these values, to give a convenient scale. This led to the empirical equation for the extra ionic energy

$$\Delta(A-B) = 23.06 (\chi_A - \chi_B)^2 \quad (\text{II.9.1})$$

and for the total bond energy, in kcal/mole

$$D(A-B) = 1/2 \left\{ D(A-A) + D(B-B) \right\} + 23.06 (\chi_A - \chi_B)^2 \quad (\text{II.9.2})$$

Pauling also studied the relationships between the electronegativity of an element, and other measurable properties. He considered the relationship between the electronegativity and the work function of a metal, and noted that a reasonable correlation between the work function ψ in electron volts and the electronegativity value was given by the expression:

$$\psi = 2.27\chi + 0.34 \quad (\text{II.9.3})$$

On the subject of metals, he also noted that the division of the periodic table into metals and non-metals appeared to be made at the point $\chi = 2$, with the metals

having electronegativity values below this, and the non-metals above.

The electronegativity of elements has also been correlated to NMR effects; Pauling reports on a study by Gutowsky⁴⁰ in which the NMR shielding of a fluorine nucleus is correlated with the electronegativity of the elements to which the fluorine is bonded.

Pauling also noted, in agreement with Mulliken at least on a qualitative level, that the first ionization energy of the element, and the electron affinity are both related in that the first I.E. can be considered to be the average of the electron attraction of the atom and the positive ion:

and the electron affinity (E.A.) as the average of the electron attraction of the atom and the negative ion:

He refined the ideas of Mulliken to explicitly include the concept of electroneutrality, which had previously been developed by Langmuir.⁴¹ This principle states that "In general, the electronic structure of substances is such as to cause each atom to have essentially zero resultant electric charge." The importance here is that electronegativity values for atoms in complexes will approximate those of the neutral atoms much more closely than those of the ions whose formal charges they were assigned in the complex. There is some dependency on the formal valence

⁴⁰ H. S. Gutowsky, J. Chem. Phys. 19, 1266, 1951

⁴¹ I. Langmuir, Science 51, 605, 1920

of the element, but this is small compared with the difference between the electronegativity of the neutral element and the free ion.^{42,43}

Jørgensen⁴⁴ proposed another electronegativity scale, based on the electron transfer spectra of complexes. Using the Pauling electronegativities as his starting point, he noted that the shift in energy of the charge transfer bands of the spectra of a single metal with a series of halides was proportional to the electronegativity differences between the halides.

halide pair	$\Delta E(\text{kK})$	$\Delta\chi(\text{Pauling})$	$\Delta E/\Delta\chi$
F:Cl	28	0.9	31
Cl:Br	6	0.2	30
Br:I	10	0.3	33

Table II.6: Comparison of Pauling electronegativity and charge transfer energy ratios for the halide pairs.

He extended this to propose that the wavenumber of the electron transfer spectrum was directly proportional to the difference in electronegativity between the metal and ligand in question. He found that it was necessary to account for the difference in spin-pairing energy on going from d^q to d^{q+1} , but that once this correction was

⁴² T. L. Bailey, J. Chem. Phys., **28**, 792, 1958

⁴³ F. A. Kröger, Some Aspects of the Luminescence of Solids, 1948 (Elsevier, Amsterdam)

⁴⁴ C. K. Jørgensen, Orbitals in Atoms and Molecules, Acad. Press, London, 1962

made, it was possible to use the technique to obtain the optical electronegativities of various central metals, based on the Pauling values for the halides. Once the values for the metals are known, these can then be used to determine the optical electronegativities of other ligands. He gave values for four ligands, along with a comparison with the Pauling values:

ligand	optical χ	Pauling χ
H ₂ O	3.5	3.5
CN ⁻	2.8	2.6
(C ₂ H ₅ O) ₂ PS ₂ ⁻	2.7	2.5
(C ₂ H ₅ O) ₂ PSe ₂ ⁻	2.6	2.3

Table II.7: Comparison of Optical and Pauling electronegativities for selected ligands.

Using bromide as the ligand, Jørgensen also determined the optical electronegativities of several of the lanthanides which had charge transfer bands in an accessible portion of the spectrum.⁴⁵ His results, when corrected for spin-pairing effects, gave:

⁴⁵ C. K. Jørgensen, Mol. Phys., 5, 271, 1962

lanthanide	χ opt
Sm(III)	0.8
Eu(III)	0.95
Tm(III)	1.45
Yb(III)	1.6

Table II.8: Optical electronegativities for selected Ln(III) ions.

Since the optical electronegativity values are usually the most experimentally accessible of the various electronegativity scales for those ligands which form complexes with transition metals, it is generally these values which are quoted in this thesis as "ligand electronegativities" χ_L . When another scale is used, it will be specified.

II.8.iii The Nephelauxetic Effect:

As early as 1926, Ephraim *et al*^{46,47,48} noted that, for a series of ligands bound to a single rare earth ion, the narrow bands were shifted according to the series:

He suggested that covalent bonds in the complex were somehow responsible for expanding the 4f shell.

⁴⁶ F. Ephraim and R. Bloch Ber., 59, 2692, 1926

⁴⁷ F. Ephraim and R. Bloch, Ber., 61, 65, 1928

⁴⁸ F. Ephraim and P. Ray, Ber., 62, 1509, 1929

This is now accepted to be a manifestation of the nephelauxetic effect; where the effective size of the metal orbitals is thought to increase due to the presence of ligand electron density between the metal orbitals and nucleus, causing an increased shielding. The degree to which the complex experiences this nephelauxetic, or "cloud-expanding" effect is quantified in the nephelauxetic parameter β . This parameter is defined by the ratio of the Racah inter-electron repulsion parameter B in the free ion with that in the complexed ion:

$$\beta = \frac{B_{fi}}{B_{ci}}$$

Jørgensen also noted that if a series of ligands was established based on their ability to increase β for a given metal, the nephelauxetic series of ligands corresponded to the Pauling electronegativity scale⁴⁹. Comparing Jørgensen's series:

with Pauling's:

the sequences are essentially the same.

Jørgensen also comments on the polarizability of the ions under consideration, however, noting that in a complex, I^- and Br^- in particular have the average radius of their outermost electrons increased significantly by the presence of the central metal.

⁴⁹ C. K. Jørgensen, Absorption Spectra and Chemical Bonding in Complexes, 1962 (Pergamon Press, London)

The shifts in the energies of the lanthanide complex terms with changing ligand are very small; the shift on going from aquo to EDTA ions in Pr(III) complexes is reported to be on the order of 1%, while for Gd(III) complexes, it is only 0.3%.⁴⁹ These represent fairly large nephelauxetic ratios, however, the largest reported by Jørgensen being $\beta = 0.91$ in Pr_2O_3 .

II.9 Hypersensitivity Mechanisms:

The majority of the spectral bands of the rare earths show very little change on going from the free ion, to the hydrated species $\text{Ln}^{3+}(\text{H}_2\text{O})_n$, to the species in a complex $\text{Ln}^{3+}(\text{L})_3(\text{H}_2\text{O})_n$. This is due to the fact that the f electrons are well shielded. Some bands have been found to vary in intensity a great deal more than the rest, however, and the transitions associated with these bands are called the "hypersensitive" transitions. These have been the subject of much speculation.

The following mechanisms for hypersensitivity have been discussed in the literature, and are reviewed by Henrie, Fellows and Chopin.⁵⁰:

1) Pseudoquadrupole:

When an ion is located in an inhomogeneous dielectric, its electric

⁵⁰ D. Henrie, R. Fellows, and G. Chopin *Coord. Chem. Revs.* 18, 199, 1976

quadrupole is enhanced. Ions in a relatively homogeneous dielectric (in a gas at low pressure, for example) show hypersensitivity. The suggested explanation for this is that the ligands may provide an inhomogeneous dielectric about the metal f electrons.

2) Charge-Transfer Coupling:

Purely charge-transfer (CT) bands are extremely sensitive to the nature of the ligand⁵¹ and so coupling these to the $f \rightarrow f$ transitions would be expected to give a built-in hypersensitivity. The CT intensities are found to increase in a stepwise manner with ligand addition.⁵² This behavior is also reported for the hypersensitive transitions.⁵³

3) Static Coupling:

The arguments that Judd used to explain the presence of any intensity at all²⁹ can equally be applied to the phenomenon of hypersensitivity. Some reason for the $4f^n-15d$ to couple preferentially with one particular ΔJ state must be found, however.

⁵¹ Henry, Fellows and Choppin, *Coord. Chem. Revs.* 18, 199, 1976

⁵² Barnes and Pincott, *J. Chem Soc A*, 1966, 842

⁵³ Poluetkov, Alakaeva and Tishchenko, *Zh. Prikl. Spektrosk.*, 17, 819, 1972

II.10 The Octupole Rule:

If a vibronic mechanism is to be used to explain the intensity of rare-earth complex spectra, some model is needed to explain the coupling between the electronic and vibronic transitions. The octupole rule⁵⁴ defines the selection rules for fundamental vibrations, and then allows them to be extended to selection rules for the coupling of electronic and vibrational modes.

The octupole rule is based on the fact that the number of degrees of freedom exhibited by a non-linear, n -atomic molecule is given by $3n$. Of these, however, 3 result in translation of the center of mass, and 3 result in rotation about the center of mass. Only $3n - 6$ are left which can result in excitation of an internal mode of the molecule.

Translation is a dipolar motion of the center of mass, and since there are 3 orthogonal modes of translation (the x , y , and z directions in cartesian coordinates) the dipole is completely exhausted by this operation, and therefore cannot excite any other modes.

⁵⁴ B. R. Hollebone and M. J. Stillman, Chem. Phys. Lett. **66**, 248 (1979) and B. R. Hollebone, Can. J. Chem., **62**, 2282 (1984)

Figure II.5 : Translation: 3 orthogonal modes exhaust the dipole.

Indeed, if the photon field is considered dipolar, it could only result in the movement of the entire molecule, since the photon field would act on the very high field gradient about the nuclei, causing a displacement of the center of mass. The field gradient due to the electrons is much lower, and so they are simply displaced along with the nucleus. No restoring force is available to hold the nucleus in place, or to bring it back, once it has experienced the dipolar field.

Figure II.6: Field gradients on an atom.

The effect on a collection of atoms, or a molecule is totally analogous.

Rotation is quadrupolar in nature, and also consumes 3 orthogonal modes (rotation about the x, y, and z axes). Once these three have been consumed, there are 2 remaining modes of the quadrupole left which may excite an internal mode.

Figure II.7: Rotation: 3 of the 5 orthogonal modes are consumed

For any form of excitation other than translation or rotation, any of the two remaining modes of the quadrupole or the higher order multipoles can be involved, depending on the symmetry available in the molecule.

In the octahedron, the dipole, consumed in translation, has the symmetry representation t_{1u} . The portion of the quadrupole consumed by rotation has the representation t_{2g} , while the two remaining modes of the quadrupole have the representation e_g ; these are the z^2 and the $(x^2 - y^2)$.

Only one of these remaining modes points along any of the M – L bonding region; this is the z^2 which can be pictorially superimposed on the octahedron as in figure II.8.

Figure II.8: z^2 representation in the octahedron: $|2e_g 0\rangle$

Two modes of the octupole affect the bonding regions in the octahedron: the t_{1u} and the t_{2u} .

buckling: $|3t_{1u} 0\rangle$

twisting: $|3t_{2u} 0\rangle$

Figure II.9: Octupolar modes on the M - L regions of the octahedron

Higher order multipoles will of course have some modes of appropriate symmetry, but these are very low in intensity and therefore decrease in importance extremely rapidly.

The octupole rule states that, based on spectroscopic evidence, the overall coupling of electronic and vibrational excitation which occurs is an octupolar (a 2^3 -pole) or one of its higher harmonics (a 2^7 -pole, 2^{11} -pole ...). The contribution from various components of the transition, such as orbital, vibrational or spin, may vary, but the sum of all the multipolar changes must be an octupole.

$$\Delta T = \Delta V + \Delta J = 3 \quad (7, 11, \dots) \quad (\text{II.10.1})$$

II.10.i Assignment of Hypersensitivity by the Octupole Rule:

The first available internal mode for the $\Delta J = 2$ hypersensitive transition is the $\Delta V = 5$ vibration, since the $\Delta V = 1$ is not an internal mode, but represents translation. Thus the vibration coupled in is pseudo-dipolar in nature. Using the example on the octahedron again, the vibration appears as in figure II.10.

Figure II.10: The $|5t_{1u} 0\rangle$ vibration on the octahedron

However, descent of symmetry arguments show the $\Delta V = 5$ vibrational term on the octahedral symmetry can be reduced to an E_u , two T_{1u} , and a T_{2u} term. One of the $|5 T_{1u}\rangle$ appears in 3 dimensions to be identical to the $|1 T_{1u}\rangle$ term, and leads to the identification of the anti-symmetric stretch as being apparently dipolar in nature.

For the $\Delta J = 1$ magnetic hypersensitive transition, the active vibrational mode is the $\Delta V = 2$ quadrupole shown in figure 7. In each case, the available mode points directly at the ligands.

In considering the multipole of the radiation involved in contributing to the hypersensitive transitions, it is necessary to bear in mind that it is changes to the nature of the ligand which cause the intensity changes. The multipole geometries allow for favorable overlap with some of the metal - ligand bonding regions, and Subduction then allows the arguments to be applied to specific geometries, if these are known. Since this work was carried out in solution, however, they are not known. Changing the solvent would allow a study of the contribution from multipoles pointing between inner sphere ligands, but towards solvent molecules in the outer co-ordination spheres, while single crystal or crystal-matrix experiments would allow for an exact knowledge of the symmetry. Neither of these was part of this study.

II.11 Hypersensitivity:

II.11.i. General Forms:

In the first description of lanthanide hypersensitivity, B. R. Judd⁵⁵ considered various a static mechanism, involving the mixing in of states other than f^n , and a dynamic mechanism involving vibronic coupling, and found that both gave an equation for oscillator strength of the form of eqn. II.5.1:

$$P = \bar{\nu} \sum_{\lambda} T_{\lambda} \langle f^n \psi J | U^{\lambda} | f^n \psi' J' \rangle^2; \lambda = 2, 4, 6 \quad (\text{II.11.1})$$

where P = oscillator strength

$\bar{\nu}$ = transition energy

$\langle f^n \psi J |$ = initial state

$| f^n \psi' J' \rangle$ = final state

As Judd noted, this means that if the T_{λ} parameters are treated as adjustable, it is not possible to determine which mechanism accounts for the observed intensities, as both fit the observations.

Judd also noted at this time that transitions having a $\Delta J = 2$ were the ones that

⁵⁵ B. R. Judd, Phys. Rev., 127, 750

gave rise to the hypersensitive transitions. He associated these transitions with an unusually large T_2 term in the above equation.

II.11.ii Vibronic Model:

If it had been possible to identify the band due to the $V = 0$ ground state vibrational term, it would be possible to eliminate the vibronic model. Unfortunately, there are no reports in the literature of this being attempted, and the resolution was not sufficient in this study for such an identification.

Hollebone and Stillman did show that for an organometallic complex of holmium, the $\Delta J = 2$ hypersensitive band at $\approx 21600 \text{ cm}^{-1}$, was associated with an excited vibrational level of the ground state⁵⁻, and so the potential for a vibronic mechanism for intensity enhancement is certainly there.

II.11.iii Static Model:

One method of identifying the static mechanism would be to study the correlation between the degree of hypersensitivity and the separation between the 4f and the 5d sub shells. A negative correlation would imply the static mixing mechanism, since the coupling would be expected to weaken with increasing subshell separation. This

correlation was not observed, however the resolution may again have been insufficient.

II.12 Correlation with Ligand Properties:

An experimental correlation between hypersensitive oscillator strength and ligand pK_a has been published⁵⁶. This is not a reliable measure, however. These ligand pK_a values have been determined using a proton as the acid, with the ligand as the base, and are not reliable for any other cation^{57,58}. The proton is much more polarizing than a large +3 ion, and so can polarize the ligand to such an extent that the symmetry of the available donor orbitals is essentially unimportant; the proton will cause them to rearrange themselves into a suitable configuration. All other species, such as the Ln^{+3} ion, must rely on the symmetry of the existing orbitals, being unable to polarize them to the extent of the proton⁵⁹. The ligand may be quite willing to give up its electron density to the metal, but may not have a low lying orbital with the appropriate symmetry to do so. In this manner, metal

⁵⁶ R. L. Fellows and G. R. Choppin, J. Coord. Chem 4, 79, 1974

⁵⁷ A.Regis, J.Corsat, Can. J. Chem. 51, 3577, 1973

⁵⁸ Pople and Hehre, Tetrahedron Letters 34, 2959, 1970

⁵⁹ A. Pulman, in an editorial note to a paper by P. Keboule, Environmental Effects on Molecular Strength and Properties, Pulman & Pulman eds. (D. Reidel Pub. Co. Dordrecht, Holland 1976)

π acidity may be more important than the σ acidity⁶⁰. Fellows and Chopin recognized this problem, and commented "...this series does not in all cases parallel the pK_a values...but rather it reflects the ligand basicity when associated with a highly polarizing +3 ion." Despite this, the trend is apparent in some cases, where the symmetries are appropriate. Carnall, Fields and Rajnak⁶⁰ published the following correlation between pK_a and intensity for a few simple ligands bound to Nd^{3+} . More complex ligands would be expected to deviate from this trend for the reasons given above.

Intensity:	ClO_4^-	>	Cl^-	>	NO_3^-
Ligand pK_a :	-10		-7		-1.4

Table II.8: correlation between pK_a and intensity for 3 simple $Nd(L)_3$ complexes.

II.13 Summary and Research Objectives:

Although the commercial development of ion exchange methods in 1945 opened up the field of rare-earth spectroscopy, there remains a great deal of argument in the literature as to the nature of their bonding.

⁶⁰ W. T. Carnall, P. R. Fields and K. Rajnak, J. Chem. Phys. **49**, 4412, 1968

There is a general consensus that the rare earth ions are hard, and that their bonding in complexes is "predominantly" ionic, but this qualitative statement gives the extent of the agreement. The actual amount of covalency is still in question. Similarly, it is agreed that the transitions observed in the absorption spectra of the rare earth metals, ions or complexes are due to transitions within the f manifold. The relative energies of the states within this manifold are also well known, at least below $40\,000\text{ cm}^{-1}$ but the mechanism which gives intensity to these formally forbidden transitions is still a matter for much debate.

In spite of their small radii, and therefore their isolation within the metal core, some of the f orbital states do couple strongly with the ligands present, giving rise to the hypersensitive transitions. The mechanism by which this effect arises is also in question. The effect has been correlated with ligand pK_a , but this only had moderate success, with some ligands deviating strongly from linearity. This is reasonable, since the Ln(III) ions are very large, and have only a very low polarizing power, but the potential for π acidity. By contrast, the proton, against which the ligand pK_a values were determined, is small, has a very high polarizing power, and no potential for π acidity.

It is evident then that it is necessary to first test whether one or more of the measurable ligand properties can be accurately correlated with the hypersensitivity of the complexes, and then to use this to assist in proposing a self-consistent and *physically meaningful* model to account for the hypersensitivity.

III. POLARIZED SPECTROSCOPY:

III.1 Introduction:

The phenomenon of polarized light, along with its practical application to spectroscopy, have been recognized long before a theoretical explanation was available for the phenomena. In 1808, Malus⁶¹ passed a single beam of light through a quartz crystal and observed that two beams exited. The following list traces the development of the science:

1808	E. L. Malus ⁶¹	Polarization of light
1811	D. F. Arago ⁶²	Optical activity proportional to wavelength
1815	J. B. Biot ⁶³	Optical activity of some organic molecules
1819	A. Fresnel ⁶⁴	Transverse wave model for light
1846	M. Faraday ⁶⁵	Magnetic optical activity
1847	W. Haedinger ⁶⁶	Discovery of circular dichroism
1865	J.C. Maxwell ⁶⁷	Electromagnetic nature of light

⁶¹ E. L. Malus, Mem. Soc. d'Arceuil 2, 143, 1808

⁶² D. F. Arago, Mem. Inst. 12, 93, 1811

⁶³ J. B. Biot, Ann. Chim. Phys. 4, 90, 1815

⁶⁴ A. Fresnel, Ann. Chim. 10, 288, 1819

⁶⁵ M. Faraday, Phil. Mag. 28, 294, 1846

⁶⁶ W. Haedinger, Ann. Phys. 70, 531, 1847

⁶⁷ J. C. Maxwell, Phil. Trans. Roy. Soc. London 155, 459, 1865

1874	J. van't Hoff ⁶⁸	Explanation for chiral carbon
1893	P. Drude ⁶⁹	Optical rotatory dispersion equations
1895	A. Cotton ⁷⁰	CD in solution
1911	A. Werner ⁷¹	Optically active inorganic complexes
1928	L. Rosenfeld ⁷²	Quantum model of optical activity
1955	H. Rudolph ⁷³	First commercial ORD spectrometer
1960	M. Grosjean ⁷⁴ M. Legrand	First commercial CD spectrometer

III.2 Polarized Light:

The explanation of polarized light relies upon the wave model for light. A ray of light can be considered to be a transverse wave having a velocity in the direction of propagation, and amplitudes perpendicular to this direction. For unpolarized light, these amplitudes occur in an infinite number of orientations, all perpendicular to the direction of propagation.

⁶⁸ J. van't Hoff, Arch. Neederland Sci. Exact. Nat. 9, 445, 1874

⁶⁹ P. Drude, Ann. Physik, 50, 595, 1893

⁷⁰ A. Cotton, Compt. Rend. 120, 989, 1895

⁷¹ A. Werner, Chem. Ber. 44, 1887, 1911

⁷² L. Rosenfeld, Z. Physik 52, 161, 1928

⁷³ H. Rudolph, J. Opt. Soc. Am. 45, 50, 1955

⁷⁴ M. Grosjean and M. Legrand, Compt. Rend. 251, 2150, 1960

The ray is described in terms of its electric and magnetic vectors. These are coupled at 90° to each other, and are transverse to the direction of propagation. This introduces an immediate degeneracy, since the electric vector may be coupled to its magnetic vector at $+90^\circ$ or at -90° .

A single ray of unpolarized light can be split into two components, each having their electric vectors in fixed planes, perpendicular to each other, and each containing the axis of propagation. Each of these is a ray of plane polarized light. This capability demonstrates the transverse nature of the light wave; no such separation is possible with longitudinal waves, such as sound waves, where the direction of vibration is not perpendicular to the direction of propagation.

Figure III.1: A ray of plane polarized light. In this case, the the y -polarized component is shown.

However, since these separated electric vectors may couple in two ways to their accompanying magnetic vectors, a ray of plane polarized light can be further separated into two distinct beams, in which the electric vectors rotate towards their magnetic vectors and the plane of polarization then traces out a helix. One traces a right handed and one a left handed helix, 90° out of phase with each other. These are beams of circularly polarized light. It should be noted that the two possible beams of plane polarized light, E_x and E_y , yield only a total of two types of CP light. There is no difference between LCP_x and LCP_y , for example.

It must be noted that polarizability is general to any transverse wave, and while the term "light" is used here, this is only due to the experimental context. More generally, the term "electromagnetic radiation" should perhaps be used, as polarization can be effected in any region, and has in practice been effected from the microwave to the soft X-ray region of the spectrum.

III.3 Applications to Spectroscopy:

III.3.i Optical Activity:

The most common use of polarized light is undoubtedly the determination of optical activity in organic compounds. A ray of monochromatic light is passed through a polarizer such as a nicol prism, and is then passed through the sample in question. The light is then passed through the analyzer, a second prism, to measure the amount by which the sample has rotated the plane of the light beam.⁶² In practice, the analyzer is rotated until a null reading is obtained, and the angle by which it must be turned is the conjugate of the angle by which the sample rotated the beam. Schematically, this can be depicted:

Figure III.2 Schematic of the determination of optical activity.

III.3.ii Optical Rotatory Dispersion:

The first major application of polarized light to spectroscopy was the application of the wavelength dependent, or dispersive, nature of optical activity. Rather than taking the optical activity measurement at only one wavelength, it could be taken across a range of wavelengths, yielding an optical activity spectrum.⁶⁹ This technique is called optical rotatory dispersion, or ORD.

The drawback of ORD is that it does not yield accurate or precise results in regions where the sample absorbs light. ORD, like optical activity measurements, uses a

null detection system, and in regions of absorption, not enough of the ray is transmitted to make detection of the exact null position feasible. More importantly, the RCP and LCP components may be absorbed to different extents, producing an output ray which is no longer plane polarized at all, and which therefore cannot produce a null reading. This "anomalous ORD" is known as the Cotton effect. ORD is only useful then in regions far from absorption peaks.

When it is properly used within its limitations, however, ORD can be a useful chemical tool. Empirical information is available from the ORD spectra of standard compounds, and by comparison with these, the chemist can obtain information on the conformation, configuration, and substituent positions of a new compound. This type of information is strictly empirical, however, and a suitable reference compound must be found. Many of these reference spectra have been catalogued by Djerassi⁷⁵.

ORD has also been exploited as a specialized GC and HPLC detector, where it responds to optically active fractions only, making positive identification of a particular peak more reliable.

III.3.iii Circular Dichroism:

The drawback of ORD was the key to the success of the next technique. The differential absorption of right and left circularly polarized light in the absorbing regions of the spectrum is the basis for the technique of circular

⁷⁵ C. Djerassi, Optical Rotatory Dispersion, McGraw-Hill, N.Y., 1960

dichroism.⁶⁶ Alternating beams of RCP and LCP light are passed through the sample. It is not the absolute amount of absorption of either which is measured, but the differential absorption of (by convention) LCP – RCP.

CD is also a useful chemical tool. It too can be used empirically to obtain structural information, and, if a suitable reference spectrum is available, it is more accurate than UV/visible spectroscopy for making a positive identification of an unknown compound.

III.3.iv Circularly Polarized Emission:

Circularly polarized emission, or CPE, can be used to yield information on low lying electronic states and ground state vibrational levels, as well as "forbidden" transitions such as singlet to triplet transitions. It is carried out by using circularly polarized light as the light source for the excitation.

III.3.v Circular Intensity Differential Scattering:

Circular Intensity Differential Scattering, or CIDS, studies the preferential scattering of RCP and LCP light by a sample at a given direction in space. This is useful, for example, in studying the handedness and pitch of oriented liquid crystals or other helical molecules⁷⁶.

⁷⁶ K. Hall, K. Wells, D. Keller, B. Samori, M. Maestre, I. Tinoco, C. Bustamante, Applications of CP Radiation Using Synchrotron and Ordinary Sources, F. Allen and C. Bustamante eds., Plenum Press, N. Y. 1985

III.3.vi Fluorescence Detected Circular Dichroism:

CIDS can pose a problem in the determination of a CD spectrum, since RCP and LCP light are scattered at different angles, and to different extents. To circumvent this problem, fluorescence detected CD, or FDCD, may be used⁷⁷. In this technique, the sample is surrounded by material which fluoresces at a broad excitation wavelength across the entire region under study, but which does not interact with the sample in any way. The fluorescence is detected, and related to the amount of light transmitted and scattered by the sample in all directions. In this manner, all non-absorbed light, in every direction, is accounted for.

III.3.vii Circular Dichroism Microspectrophotometry:

Even microscopy has its polarized analogue. The CD microscope (or more properly microspectrophotometer), CDM, can be used where the CD spectrum of a very small area is required, without separating it from the matrix. Living cells are an example of the applicability of the CDM. It is achieved by using CP light with a Zeiss photometer microscope.

⁷⁷ M. Maestre, D. Keller, C. Bustamante, and I. Tinoco, Applications of CP Radiation Using Synchrotron and Ordinary Sources, F. Allen and C. Bustamante eds., Plenum Press, N. Y. 1985

III.3.vii.a Differential Imaging CD Microscopy:

The differential imaging CD microscope takes this one step further, using CIDS to provide an image of the sample, showing the differential images provided by RCP and LCP light.

III.4 Magnetic Effects:

In 1846, Michael Faraday discovered that while natural optical activity was confined to a small group of specialized compounds, all compounds were optically active when placed between the poles of a magnet⁶⁵. This meant that all of the techniques which exploited the interaction of polarized light and optically active compounds could now be used on all compounds, with the addition of a magnet to the apparatus used. The techniques became universally applicable.

The development followed that of the non-magnetic analogues. MORD was the first to be used, followed by MCD, and then the more specialized techniques based on the principles of the first two. This study uses MCD spectroscopy as the means for obtaining information of the rare earth systems under study, and the details of magnetic optical activity and MCD are presented in the next section.

III.5 Magnetic Circular Dichroism:

Magnetic circular dichroism (MCD) spectroscopy is a special case of the Faraday effect, which is exhibited by all substances. The Faraday effect can be denoted, in a non-absorbing region, by:⁶⁷

$$\phi = V(\nu) \int_0^l B(l) dl \quad (\text{III.5.1})$$

ϕ is the rotation of the plane of the polarized light

l is the sample length

$V(\nu)$ is the Verdet constant, characteristic of the sample material

$B(l)$ is the applied magnetic field

In most cases, the magnetic field is kept constant over the length of the sample, and so the equation simplifies to:

$$\phi = V(\nu) B l \quad (\text{III.5.2})$$

MCD, however, is concerned with the effect as it occurs in the absorptive regions of the sample. If the refractive index of left-handed circularly polarized light is denoted n_- , and that of right-handed CP light as n_+ , the angle of a beam of plane polarized light would be rotated by an angle⁷⁸

$$\phi = \frac{\pi \nu l \Delta n}{c} \quad \Delta n = n_- - n_+ \quad (\text{III.5.3})$$

⁷⁸ P. J. Stephens, J. Chem. Phys., 52, 3489, 1970

Historically, in the MCD experiment, the plane polarized light was split into the two beams of circularly polarized light which were passed alternately through the sample and then recombined prior to detection. The measurable parameter in that case was the degree of ellipticity of the recombined beam, denoted θ .⁷⁹

Modern MCD experiments no longer measure the angle of rotation or ellipticity of a incident plane polarized beam, but measure the difference in absorption of right and left CP light.⁷⁹ For a transition $A \rightarrow J$, assuming J to be unpopulated at ambient temperature, the spectrum can be characterized by:

$$\Delta I(z) = (c/4\pi) (\Delta\hat{n}/\hat{\mu}) E_0^{02} \exp \{ -2\omega\Delta kz/c \} \quad (\text{III.5.4})$$

$$I_{\pm}(z) = (c/4\pi) (\hat{n}_{\pm}/\hat{\mu}) E_0^{02} \exp \{ -2\omega\Delta kz/c \} \quad (\text{III.5.5})$$

where $\hat{n} = n - ik$, and Δk is the difference in absorption coefficients ($k_- - k_+$), given by:

$$\Delta k = -4/3 \gamma N_a^0 \left\{ \frac{A(A \rightarrow J)}{h} f^1 + \left[B(A \rightarrow J) + \frac{C(A \rightarrow J)}{kT} \right] f^0 \right\} \quad (\text{III.5.6})$$

where

$$\gamma = \pi^2 \omega^2 / \hbar \Delta\hat{n}$$

⁷⁹ S. B. Piepho and P. N. Schatz, Group Theory in Spectroscopy, (John Wiley & Sons), 1983.

To translate this phenomenological form into a theoretical model, $\mathcal{A}$, $\mathcal{B}$ and $\mathcal{C}$ are interpreted as arising from the differential rotation of charge around the imposed magnetic field during the transition. This generates a preferred transient magnetic moment aligning with or against the field, resulting in a positive or negative differential signal respectively.

The MCD terms are assigned the following meanings in describing the spectrum. They are given by:⁸⁰

$$\mathcal{A}(I \rightarrow J) = -\frac{g}{4a_A} \sum_{\substack{a^0 \\ j^0, j^{0'}}} [\langle a^0 | m_- | j^0 \rangle \langle j^{0'} | m_+ | a^0 \rangle - \langle a^0 | m_+ | j^0 \rangle \langle j^0 | m_- | a^0 \rangle] \\ * [\langle j^0 | \mu_z | j^{0'} \rangle - \langle a^0 | \mu_z | a^0 \rangle \delta_{j^0 j^{0'}}] \quad (\text{III.5.7})$$

$$\mathcal{B}(I \rightarrow J) = -\frac{g}{2a_A} \sum_{a^0, j^0} \text{Re} \left\{ \sum_{k^0 \neq J} [\langle a^0 | m_- | j^0 \rangle \langle k^0 | m_+ | a^0 \rangle - \langle a^0 | m_+ | j^0 \rangle \langle k^0 | m_- | a^0 \rangle] * \langle j^0 | \mu_z | k^0 \rangle / \omega_{k^0}^0 \hbar \right. \\ \left. + \sum_{k^0 \neq A} [\langle a^0 | m_- | j^0 \rangle \langle j^0 | m_+ | k^0 \rangle - \langle a^0 | m_+ | j^0 \rangle \langle j^0 | m_- | k^0 \rangle] * \langle k^0 | \mu_z | a^0 \rangle / \omega_{k^0}^0 \hbar \right\} \quad (\text{III.5.8})$$

$$\mathcal{C}(I \rightarrow J) = \frac{g}{4a_A} \sum_{a^0, j^0} [\langle a^0 | m_- | j^0 \rangle \langle j^0 | m_+ | a^0 \rangle - \langle a^0 | m_+ | j^0 \rangle \langle j^0 | m_- | a^0 \rangle] * \langle a^0 | \mu_z | a^0 \rangle \quad (\text{III.5.9})$$

⁸⁰ P. J. Stephens, Ann. Rev. Chem. Phys., 35, 197, 1974

The existence of an A term requires excited state degeneracy, which is lifted by the magnetic field. The ground state may be degenerate or non-degenerate. The intensity of an A term is, to a first approximation, inversely proportional to the zero-field linewidth of the transition, denoted Γ^{-1} . Pictorially, the A term can be shown as in figure III.3.

Figure III.3: Pictorial description of the MCD A term.

The C term requires ground state degeneracy, and is inversely proportional to the temperature $(kT)^{-1}$. Pictorially, this is shown:

Figure III.4: Pictorial representation of the MCD C term

The B term is present for all transitions regardless of degeneracy, and is inversely proportional to the zero-field state separations $(\Delta E^0)^{-1}$. It has the same appearance as a C term, but can be distinguished based on the temperature dependence of the C term. The B term is independent of temperature.

The equations describing each of these terms must be tensorial in nature. They are traditionally solved by scalar techniques, however, which causes them to lose all of their phase information.⁷⁹ The standard phases are arbitrarily re-inserted to match the experimentally observed phases. The drawback to this empirical approach is that it does not allow the prediction of phases for new compounds.

MCD spectroscopy yields the same information as absorption spectroscopy in terms of the position (energy) of an absorption band. In many cases, however, the differential intensities offer considerably more information, because they carry the magnetic moment in addition to the square of the electric moment. In the first case, it is often possible to detect bands in the MCD that were too weak to be detected by absorption spectroscopy; this occurs when the absorption is small, but the magnetic difference between the absorption of left and right circularly polarized light is relatively large. When two transitions overlap in the absorption MCD has a chance of resolving them, as well, since they may have opposite magnetic properties and hence MCD sign.

Since the magnetic field splits the Zeeman levels of degenerate states, MCD can contribute new information that is not available at all from the absorption spectrum. Since A and C terms depend on the excited and ground state degeneracies, respectively, bands can be positively assigned based on their degeneracies. In organic molecules in particular, this is useful for distinguishing singlet $\rightarrow$ singlet transitions from singlet $\rightarrow$ triplet ones.

The fact that electric dipolar transitions have a low differential intensity in the MCD, because they occur without charge rotation, is responsible for another potential advantage of MCD. In spectra of the d-block complexes, the ligand field transitions are often obscured by much more intense charge transfer bands. These dipolar CT bands are much weaker in the MCD, however, and the ligand field transitions can usually be resolved.

III.6 Tensorial Model of Polarized Events:

An MCD experiment is truly a 3-dimensional experiment; for the interaction of the wave functions of a molecule with a circularly polarized photon, a set of relative properties can be defined as:

The phase coherence:

A 1-dimensional phenomenon, ranging from completely in phase to completely (180°) out of phase, or from +1 to -1.

The sense of motion: A 2-dimensional phenomenon, left or right, positive or negative

The chirality: A 3-dimensional phenomenon, the circular direction when viewed down the axis of propagation, right or left handed, or counter-clockwise or clockwise.

For any photon with known propagation, these three binary conditions can be combined in eight different ways to define the wavefunctions, although the resultant is one sign. The simplest available three-dimensional closed pathways are three orthogonal Mobius loci. These Mobius pathways have therefore been defined as the "natural coordinates", and are orthonormal to each other. The three binary choices define the required geometric properties of the paths: the chirality, denoted χ , the sense of motion, denoted s , and the coherence phase, denoted c . This means that for any given state J, M_J , there are 2^3 , or 8 possible paths, as required by the 3-dimensional phenomena defined above. Defining the phase, sense and chirality amounts to selecting one of the 8 possibilities for ψ .

These eight possibilities, which can be represented by eight fundamental, "natural" Mobius pathways on loci, are⁸¹:

$(+, +, +) ; (+, -, -) ; (-, +, -) ; (-, -, +)$ which yield a positive sign overall, and
 $(-, -, -) ; (-, +, +) ; (+, -, +) ; (+, +, -)$ which lead to an overall negative sign.

⁸¹ K. M. E. Miedzinska, personal communication

A change in any or all of these conditions will result in a change in the sign of the MCD transition (a change in any two will result in no observed change). The chirality and sense of motion may be in one of two possible conditions: they may each be either positive or negative. The coherence phase, however, in addition to its sign, may vary in value between its "in phase" and "out of phase" conditions.

In order to describe the influence of these geometric conditions, for any transition we can write the intensities as path integrals for the motion of the state vector on these pathways.. The normalized value of the magnetic moments is determined by the integrated projection on the magnetic field direction:

$$\oint \oint \oint \psi_z^* \hat{O}_z \psi_z d\tau = P_z \quad (\text{III.5.10})$$

Where P is the transition probability, and the operator represents the transient magnetic moment needed to convert the ground state moment to its excited state, via the allowed geometric change.

In any system in which electron–nuclear coupling exists, for an inelastic interaction between the photon and the molecule (ie. an absorption process) to occur, mass, the position of the center of mass, and rotation about the center of mass, must all be conserved. The operator $\hat{O}$, in this case the photon, selects the coupled excited state for which this is the case. In order for there to be interaction between the atomic state and the photon, they must couple within the same event space, in other words have a common origin, similar energies, the same chirality and sense of motion, and

similar phase (although uncertainty in the phase makes an exact match meaningless).

While this exact matching of the chirality and sense of rotation is necessary for the rotating photon to do work on the ground state, the need for coherence is less rigorous. However, if the photon and the molecule are considered separately, the wavelength of the photon would appear to be approximately 10^4 times the size of the molecule, and such a large difference would make the potential for an event very small, with the photon most often passing through the space without interaction. The refractive index of space within a molecule near a transition is $\sim 10^4$ times that of free space, however, and so the photon is slowed from its speed in vacuum. Since the energy of the photon is invariant, the ratio $c\lambda^{-1}$ must remain constant, and its wavelength must also decrease by 10^4 .

On a Mobius locus, the state vector varies in length from 0 to infinity, as it sweeps around the principle axis from $\phi = 0$ to $\phi = 2\pi$ radians, as in figure III.5

Figure III.5: The state vector on a Mobius locus

As the vector approaches infinity, all of the kinetic energy is converted to potential energy, and the tangential velocity reaches a minimum. At this point, the state vector has three important properties; it lies entirely in the horizontal plane, it has reached its maximum length, and the uncertainty in its velocity is at a maximum. If the state and wave vectors meet in the plane at this point, where the state vector is most easily redirected, there is a good match in the length of the vectors, and therefore there is the greatest likelihood of interaction. As the wave vector begins to do work on the state vector, the state vector is accelerated onto a new path with greater pitch and the wave is slowed along its propagation up the axis. If the two vectors arrive together at an excited state node, the incoming wave stops completely, and is absorbed, otherwise the wave vector "unwraps", and is scattered.

IV. EXPERIMENTAL:

IV.1 Experimental Design:

The properties of MCD spectroscopy make it a good tool for exploring the electronic spectra of the rare earth elements. Because it is a direct measure of the direction and magnitude of the transient magnetic moment of any transition, it should be able to shed some light on the mechanism which gives intensity to the $f \rightarrow f$ transitions, and which causes the phenomenon of hypersensitivity. Conversely, the "atomlike" nature of the spectra of the complexes of the rare earths make them useful for investigating the problem of identifying and classifying the effects of ligand bonding without the complicating factor of ligand field splittings.

In the case of $f \rightarrow f$ transition hypersensitivity, the charge transfer coupling mechanism should be the simplest to test, since MCD would pick up this coupling only very weakly, and so if it is the major cause, the degree of hypersensitivity should appear much less in the MCD than in the absorbance spectra.

The "pseudoquadrupole" mechanism, by contrast, would be expected to give a much enhanced hypersensitivity in the MCD, as the quadrupole represents the rotation of charge necessary for observable events in the magnetic domain. This should also be immediately obvious from the MCD spectra.

The static and vibronic coupling mechanisms would be expected to be more difficult

to distinguish. As discussed previously, the elimination of one or the other of these mechanisms will require that the experiment consider the separation between the 4f and 5d levels, and the vibrational levels of the ligands being used. In both cases, a correlation with the degree of hypersensitivity would be necessary.

An effective method for testing each of these models is to investigate each metal with a series of simple, structurally related ligands of varying χ_L . Except for the chloride, the ligands were all anions of oxyacids in which the χ_L was varied by varying the substituents. By using ligands which were as structurally simple as possible, spectral complications due to vibronic effects were minimized. The ligands used were:

Ligand	Formula	χ_L ⁸²
acetylacetate	$[\text{HC}(\text{CH}_3\text{CO})_2]^-$	2.7
chloride	Cl^-	3.00
acetate	CH_3COO^-	3.38
trichloroacetate	CCl_3COO^-	≈ 3.4
trifluoroacetate	CF_3COO^-	3.55
nitrate	NO_3^-	4.1

Table IV.1. Ligands used in this study.

⁸² B. R. Hollebone, J. Chem Soc., 1971, 481

The acetate based ligands, which have the potential to be bidentate, and are likely to bind in the same manner across the series, allow the distinction between changing electronegativity and geometric effects.

Figure IV.1: Structure of the acetate ligands used in this study.

The ligands used were all hard, ranging from the hardest, NO₃⁻, to the softest, acetate, which is still moderately hard. These bind most easily with the rare earth metals, which are themselves hard metals. Some studies have been reported using softer ligands, but these have to be carried out under rigorously anhydrous conditions, as the metals will preferentially bind with the water.^{35,36}

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MICROCOPY RESOLUTION TEST CHART
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STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

IV.2 Experimental Procedure:

IV.2.i Reagents:

All of the metals were purchased from the Aldrich Chemical Company as the oxides Ln_2O_3 , listed at 99.9% purity or above. They were used without further purification. The mineral acids and the acetic acid were purchased from Anachemia, as reagent grade. The trifluoroacetic acid (TFA) was purchased from Aldrich, as the 99+ % spectro grade. All were used without further purification.

The metal complexes were prepared by dissolving the metal oxide in a 5 molar solution of the appropriate acid. The amount of metal used was calculated to provide a 1 molar solution of the metal complex. In cases where the metal complex was less soluble than this in the acid, the spectra were taken at the solubility limit, and the concentration was obtained by comparison of the UV/visible spectrum with the spectrum of a known concentration of another complex of the same metal. Comparison of the peak areas of the non-hypersensitive bands allow determination of the concentration of the complex.

IV.2.ii Spectra:

Absorption spectra were run on a Perkin-Elmer Lambda 4B spectrometer with a range of 190 nm to 900 nm., or $11\,111\text{ cm}^{-1}$ to $52\,631\text{ cm}^{-1}$.

MCD spectra were run on a custom built MCD spectrometer, consisting of optics taken from a Cary 14 UV/visible spectrometer, a 14 KG electromagnet, and custom electronic components, controlled by a Motorola microcomputer, using the program MCD3.(Fig. IV.2)

Figure IV.2: Schematic of the MCD spectrometer used

The microprocessor control was designed to accumulate spectral data at a given energy until the standard deviation between subsequent data points reached a predetermined acceptable value, selected by the operator, and then to proceed to the next energy point, and begin the accumulation process again. The size of the steps is determined by the computer based on the difference in intensity values between adjacent points. In this manner, points are closely spaced on spectral peaks, and more widely spaced where there are no features, allowing the best spectrum to be taken in the least amount of time.

Figure IV.3: Schematic of the processor control of the spectral quality.

The experiment was run as a single beam experiment with corrections for the baseline made later. The solvent was subsequently run, and subtracted using the subroutine MERGE to do a digital subtraction.

This subroutine initially linearizes the data and the reference files, and cuts the number of points to 500. It then accepts two lockpoints from the operator. These points are chosen by the operator, and are selected such that they are as far as possible from any spectral features. The subroutine adjusts the slopes of the two spectra to be equal at those points, and the offset between the two files at the lockpoints is removed. This helps to eliminate effects due to strain in the quartz cuvettes used. The reference spectrum is then subtracted from the data, and an output file is produced.

Plotting of the output files is done using the routine PLOT2. This routine allows the output spectra to be scaled in the x and y directions independently.

V. DATA AND RESULTS:

V.1 Complex Solutions:

The Neodymium, samarium, and erbium complex spectra were taken of 1.0M solutions of the complexes. The dysprosium complexes were less soluble than that, however, and so were run at their saturation limit. An excess of the metal oxide was suspended in a 5% solution of the appropriate acid, and the suspension was brought to the boil, and boiled for 5 minutes. The suspension was then sonicated for 20 minutes, and allowed to stand overnight. The suspensions were then filtered through Whatman #42 filter paper (fine grade). Since these complexes were not used in the quantitative calculations, exact knowledge of their concentrations was not critical.

The complete catalogue of spectra used in this study is given in appendix A. For clarity, only the composite tracings of those which show the actual measurements used in the calculations of the degree of hypersensitivity are presented within the body of the thesis.

V.2 Complexes:

Assignments of the spectral bands were all made based on the study by Carnall, Fields and Rajnak.¹³ The lifting of the degeneracy in M_J by the magnetic field meant that when states were closely spaced, their manifolds frequently overlapped in the MCD. Only those which were well separated were used for the calculations, therefore.

V.2.i Neodymium Complexes:

The neodymium complexes studied were $\text{Nd}(\text{Cl})_3 \cdot x \text{H}_2\text{O}$, $\text{Nd}(\text{OAc})_3 \cdot x \text{H}_2\text{O}$, and $\text{Nd}(\text{NO}_3)_3 \cdot x \text{H}_2\text{O}$. $\text{Nd}(\text{III})$ is an f^3 system, and the ground state is $^4I_{9/2}$. The following regions are expected to show some degree of hypersensitivity, either of the electronic type associated with a ΔJ of 2, or the magnetic type, associated with ΔJ of 1.

Figures V.1.a and V.1.b show the comparison between the absorption and the MCD spectra of three $\text{Nd}(\text{III})$ complexes. In figure V.1.a, it is apparent that the bands centered at $580 \text{ \AA}$ ($\approx 17\,100 \text{ cm}^{-1}$) shows virtually no dependence on the nature of the ligand, while figure V.1.b shows that the band at $17\,100 \text{ cm}^{-1}$ in the MCD spectrum has not only changed in intensity, but has actually flipped sign from positive to negative on going from the chloride to the nitrate complex.

Transition to	ΔJ	Energy Range(cm^{-1})	Series Trends lowest to highest χ_L
$^4F_{7/2}$	-1	13 500	A small relative intensity shift on a small side band at approximately $13\,400\text{ cm}^{-1}$.
$^2H_{11/2}$	+1	15 900	A very weak band; impossible to determine whether the intensity is changing.
$^4G_{5/2}$	-2	17 300	Both this band and the next occur in the same region of the spectrum. There are pronounced
$^2G_{7/2}$	-1	17 400	intensity changes to the low energy side of the manifold, and a flip in sign at approximately $17\,600\text{ cm}^{-1}$.
$^4G_{7/2}$	-1	19 200	A flip in sign is apparent at approximately $19\,200\text{ cm}^{-1}$, but an instrument malfunction obscures the details.
$^4G_{11/2}$	+1	21 600	A side band appears for the chloride at approximately $21\,200\text{ cm}^{-1}$ which is absent for the acetate.
$^2D_{5/2}$	-2	23 900	A weak band; intensity changes are difficult to determine.
$^2I_{11/2}$	+1	28 600	A band at approximately $28\,500\text{ cm}^{-1}$, appears to have flipped in sign.
$^4D_{7/2}$	-1	30 500	No intensity shifts are apparent.

Table V.1. Observed features in the MCD spectra of Nd(III) complexes.

Figure V.1.a Absorption spectra of $\text{Nd}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ (—), $\text{Nd}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (■ ■ ■), and $\text{Nd}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (xxx) from 590 Å to 540 Å.

Figure V.1.b MCD spectra of $\text{Nd}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ (—), $\text{Nd}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (■ ■ ■), and $\text{Nd}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (xxx) from 17 000 cm^{-1} to 18 500 cm^{-1} .

V.2.ii Samarium Complexes:

The samarium complexes studied were $\text{Sm}(\text{AcAc})_3 \cdot x\text{H}_2\text{O}$, $\text{Sm}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$, $\text{Sm}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$, $\text{Sm}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$, $\text{Sm}(\text{TFA})_3 \cdot x\text{H}_2\text{O}$, and $\text{Nd}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$. Sm is an f^6 system, and the ground state is $^6\text{H}_{5/2}$. The following regions are studied for their potential magnetic and electronic hypersensitivity.

Figures V.2.a, V.2.b, and V.2.c show the MCD spectra of a series of samarium complexes, in spectral regions where the intensity changes can be quantified. Figures b and c are shown separately for clarity; they represent the same spectral region. In figure V.2.a, the band at $\approx 26\,300\text{ cm}^{-1}$ shows an MCD sign change from positive to negative on going from the acetate to the trifluoroacetate, while the band at $\approx 26\,600$ changes from negative to positive. This represents a transition to the $^4\text{P}_{7/2}$ state. In figures V.2.b and c, the side band at $\approx 28\,700\text{ cm}^{-1}$ increases in intensity on going from the acetate to the nitrate. The band at $29\,100$ decreases in intensity on going from the Acetate complex to the nitrate complex.

Transition to	ΔJ	Energy Range(cm^{-1})	Series Trends lowest to highest χ_L
$^4F_{3/2}$	-1	18 900	Very weak band. No visible changes.
$^4G_{7/2}$	+1	20 000	Very weak band. No visible changes.
$^4I_{9/2}$	+2	20500	The side band at lower energy increases in intensity and begins to dominate.
$^4G_{9/2}$	+2	22 700	No apparent change.
$^4F_{7/2}$	+1	24 800	The band at higher energy increases slightly in relative intensity.
$^4P_{3/2}$	-1	25 000	The band at higher energy decreases in relative intensity.
$^4P_{7/2}$	+1	26 700	There is a sign change apparent in the band at $\approx 26\,300\text{ cm}^{-1}$, and another at $\approx 26\,600\text{ cm}^{-1}$.
$^4D_{3/2}$	-1	27 700	The band at $\approx 27\,700$ increases in intensity.
$^4H_{7/2}$	+1	28 700	The band increases in intensity.
$^4D_{7/2}$	+1	29 100	The band decreases in intensity.

Table V.2. Observed features in the MCD spectra of Sm(III) complexes.

Figure V.2.a MCD spectra of $\text{Sm}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (■■■), $\text{Sm}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ (---), and $\text{Sm}(\text{TFA})_3 \cdot x\text{H}_2\text{O}$ (.....) from $26\,000\text{ cm}^{-1}$ to $27\,250\text{ cm}^{-1}$.

Figure V.2.b MCD spectra of $\text{Sm}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ (■ ■ ■), $\text{Sm}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ (— — —), and $\text{Sm}(\text{TFA})_3 \cdot x\text{H}_2\text{O}$ (· · · · ·) from 28 500 cm⁻¹ to 29 750 cm⁻¹.

Figure V.2.c MCD spectra of $\text{Sm}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ (---), and $\text{Sm}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (xxx) from 26 000 cm⁻¹ to 27 250 cm⁻¹.

V.2.iii Dysprosium Complexes:

The dysprosium complexes studied were $\text{Dy}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ and $\text{Dy}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$. $\text{Dy}(\text{III})$ is an f^9 system, having the ground state $^6\text{H}_{15/2}$. The following regions are expected to show hypersensitivity:

Transition to	ΔJ	Energy Range(cm^{-1})	Series Trends lowest to highest χ_L
$^6\text{I}_{13/2}$	-1	25 800	There appears to be a band in the chloride spectrum which is either absent in the acetate spectrum, or has flipped to negative, and is obscured by a band at slightly higher energy.
$^6\text{K}_{17/2}$	+1	26 400	A band at $26\,300\text{ cm}^{-1}$ in the chloride spectrum appears to be absent in the acetate spectrum.
$^6\text{M}_{17/2}$	+1	30 900	The band at $\approx 30\,800\text{ cm}^{-1}$ decreases in relative intensity

Table V.3 Observed features in the MCD spectra of $\text{Dy}(\text{III})$ complexes.

V.2.iv Erbium Complexes:

The erbium complexes studied were $\text{Er}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$, $\text{Er}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$, $\text{Er}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ and $\text{Er}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$. $\text{Er}(\text{III})$ is an f^{11} system, having the ground state $^4\text{I}_{15/2}$. The following regions are expected to show hypersensitivity:

Transition to	ΔJ	Energy Range(cm^{-1})	Series Trends lowest to highest χ_L
$^4\text{G}_{11/2}$	-2	19 300	A band at $\approx 19\,000$ flips from positive for the chloride to negative for the nitrate.

Table V.4 Observed features in the MCD spectra of $\text{Er}(\text{III})$ complexes.

V.3 Correlations with Ligand Electronegativity:

For those hypersensitive bands which are relatively well separated from the surrounding bands, it is possible to attempt a quantitative correlation of MCD intensity with ligand electronegativity χ_L . Figure V.3, showing the correlation for neodymium complexes, is nearly linear for the three ligands used: Cl^- , Ac^- , and NO_3^- . Figure V.4, showing the plot for the samarium complexes, showing

the ligands Ac^- , TCA^- , Cl^- , and NO_3^- , deviates much more strongly from linearity, but the trend is still clear.

Figure V.3 Plot of χ_L vs MCD intensity for 3 Nd(III) complexes.

Figure V.4 Plot of χ_L vs MCD intensity for 4 samarium complexes.

VI. DISCUSSION:

VI.1 Introduction:

The use of MCD spectroscopy in examining the electronic and vibronic transitions of the rare earth ions raises the problem that the current theory does not incorporate the definitions of chiral wavefunctions and operators needed to assign the observable behavior of molecules with natural or imposed optical activity when probed with circularly polarized light. The language of spectroscopy is only set up to describe the energy of the band center and to classify the scalar spectral intensity. In the case of the rare earth ions, these absorption intensities cannot be related to any physically determinable properties of the free ion or the complex. The theory is even less able to deal with the question of differential intensities, since these carry with them a sign, as well as a magnitude.

VI.2 Definitions for Spectroscopic Interpretation:

To fully explain all of the information available from the MCD spectra, it is necessary to set up the wave functions for the free ions, subduced onto the complexes, with all of their vectorial properties explicitly assigned based on physical requirements, rather than assuming, as has been the case in the past, that all normalization coefficients are positive. It is necessary to choose parameters for the wave functions which are physically well defined, and which can be easily related to physically measurable properties.

For this reason, the wave functions and all of the operations, including the Hamiltonians and the transition moments, will be set up following the chiral formalism described above, and using electromagnetic units, rather than the traditional mechanical ones. These allow a fully vectorial description in terms of familiar electronic and magnetic phenomena.

The following terms are used in this section in the dimensional analysis of the wavefunctions. They have their usual definitions from common electromagnetic theory, which are given here for clarity.⁸³

Inductance: The ability of the system under consideration to withstand changes in current.

units: μI

Permeability (magnetic): State function describing the inherent ability per unit length of a material (including vacuum) to permit the establishment of magnetic lines of force. Quantified as the amount of induction which takes place for a given applied magnetic field.

units: μ

Capacitance: The ability of a system to oppose changes in the voltage across a circuit. Quantified as the amount of charge which must be added to a body to

⁸³ Halliday, David and Resnick, Robert; Physics 3rd ed. (John Wiley & Sons, N.Y.) 1978.

raise its potential by one unit.

units: ϵl

Permittivity (Electrical): State function describing the ability of a substance to maintain the separation of charges under an imposed voltage.

units: ϵ

Moment of Inertia: The ability of a given object to resist changes in its angular velocity ω for a given applied torque.

units: I

Natural Frequency (LC circuit): The frequency of the oscillation of the total energy in the system from its starting point, through totally capacitive, through totally inductive, and back to its starting point.

units: ω

Time Constant (LC circuit): The time required for the total energy in the system to cycle from its starting point, through totally capacitive, through totally inductive, and back to its starting point once.

VI.3 MCD Response of Lanthanide Complexes:

The lanthanide metal complexes used in this study all showed narrow MCD transitions, having bandwidths on the order of 5cm^{-1} to 20cm^{-1} . These are centered about the positions quoted in the literature for the positions of the bands in the

absorption spectra for these complexes¹³. This is as expected, and in agreement with the concept that the molecular spectra of rare earth complexes are "atom like" in their bandwidths, and that the 4f electrons are inner, rather than valence electrons.

The lifting of the Zeeman degeneracies in M_J by the magnetic field is apparent in all of the spectra, although for the closely spaced states, it is difficult to tell which of the bands is associated with a particular transition. For a set of widely spaced bands, however, it is possible to count the number of bands associated with a particular transition. This is apparent in the spectrum of Nd^{3+} , where the transitions are relatively widely spaced.

final state	expected degeneracy	observed degeneracy
$^4F_{3/2}$	4	2
$^4F_{5/2}$	6	5
$^4F_{7/2}$	8	4
$^4F_{9/2}$	10	3

Table VI.1: Observed number of bands and expected degeneracy of Nd^{3+} complexes.(figure A.1)

In all cases, it is evident that not all of the expected bands appear in the spectrum. It is not known whether the resolution is insufficient, or whether there are selection rules which select some of the M_J values, while others are not active in the MCD.

VI.4 Electronic Basis Functions of States:

An understanding of the nature of the polarized transitions in the rare earth complexes must first be approached with an understanding of the chiral nature of the states themselves. For this reason, it is necessary to take a new look at the physical nature of the energy levels of the system, using a model that allows the vectorial structure of the system to be described *explicitly*, since this is the only way that the sign of the MCD transitions can be included.

The total energy of any state of the system for each f^N configuration can be described in electromagnetic as opposed to mechanical terms. The energy contained in the system oscillates from the magnetic (inductive) to the electric (capacitive). At its farthest limit, which is by definition out near the ligand, the energy is all potential in mechanical terms, and all capacitive in electromagnetic ones. In near the nucleus, it is mechanically all kinetic, and electromagnetically all inductive. The traditional description given by:

$$\mathcal{H} = T + V \quad (\text{VI.4.1})$$

can be interpreted using *electromagnetic* definitions by:⁸²

$$\mathcal{H} = U_T = U_M + U_E = 1/2 L \dot{\phi}^2 + 1/2 q^2/C \quad (\text{VI.4.2})$$

Comparison between a mechanical system, and this electromagnetic one gives the following analogies:

	Mechanical Energy	Electromagnetic Energy	
Potential	$U_p = 1/2 kx^2$	$U_e = 1/2 q^2/C$	Capacitive
Kinetic	$U_k = 1/2 mv^2$	$U_m = 1/2 Li^2$	Inductive
	$v = dx/dt$	$i = dq/dt$	

Table VI.2.a: Comparison between mechanical and electromagnetic descriptions of energy

where the comparison suggests the one to one transformation shown in table VI.2.b:

x	$\Rightarrow$	q
v	$\Rightarrow$	i
$1/k$	$\Rightarrow$	C
m	$\Rightarrow$	L

Table VI.2.b: Transformation between mechanical and electromagnetic units.

The atomic states are be assumed to have zero resistance for the vector current i , since there is no loss of energy as time progresses.

To avoid exchange of energy with the surroundings, the energy content of the state must remain constant, therefore:

$$dU/dt = \frac{d}{dt} \left[1/2 L i^2 + 1/2 q^2/C \right] = 0 \quad (\text{VI.4.3})$$

$$dU/dt = \left[1/2 L (2i) \frac{di}{dt} + 1/2 (1/C) (2q) \frac{dq}{dt} \right] = 0 \quad (\text{VI.4.4})$$

which gives

$$L i \frac{di}{dt} + q/C \frac{dq}{dt} = 0 \quad (\text{VI.4.5})$$

now, using the fact that $q = it$, and that $dq/dt = i$, the expression can be written in terms of the current i :

$$L i \frac{di}{dt} + i^2/C = 0 \quad (\text{VI.4.6.a})$$

which on rearrangement and simplification and rearrangement becomes

$$\frac{di}{i} = \frac{-1}{LC} t dt \quad (\text{VI.4.6.b})$$

This expression is the conventional description of oscillating current in an LC circuit, and may be used to model an atomic or molecular state.

The solution is the so called "conserved current"⁸⁴ carrying no dimensions or units

⁸⁴ Anthony Sudbery, Quantum Mechanics and the Particles of Nature — An Outline for Mathematicians —, Cambridge University Press (Cambridge U.K.), 1988.

and taking the form of the wave function:

$$i = \exp \left\{ \frac{-t^2}{2LC} \right\} \quad (\text{VI.4.7})$$

this is a solution of the general form:

$$y = \exp \left\{ -Ax^2 \right\}$$

which is as a Hermite function.

A hermite function is defined as a coupled pair of tensors in the vectorial square of the spatial parameter x . Polynomials of this type describe a vector space which contains a function and its complex conjugate. This double space is generally considered to be annular, with the vectors of motion x , and their complex conjugates x^* , inverted to each other at all points. Thus, for each full wave function and its complex conjugate there is an internal conjugacy of counter-rotating currents in specific inverted orientation. Both the wave function and its complex conjugate must coexist at all points for a steady state to exist. Wave theory requires the destructive interference of the electromagnetic radiation by coupled counteracting rotation of charge, or this radiation would be emitted from the state.

The energy expression is more commonly solved for the charge q , which yields a solution of the form

$$q/q_m = \cos \left[\frac{t}{\sqrt{LC}} + \phi \right] \quad \text{where } \phi \text{ is a phase angle.}$$

The spatial dimensions for inductance, L , are μl , and those for capacitance, C , are ϵl . These can be substituted into the equation for current. The hermitian nature of the expression is seen in the reversal of the dimension of time, which represents progression "backwards" along the path. If we are dealing specifically with the initial state of the transition, in which we will be concerned with the dimensional analysis only, we can write:

$$i_1 = \exp \left\{ \frac{-(t^* \times t)_1}{2 \mu_1 \times \epsilon_1 l_1^2} \right\} \quad (\text{VI.4.8})$$

These wave functions of current can be substituted into the standard form of the expectation integral, where the operator carries the dimensions of action.:

$$\iiint i^* \hat{O} i \, d\tau$$

The dimensions of the overall expression are those of *action*, or energy times time. This leads to:

$$\iiint \exp \left\{ \frac{-t^* \times t}{2 \mu \times \epsilon l^2} \right\}^* \hat{O} \exp \left\{ \frac{-t^* \times t}{2 \mu \times \epsilon l^2} \right\} d\tau \quad (\text{VI.4.9})$$

In a geometric sense, the complex conjugate has the effect of reversing the direction of the current, so that i and i^* are of equal magnitude and opposite directions at all times. One aspect of the symmetry requirement can be reflected by a change in the sign of the exponential.

The conjugacy across the operator defines only one reversal, that of chirality. Within each wave function the signs of the conjugate reversals are assigned when the roots of the exponential powers of t are extracted.

Returning to the description of the state in units of inductance and capacitance, we can write this in the fully expanded form:

$$\oint_M \oint_M \oint_{M^*} \exp \left\{ \frac{t^* \times t}{2 (\sqrt{LC})^2} \right\}^* \hat{O} \exp \left\{ \frac{-t^* \times t}{2 (\sqrt{LC})^2} \right\} d\pi \quad (\text{VI.4.10})$$

The key here is that t , L , and C are all vectors, and so the root of the expression $\frac{t^2}{(\sqrt{LC})^2}$ is not simply the scalar real positive root, $\frac{t}{(\sqrt{LC})}$. The appropriate conjugate orientations for both must be chosen. In this case, the product must be depicted as the vector product of conjugate terms:

$$\frac{t^2}{(\sqrt{LC})^2} = \left[\frac{t}{(\sqrt{LC})} \right]^* \times \left[\frac{t}{(\sqrt{LC})} \right]$$

Each occurrence of $\frac{t^2}{(\sqrt{LC})^2}$ must be separated into its two Mobius inverted, conjugate paths of motion for the electronic vectors L and C which define the state.

When the operator, in this instance the photon, acts on the state, it can accelerate only one of these vectors on its path, since it is orthonormal to the conjugate one. It increases the value of the inductive term, L of the current which has the same original orientation as the photon. It does not affect the conjugate current, and so

the two are dephased from each other. Since the two currents are initially coupled, however, the unaccelerated current will attempt to equilibrate with the accelerated one. If this is achieved, the result is a new state, and a transition is said to have taken place. If not, the photon is released again, and the state remains unchanged.

VI.5 Complete Tensorial Energy Basis Functions of States:

Complete basis energy functions can be constructed by including the dimensions and units of action explicitly in the expression. The expression for these functions can be multiplied by the dimensions of ml^2t^{-1}/ml^2t^{-1} , the units of Planck's constant. Upon rearrangement, this yields an expression of "conserved current"⁸⁴ of the form:

$$i = \frac{\hbar t^3}{2 ml^2 (\sqrt{LC})^2} \quad (VI.5.1)$$

and given that (ml^2) are the dimensions of the moment of inertia, the expression can be arranged to read:

$$i = \frac{\hbar t^3}{2(\sqrt{ILC})^2} \quad (VI.5.2)$$

This basis function of conserved current contains the mechanical, electrical and magnetic attributes of the energy, all explicitly stated.

At this point, a new constant can be defined, by analogy with ϵ and μ . Bearing in mind that ϵ and μ are the state functions describing the capacitance and inductance of the system, a state function γ can be defined as the mass permittivity, or the ability of a system to maintain constant acceleration under an applied force.

$$C = \epsilon l$$

$$L = \mu l$$

$$I = \gamma l$$

This allows the description to be stated entirely in terms of the state functions describing the energy level.

$$i = \frac{\hbar t^3}{2(\sqrt{\gamma\mu\epsilon})^2(\sqrt{I^3})^2} \quad (\text{VI.5.3})$$

If we wish to examine the change in conserved current on undergoing a transition from one state to another, this can be expressed within the familiar expression:

$$\iiint i_f^* \hat{O} i_i d\tau \quad (\text{VI.5.4})$$

This leads to:

$$\iiint \exp \left\{ \frac{\hbar t_f^3}{2(\sqrt{ILC})_f^2} \right\}^* \hat{O} \exp \left\{ \frac{-\hbar t_i^3}{2(\sqrt{ILC})_i^2} \right\} d\tau \quad (\text{VI.5.5})$$

If the ratio of the two currents is considered, the expression is:

$$\frac{i_f}{i_i} = \exp \left\{ \frac{2}{2} \frac{t_i^3 \sqrt{\overrightarrow{\Pi C}}_f^2}{t_f^3 \sqrt{\overrightarrow{\Pi C}}_i^2} \right\} \quad (\text{VI.5.6})$$

It can be clearly seen, therefore, that the transition is dependent on the ratio of the inertia, inductance, and capacitance of the initial and final states.

In terms of the vectors state function constants, this can be written:

$$\begin{matrix} \oint \\ \mathbf{M}_f \end{matrix} \begin{matrix} \oint \\ \mathbf{M} \end{matrix} \begin{matrix} \oint \\ \mathbf{M}_i \end{matrix} \exp \left\{ \frac{-\hbar t^2}{2(\sqrt{\gamma \mu \epsilon l^3})_f (\sqrt{\gamma \mu \epsilon l^3})_f} \right\}^* \hat{O} \exp \left\{ \frac{-\hbar t^2}{2(\sqrt{\gamma \mu \epsilon l^3})_i (\sqrt{\gamma \mu \epsilon l^3})_i} \right\} d\pi \quad (\text{VI.5.7})$$

For a successful transition, the photon has accelerated one of the conjugate currents in $(\overrightarrow{\Pi C})_i$, and the resulting rearrangement to a new conserved current condition has yielded the final state.

A brief consideration of the symmetry of the operator can also be instructive. The fully symmetric operator A_{1g} links ψ with ψ^* and yields the traditional Hamiltonian. The electric dipole portion of the photon is responsible for the absorption intensity, and is represented by the dipole operator, having the symmetry T_{1u} . The MCD intensity is the result of the operation of the magnetic dipole, or electric quadrupole, portion of the photon, and has the symmetry T_{2g} . The full vectorial expression of MCD transition probability can therefore be written:

$$\int_{M_f} \int_{M_i} \exp \left\{ \frac{-\hbar t^2}{2(\sqrt{\gamma \mu \epsilon l^3})_f (\sqrt{\gamma \mu \epsilon l^3})_f} \right\}^* (\hat{T}_{2g}) \exp \left\{ \frac{-\hbar t^2}{2(\sqrt{\gamma \mu \epsilon l^3})_i (\sqrt{\gamma \mu \epsilon l^3})_i} \right\} dx$$

(VI.5.8)

VI.6 Application of the Model to Spectral Intensities:

The experimental results show that the hypersensitive transitions vary in intensity with the changing nature of the ligand, and therefore any model explaining these phenomena must focus on the metal–ligand interaction and bonding region.

The ligand which is bound to the metal in question can potentially affect all three features, I, L, and C. In the ground state, the f electron is tightly bound to the metal ion, since the ligand field splitting of the ground state is negligible. The electron in the excited state is much less tightly bound, however, and so delocalization onto the the ligand is expected to contribute to its electromagnetic structure. Once the photon has found coherence with the state vector, and established the inductive term in its own orientation, the increased capacitance of the excited state due to the dielectric constant of the ligand causes a time delay in the transition, and the rearrangement of the current in the complex appears to be out of phase with the photon. This causes the observed sign change in the MCD signal.

Traditional quantum models do not indicate ways to measure the inertia, capacitance and inductance of the electronic states of a molecule experimentally, and so a range of conventionally defined parameters had to be chosen such that they would provide a good model for testing the fundamental parameters. In this study,

therefore, the well established parameter of ligand electronegativity χ_L was used as the observable independent parameter. Changes in χ_L would be expected to parallel changes in the capacitive term C of the state, since the hardness, by definition, is a measure of how tightly the electrons are bound in the bonding region, and the capacitance is a measure of the ability of a region to retain electrical charge.

The time dependence of eqn. (VI.5.6) is consistent with a capacitive model of the electronic states and transitions. Changing the capacitance would be expected to change the amount of time required for the electron to follow the electric field of the photon during a transition. If the ligand is soft, and the dielectric constant is large the state vector will be delayed with respect to the photon vector. The photon will take time to interact with the complex, and the time required will depend on the capacitance of the metal–ligand bonding region.

The dependence of the equation on t^3 means that a small change in ligand electronegativity, resulting in a small change in the bond capacitance, will result in a large change in the time required to "discharge" the capacitance of the ground state, or move the charge density in that region. The time delay results in a loss of phase coherence, and therefore a change in the intensity and sign of the MCD transition.

VI.7 Relationship with Traditional Models for Intensity:

MCD intensity represents the transient magnetic moment required for a change in the magnetic pseudodipole in going from the initial to the final state. Since a magnetic pseudodipole arises from an electric quadrupole, MCD is actually a

quadrupolar phenomenon. In fact, transitions which are apparently almost purely dipolar in nature, such as the charge transfer transitions in some d-block complexes, show little or no MCD intensity. Thus the simple fact that the f-f transitions have significant MCD intensities, and that the hypersensitive $\Delta J = 2$ transitions have intensity ratios similar to those in the absorption spectra, suggests that neither the transitions themselves, nor the manner in which they "borrow" intensity, are a purely dipolar phenomenon; some higher multipole must be responsible for the observed intensity.

VI.7.i Charge Transfer Coupling:

The charge-transfer coupling mechanism involves an almost purely dipolar mechanism, and so does not fit this multipole order criterion. It can therefore be dismissed. The remaining three mechanisms bear examining in light of the newly discovered phenomenon of magnetic hypersensitivity.

VI.7.ii Pseudoquadrupole Mechanism:

Although the title "pseudoquadrupole" would suggest a mechanism which would be active in the MCD, this mechanism is not helpful in explaining data already in the literature. It presupposes the existence of an inhomogeneous dipole around the lanthanide ion. This is not supported by work on rare earth complexes in gases at low pressures, where the dielectric is relatively homogeneous, but $\Delta J = 2$ hypersensitivity persists⁸⁵. There are also no selection rules to suggest why the

⁸⁵ D. Henrie, R. Fellows, and G. Chopin Coord. Chem. Revs. 18, 199, 1976

inhomogeneous would affect only certain, well defined, values of ΔJ , while leaving others unchanged. This study further discounts the pseudoquadrupole mechanism, since it can offer no reason for some of the transitions to show hypersensitivity only in the MCD, while others show hypersensitivity in both.

VI.7.iii Static Coupling:

A static coupling mechanism requires that orbitals other than the 4f be coupled in order to give intensity to the transitions. This means that the metal 5d or 6s be coupled in, or an energy level from the ligand.

The octupole rule can be used to predict which energy level would need to be involved, since the overall order of the transition must be 3. This means that for a $\Delta J = 2$ transition, the static level involved would have to be removed from the 4f by a value of 1. This means that a d state, presumably the 5d would be the one actively giving intensity to the hypersensitive transitions. This is logical since 5d lies closest to the 4f level.

For the same reasons, the $\Delta J = 1$ transitions, the level involved must be a p level. The 6p level is very far removed from the 4f, however, and would not be expected to contribute any appreciable intensity to it. The separation is of the order of $125\,000\text{ cm}^{-1}$ to $175\,000\text{ cm}^{-1}$. The ligands could, under some circumstances, contribute an appropriate p level from which the necessary intensity could be borrowed. The relationship between magnetic hypersensitivity and ligand electronegativity would then seem to be explained. There are two inconsistencies in this model, however.

Firstly, the electronegativity used in the correlations is that of the first available ligand orbital, not necessarily the first available p orbital. It is very rare that a pure p orbital can be defined in a polyatomic ligand. United atom models⁸⁶ usually indicate a mixed character to the Lewis base pair being donated towards the metal ion from the ligand. Since the χ_L used for the plots is for the first available ligand orbital, a ligand p orbital involved to the exclusion of all others in contributing to the intensity of the $\Delta J = 1$ band would result in non linearity of these plots.

Secondly, to explain the presence of any intensity at all, the static coupling mechanism also needs to invoke coupling of an s orbital, to explain the intensities for the $\Delta J = 0$ bands. The 6s orbital on the metal lies at 80 000 cm^{-1} to 125 000 cm^{-1} above the 4f, and so would not appear to be readily available for coupling. The availability of ligand s-like orbitals would also depend strongly on the electron configuration of the ligand, and yet these bands show little to no dependence on the nature of the ligand.

The $\Delta J = 3$ bands pose even more of a problem; they require the coupling in of another f orbital. The only possible orbital is the 5f, and it is removed from the 4f by more than 250 000 cm^{-1} , yet the $\Delta J = 3$ bands show intensities comparable to the others.

The static mechanism seems to fail both in accounting for the linearity of the plots of MCD intensity vs. ligand electronegativity, and in explaining the presence in the spectrum of the $\Delta J = 0$ and $\Delta J = 3$ bands. The coupling mechanism between the

⁸⁶ B. R. Hollebone J. Chem. Soc.(A), 1971, 3008 – 3027 (Parts I, II, and III)
and J. Chem. Soc. Dalton, 1974, 1889 – 1898 (Part IV)

metal and the ligands cannot be selectively used only when expedient, but must be applied equally. When this is done, its predictions of the static mechanism become very poor.

VI.7.iii Vibronic Coupling:

The vibronic model allows for different vibrations to be coupled exclusively to different electronic transitions. Each class of vibrationally coupled transitions would therefore obtain its own intensity rules from a different vibrational source, and so different behavior for each is rationalized, and in retrospect, should have been expected.

These selection rules can all be derived from the octupole rule allows the order of the vibration to be assigned for each group of electronic transitions, based on the ΔJ value of its electronic component. The total must always add up to 3.

For the hypersensitive transitions associated with $\Delta J = 2$, the vibration which is required is a $\Delta V = 1$, or a dipolar vibration. As described earlier, the dipole is consumed in translation, however, and so it is its first harmonic, the $\Delta V = 5$ "pseudo dipole" which is active. The dipolar nature of the intensity enhancing mechanism explains why this particular class of transition is hypersensitive in the absorption spectrum. It is not a true dipole, however, and so the restoring forces within the structure which are necessary to keep it from being a displacement itself are present.

For the $\Delta J = 1$ transitions, the vibration involved is the $\Delta V = 2$. This is a quadrupole displacement of nuclei, having the same symmetry as a rotation of charge, and so the MCD is particularly sensitive to it, while the absorption process is not. This explains why the $\Delta J = 1$ transitions show hypersensitivity only in the MCD spectra.

This model would predict that the hypersensitivity should extend to higher harmonics of ΔJ ; $\Delta J = 3, 5, 7, 9, \dots$ for the magnetic hypersensitivity, and $\Delta J = 2, 6, 10, 14, \dots$ for the electronic hypersensitivity. This was not apparent from the experiments carried out, but neither can it be ruled out. Some of the $\Delta J = 5$ or 6 bands can be seen in the spectra, but the effect on these higher order harmonics would be expected to be smaller, and without a deconvolution, these changes could remain unnoticed.

The fact that there is any intensity in either the absorption or the MCD spectra means that all transitions, regardless of the ΔJ value associated with them, are borrowing intensity from some source, since the $f \rightarrow f$ transitions are Laport forbidden. Any mechanism postulated to account for the hypersensitivities must then be examined with respect to the broader question of providing any intensity at all.

There remain therefore the $\Delta J = 0$, and the $\Delta J = 3$ transitions to account for. The $\Delta J = 0$ transition would be coupled to the $\Delta V = 3$ vibration. This is an octupolar vibration, and is certainly present and available to contribute intensity to the transitions. It is not hypersensitive in either the electronic or magnetic domains, however, since it does not involve the apparent translation or rotation of charge

equivalent to the actual motion of nuclei. It is possible that if the transitions were examined in the presence of a magnetic *and* an electric field (a full Stark experiment which would lift the final Kramers degeneracies) that the hypersensitivity associated with the $\Delta J = 0$ would be apparent. This would involve the construction of a capacitor at the sample holder of the MCD spectrometer, aligned to produce an electric field at right angles to the magneto-optic axis. This predicted behavior appears to be an interesting and promising area of research.

The $\Delta J = 3$ transitions would be coupled with a $\Delta V = 0$ vibration to satisfy the octupole rule. This is not possible, of course, since the "zero-pole" is not an internal mode, but represents a change in the mass of the system. The vibration actually involved would therefore be the $\Delta V = 4$ hexadecapole. In cubic complexes, and those related by symmetry descent, this is always the A_{1g} breathing mode, which is always defined in all symmetries. Thus, this transition would always be visible but weak, since it does not mimic dipole or quadrupole movement of charge.

In this manner, all of the higher ΔJ transitions can be accounted for by remembering that in 3 dimensions, the transitions of higher than 3 simply map back onto the original 4 values of 0 through 3 inclusive. In this manner, all of the transition intensities can be accounted for.

Certainly a vibronic mechanism can account for a lifting of the parity restriction. Pure f^N states are centrosymmetric, but a vibration can distort the symmetry of the ligand cage. This in turn distorts the electron density, changing it from a purely f^N , and giving allowedness to the vibration.

This leads directly to the model of the metal – ligand bonding region as a capacitor. Firstly, the ligand electronegativity χ_L determines how tightly the ligand holds the electron density to itself, and therefore the energy of the vibration, and secondly the χ_L determines the ease with which the electron density can be shifted in space, as required for a transition.

The first case leads directly to the relationship between χ_L and the amount of intensity that the vibration can give to the electronic transition, and therefore the relationship between χ_L and the hypersensitivity.

The second case explains why the magnetic hypersensitivity shows a change in the MCD sign. The transition from one electronic state to another takes real time, and although the time is short, it is not negligible. In the case of a large metal, it can be quite significant. The transition occurs only after a time lag from the incidence of the photon, and therefore an "out of phase" condition occurs.

A final confirmation of the involvement of a vibronic coupling mechanism could be obtained by observing the vibrational structure of the transitions in the MCD. While some vibrational structure is apparent, however, the spectra are too complex to allow for a positive identification of the vibrational bands. A spectrometer with better resolution and computer software designed to provide accurate deconvolution of MCD bands are presently being developed, and should help to achieve this end.

VII. CONCLUSIONS:

Based on the existence of hypersensitivity, it is unquestionable that the rare earth ion responds to its surroundings. The appearance of the $\Delta J = 2$ hypersensitivity in the MCD allows for a re-evaluation of the mechanism through which the metal ion and the ligands interact.

To describe the interaction of the rare earth ion with the surroundings, it is possible to set up the Hamiltonian using electromagnetic units, rather than the traditional units of mechanical energy. Extending this to the Schrödinger operator form yields equation (VI.5.7):

$$\left\langle \begin{matrix} \phi \\ \mu_f \\ \mu_i \end{matrix} \right| \exp \left[\frac{-\hbar t^2}{2(\sqrt{\gamma \mu \epsilon l^3})_f (\sqrt{\gamma \mu \epsilon l^3})_i} \right]^* \hat{O} \exp \left[\frac{-\hbar t^2}{2(\sqrt{\gamma \mu \epsilon l^3})_i (\sqrt{\gamma \mu \epsilon l^3})_f} \right] d\tau \quad (VI.5.7)$$

From this equation, the time dependence of the process is clear, supporting the concept of modeling the metal-ligand bonding region as a capacitor. The operator, the photon, must "discharge" the initial state before a transition can occur.

MCD intensity depends on the change in the magnetic dipole in going from the initial to the final state. Since a magnetic dipole arises from an electric quadrupole, MCD is a quadrupolar phenomenon. In fact, transitions which apparently almost purely dipolar in nature, such as the charge transfer transitions in some d-block

complexes, show little or no MCD intensity. Thus the simple fact that the hypersensitive transitions appear in the MCD, and that their intensity ratios are similar to those in the absorption spectra means that neither the transitions themselves, or the manner in which they "borrow" intensity for the $\Delta J = 2$ transitions is a purely dipolar phenomenon. Some higher order multipole is at work.

The fact that there is any intensity in either the absorption or the MCD spectra means that all transitions, regardless of the ΔJ value associated with them, are borrowing intensity from some source, since the $f \rightarrow f$ transitions are Laport forbidden. Any mechanism postulated to account for the hypersensitivities must then be examined with respect to the broader question of providing any intensity at all.

Though the title of pseudoquadrupole would suggest a mechanism that would be active in the MCD, this mechanism was not helpful in explaining the data. It depends on the existence of an inhomogeneous dielectric around the lanthanide ion, something that was not supported by work on the rare earth complexes in gases at low pressures, where the dielectric is relatively homogeneous, while the hypersensitivity persists⁵. In addition to this, there are no selection rules to suggest why the inhomogeneous dielectric would affect only certain well defined values of ΔJ , while leaving others unchanged, and no reason for some of the transitions to show hypersensitivity only in the MCD, while others show hypersensitivity in both the MCD and the absorption spectra.

The static coupling and the vibronic coupling mechanisms can both explained the initial observations, though for different reasons.

A static coupling mechanism required that states other than the 4f be coupled in order to give intensity to the transitions. The octupole rule was used to select the necessary level, and it was found that the 5p, 5d, 6s, and 5f were required. The large energy separation between these levels and the 4f led to the rejection of this model.

The vibronic model allowed for different vibrations to be coupled to various electronic transitions. Each class of electronic transition would therefore obtain its intensity from a different vibrational source, and so different behavior for each is rationalized.

The octupole rule was again used to predict the order of the vibration to be assigned for each group of electronic transitions, based on the ΔJ value of its electronic component.

For the hypersensitive transitions associated with $\Delta J = 2$, the required vibration was found to be a $\Delta V = 1$, or a dipolar vibration. The dipole is consumed in translation, however, and so it is its first harmonic, the $\Delta V = 5$ "pseudo dipole" which is active. The dipolar nature of the intensity enhancing mechanism explains why this particular class of transition is hypersensitive in the absorption spectrum. It is not a true dipole, however, and so the restoring force necessary to keep it from being a displacement itself is present.

For the $\Delta J = 1$ transitions, the required vibration was found to be the $\Delta V = 2$. This is a quadrupole, and so the MCD is particularly sensitive to it, while the

absorption is not. This explained why the $\Delta J = 1$ transitions show hypersensitivity only in the MCD spectra.

The model predicted that the hypersensitivity should extend to higher harmonics of ΔJ ; $\Delta J = 5, 7, 9, \dots$ for the magnetic hypersensitivity, and $\Delta J = 6, 10, 14, \dots$ for the electronic hypersensitivity. This was not apparent from the experiments carried out, but neither could it be ruled out. Some of the $\Delta J = 5$ or 6 bands can be seen in the spectra, but without a deconvolution, these changes could have remained unnoticed.

The $\Delta J = 0$ transition was coupled to the $\Delta V = 3$ vibration. This is an octupolar vibration, and is certainly present and available to contribute intensity to the transitions. It would be expected to show hypersensitivity only if the transitions were examined in the presence of a magnetic and an electric field (a full Stark experiment which would lift the final Kramer's degeneracies).

The $\Delta J = 3$ transitions were coupled with a $\Delta V = 0$ vibration to satisfy the octupole rule. The "zero-pole" is not an internal mode, but represents a change in the mass of the system, and so the vibration actually involved was therefore be the $\Delta V = 4$ hexadecapole.

In this manner, all of the transition intensities can be accounted for.

The vibronic mechanism accounted for a lifting of the parity restriction. Pure f^n states are centrosymmetric, but the vibration distorted the symmetry of the ligand

cage. This in turn distorted the electron density, changing it from a purely f^N , and gave allowedness to the vibration.

This led directly back to the model of the metal – ligand bonding region as a capacitor. The ligand electronegativity χ_L determined how tightly the ligand held the electron density to itself, and therefore the energy of the vibration, and the ease with which the electron density could be shifted in space, as required for a transition.

This led to the relationship between χ_L and the intensity of the transition, and therefore the relationship between χ_L and the hypersensitivity.

It also explained why the magnetic hypersensitivity showed a change in the MCD sign. The transition from one electronic state to another took real time, and although that time was small, it was not negligible. In the case of a large metal, this time can be quite significant. The transition occurred therefore only after a time lag from the incidence of the photon, and therefore an "out of phase" condition occurred.

This study led to the conclusion that a vibronic mechanism accounts for the observable features of rare earth spectra, both in the absorption and MCD domains, and that the hypersensitivity is proportional to the ligand electronegativity χ_L . Further work is needed to examine a wider selection of ligands for their electronegativity correlations. A sequence of geometrically similar ligands whose electronegativity is changed by changing substituents at positions removed from the

bonding site would allow the effect to be determined without interference from changing coordination number and geometry.

A band fitting program is also necessary for further experiments. The MCD spectra yield a large amount of information, and much of it was impossible to interpret quantitatively without a reliable fitting program. A significant increase in the amount of memory available on the computer that drives the spectrometer has made it possible to develop this program in the near future.

Finally, a new MCD spectrometer is currently being developed, and should prove more sensitive and more reliable than the one which was used for these experiments. The combination of these two should allow the qualitative information quoted for this study to be quantified.

Figure A.1: $\text{Nd}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.2: $\text{Nd}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 20 000 cm^{-1} to 30 000 cm^{-1}

Figure A.3: $\text{Nd}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 29 000 cm^{-1} to 39 000 cm^{-1}

Figure A.4: $\text{Nd}(\text{AC})_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.5: $\text{Nd}(\text{AC})_3 \cdot x\text{H}_2\text{O}$ from 20 000 cm^{-1} to 30 000 cm^{-1}

Figure A.6: $\text{Nd}(\text{AC})_3 \cdot x\text{H}_2\text{O}$ from 29 000 cm^{-1} to 39 000 cm^{-1}

Figure A.7: $\text{Sm}(\text{AcAc})_3 \cdot x\text{H}_2\text{O}$ from 15 000 cm^{-1} to 25 000 cm^{-1}

Figure A.8: $\text{Sm}(\text{AcAc})_3 \cdot x\text{H}_2\text{O}$ from 25 000 cm^{-1} to 35 000 cm^{-1}

Figure A.9: $\text{Sm}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 15 000 cm^{-1} to 25 000 cm^{-1}

Figure A.10: $\text{Sm}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 24 000 cm^{-1} to 34 000 cm^{-1}

Figure A.11: $\text{Sm}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 15 000 cm^{-1} to 25 000 cm^{-1}

Figure A.12: $\text{Sm}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 24 000 cm^{-1} to 34 000 cm^{-1}

Figure A.13: $\text{Sm}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ from 15 000 cm^{-1} to 25 000 cm^{-1}

Figure A.14: $\text{Sm}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ from 24 000 cm^{-1} to 34 000 cm^{-1}

Figure A.15: $\text{Sm}(\text{TFA})_3 \cdot x\text{H}_2\text{O}$ from 15 000 cm^{-1} to 25 000 cm^{-1}

Figure A.16: $\text{Sm}(\text{TFA})_3 \cdot x\text{H}_2\text{O}$ from 28 000 cm^{-1} to 38 000 cm^{-1}

Figure A.17: $\text{Sm}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ from 15 000 cm^{-1} to 25 000 cm^{-1}

Figure A.18: $\text{Sm}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ from 25 000 cm^{-1} to 35 000 cm^{-1}

Figure A.19: $\text{Dy}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.2(b): $\text{Dy}(\text{Cl})_4 \cdot x\text{H}_2\text{O}$ from 19 000 cm^{-1} to 29 000 cm^{-1}

Figure A.21: $\text{Dy}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 28 000 cm^{-1} to 38 000 cm^{-1}

Figure A.22: $\text{Dy}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 35 000 cm^{-1} to 45 000 cm^{-1}

Figure A.23: $\text{Dy}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.24: $\text{Nd}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 20 000 cm^{-1} to 30 000 cm^{-1}

Figure A.25: $\text{Dy}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 29 000 cm^{-1} to 39 000 cm^{-1}

Figure A.26: $\text{Dy}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 35 000 cm^{-1} to 45 000 cm^{-1}

Figure A.27: $\text{Er}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.28: $\text{Er}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 20 000 cm^{-1} to 30 000 cm^{-1}

Figure A.29: $\text{Er}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 29 000 cm^{-1} to 39 000 cm^{-1}

Figure A.30: $\text{Sm}(\text{Cl})_3 \cdot x\text{H}_2\text{O}$ from 32 500 cm^{-1} to 42 500 cm^{-1}

Figure A.31: $\text{Er}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.32: $\text{Er}(\text{Ac})_3 \cdot x\text{H}_2\text{O}$ from 20 000 cm^{-1} to 30 000 cm^{-1}

Figure A.33: $\text{Er}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.34: $\text{Er}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ from 20 000 cm^{-1} to 30 000 cm^{-1}

Figure A.35: $\text{Sm}(\text{TCA})_3 \cdot x\text{H}_2\text{O}$ from 29 000 cm^{-1} to 34 000 cm^{-1}

Figure A.36: $\text{Er}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ from 11 000 cm^{-1} to 21 000 cm^{-1}

Figure A.37: $\text{Er}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ from 20 000 cm^{-1} to 30 000 cm^{-1}

Figure A.38: $\text{Sm}(\text{NO}_3)_3 \cdot 11\frac{1}{2}\text{H}_2\text{O}$ from 29 000 cm^{-1} to 39 000 cm^{-1}

END

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