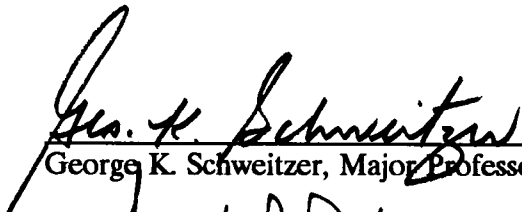
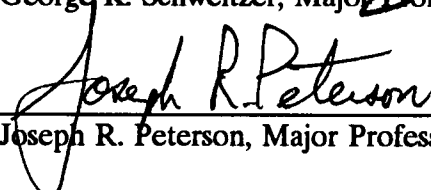


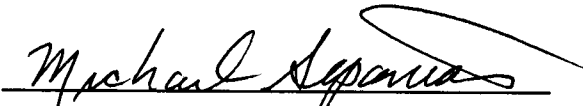
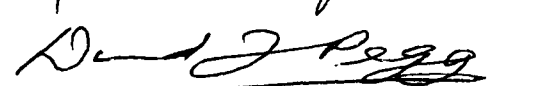
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Joseph R. Peterson, Major Professor

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and Dean of the Graduate School

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A STUDY OF LANTHANIDE FLUORESCENCE SHIFTS  
CAUSED BY NEAR NEIGHBOR PERTURBATION

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Nathan Aaron Stump

December 1991

## DEDICATION

The author dedicates this work and the effort behind its completion to his parents,  
Ned and Nancy.

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Much work has gone into the completion of this dissertation. The author would like to thank those people whose help facilitated its realization.

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## ABSTRACT

Lanthanide ions, unlike ions formed by the d-block elements, characteristically exhibit narrow electronic spectral features, usually on the order of one to two wavenumbers. The spectral position and intensity of these features are dependent upon the environmental symmetry of the lanthanide ion. Any perturbation in the coordination sphere, such as a change in bond distance, or a shift to another geometrical polyhedron, will ordinarily cause a change in the observed spectrum. These two characteristics (narrow line spectra and environmental sensitivity) make the lanthanide ions particularly useful for the study of symmetry, coordination, and crystal structure in solid and dissolved compounds in which they are a major or a minor constituent. Such compounds could also be employed for the study of impurities, coordination numbers, absorption of solvent molecules, and anything else that might perturb the environment around the lanthanide ion. The present work describes the theoretical background required, the instrumentation employed, the syntheses attempted, and the spectral evaluations completed for several europium-containing molecules. A special emphasis was placed upon europium-containing chelates. Europium was chosen because of its simple-appearing electronic spectrum and its readily excited emission in the visible region of the electromagnetic spectrum.

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## CHAPTER I

### INTRODUCTION

Since the discovery of the lanthanide elements about two centuries ago, they have been the topic of many investigations. Some of the characteristics of these elements have been exploited in areas of the technological world, while other characteristics have been studied for their scientific uniqueness alone. This chapter will introduce the reader to the lanthanide elements and some of their spectroscopically interesting characteristics, especially those of europium(III), to which the greater part of this work is devoted.

#### A. Elemental Characteristics

The term lanthanide is usually used to designate the elements with atomic numbers of 57 through 71. These elements are grouped because all show similar physical and chemical characteristics. These similarities arise from resemblances of the electronic structures in each of the elements. The electrons of a lanthanide atom fill sublevels to yield an electronic configuration equal to that of xenon plus the filled 6s sublevel and different numbers of electrons occupying the 4f sublevel. (It is sometimes suggested that the 4f and 5d sublevels are close enough in energy that one electron may occupy a 5d orbital rather than a 4f orbital, but in this work it will be assumed that the 4f sublevel is the only partially filled sublevel.) Lanthanide ions are most often found in oxidation state III. This results from the removal of the two 6s electrons and one 4f electron.

In the elemental state most lanthanide elements are silvery white metals, but the ionic forms can show a variety of colors ranging from white to pink to violet, which arise from absorption of visible light to excite the ion from its ground state to an excited level. The elements in the form of ionic salts are extracted from ores such as bastnasite and

monazite.<sup>1</sup> Industrially, the compounds of these elements are used as phosphors, optical amplifiers, commercial dyes, superconductors, and other similar employments (most taking advantage of the low energy transitions from which the colors originate).<sup>1</sup>

The chemistry of the lanthanide ions resembles that of other ions with large charge density (usually designated "hard" ions). The ions tend to be easily hydrolysed in aqueous solution at a pH greater than about 6, and the hydrous oxides and hydroxides formed will ordinarily be readily decomposed in the presence of strong acids. The ions also weakly or moderately complex with oxygen or nitrogen donor ligands.

Coordination numbers which are usually taken as characteristic for the coordinatively saturated lanthanide ions are eight or nine. The larger ions ( $\text{La}^{3+}$  through  $\text{Sm}^{3+}$ ) will usually exhibit nine coordination sites, while the smaller ions ( $\text{Gd}^{3+}$  through  $\text{Lu}^{3+}$ ) will exhibit eight. The precise crossover point (somewhere in the range of  $\text{Sm}^{3+}$  through  $\text{Gd}^{3+}$ ) will depend upon the ligand types and other subtle factors which determine whether eight or nine coordination is the more stable. Most of the compounds studied by the author have been crystallized from solution and tend to retain the coordination number of eight or nine.

The lanthanide ion electronic configuration and coordination situation is of specific interest to the spectroscopist. The first characteristically gives rise to narrow spectral features with widths resembling those shown by free ions. The second shifts the electronic levels which in turn gives rise to energy shifts in the observed transitions.

## B. Spectroscopy

The electronic spectroscopy of lanthanide compounds deals with the normally forbidden intra-4f transitions.<sup>2</sup> These transitions can be forbidden through the Laporte or parity selection rule. They become observably allowed through the formation of an

induced dipole which allows the transition due to the loss of the inversion center of the ion. A similar disregard for the selection rule results in the colors seen arising from the intra-d transitions of the transition metals.

The structure of a lanthanide ion-containing molecule is reflected in the energies of the electronic levels exhibited by the ion. The coordinated entities surrounding the lanthanide ion form an electrostatic field which will slightly perturb the lanthanide's 4f electrons. These slight perturbations will give rise to shifts in the 4f electronic levels and to full or partial loss of degeneracy of some of the levels. The narrow line spectra of the lanthanides allow for moderately easy evaluation of the shift of these lines.<sup>2</sup>

The europium(III) ion is particularly well suited for use in gaining structural information. Transitions to the ground level from several higher electronic levels are observed in the visible region of the electromagnetic spectrum. The previously mentioned transitions arise from levels with minor possible crystal field splitting (that is, the electronic states of the ion may be split into two to thirteen sublevels). The electronic levels involved in the most intense and easily resolvable transitions are split into five or less sublevels. The presence or absence and extent of the splitting assist in the assignment of spectral lines to specific transitions.

Another advantage of europium(III) emission spectroscopy is the variety of excitation sources that can be employed. The europium(III) ion has several absorption bands in the visible wavelength region including strong absorptions at 390 and 465 nm. If these are not acceptable, the ion can be excited by transfer of energy from an ultraviolet absorbing molecule or molecular ion complexed with the ion. All three of the above-mentioned excitation modes can be realized with a xenon arc lamp. Increased power can be obtained from an argon ion laser in the form of narrow line emission at 465.8 nm and

certain ultraviolet wavelengths. However, the added intensity may not greatly increase fluorescence intensities unless the laser line emission falls upon a broad absorption feature of a ligand or coincides with the narrow absorption features of the europium(III) ion. Low-intensity broad-band mercury arc lamps also work well for excitation in the ultraviolet. All of the above-mentioned sources have been employed by the author to excite europium(III)-containing molecules and molecular ions.

For an experimental technique such as spectroscopy to be of use in inorganic chemistry, it should yield information about the fundamental characteristics of an inorganic compound. Lanthanide ions, with their narrow spectroscopic features and their spectral sensitivity to the coordination situation, are well suited to monitor changes in the basic structure of a molecule or molecular ion.

### C. Investigated Compounds

The author limited the compounds which were studied to europium(III)-containing molecules and molecular ions. Emphasis was placed upon chelates formed between europium(III) ions and polydentate ligands. This priority was used to allow for simple excitation with ultraviolet sources and for moderately simple wet synthetic procedures. These molecules permitted the study of the effects of very slight changes in the molecular environment. One such effect is the change in the geometric positioning of complexed entities around the lanthanide ion. Another is the effect resulting from the change in complexed (often anionic) or non-complexed (usually cationic) counterions. A third interesting structural change is the geometric placement and amount of adsorbed solvent molecules. Other similar changes can be studied through this method.

Investigations of the use of europium(III) as a probe ion in simple solid-state molecules of other lanthanide and transition metal ions were also carried out. When a

europium ion is placed in a rigid lattice, its local environment is determined by the structure of the lattice. This structure can then be determined and studied by the shifts in the emission spectrum of the Eu(III) ion. The present studies employed several simple hydrated inorganic salts such as sulphates and phosphates of other metal ions.

#### D. Proposed Course of Study

The aim of the work described in this dissertation was the advancement and refinement of the use of lanthanide emission spectroscopy for the study of structural changes in molecules and molecular ions. This study was designed to build upon that work already completed and to clear up some of the confusion noted in some previous investigative reports. An understandable treatment of the theoretical background needed for lanthanide spectral interpretation was to be provided, synthetic and instrumental procedures were to be enhanced, and an interpretive method for the description of spectral shifts developed.

## CHAPTER II

### THEORETICAL BACKGROUND

Before the electronic spectra of lanthanide compounds can be considered, an understanding of the theory which is used to describe these spectra is required. In this chapter the author attempts to present an understandable treatment of the theories used for the spectra evaluation of lanthanide molecules. For additional examples of the group theoretical calculations done in this chapter, refer to Appendix A.

#### A. Determination of States

The lanthanide ions have a primary oxidation state of +3, and have ground-state electron configurations of  $[\text{Kr}] 4d^{10} 4f^x 5s^2 5p^6$  ( $x = 0$  to 14). The ground and excited states or energy levels of the ions can be considered as electron configurations of the unfilled sublevels, in this case the 4f sublevel. Each of the electrons in a configuration can be labeled by a unique set of numbers, called quantum numbers. In a field free environment, three quantum numbers are required. The first is the electronic level ( $n$ ) which can have any positive integer value, the second designates the sublevel ( $\ell$ ) which has an integer value between 0 and  $n-1$ , and the third is the spin angular momentum ( $s$ ) which can only equal  $1/2$ . In the case of solid or dissolved lanthanide ions, field free environments are useful only as a first approximation. If a field is applied (magnetic or electrostatic), four quantum numbers are applicable. The first two are the level ( $n$ ) and sublevel ( $\ell$ ) discussed above, the third is the magnetic angular momentum ( $m_\ell$ ) which can have any integer value between  $n-1$  and  $-(n-1)$ , and the fourth is the spin angular momentum ( $m_s$ ) having either the value  $+1/2$  or  $-1/2$ . The later two arise from alignment

of the momenta with, or opposed to, the applied field.

In a specific electron configuration (starting with the approximation of the field free environment) the  $\ell$  values of the electrons can be added vectorially to give an approximation of the total orbital angular momentum ( $L$ ) of the ion. The same can be done to the  $s$  values, yielding an approximation of the total spin angular momentum ( $S$ ). Each of the states can be labeled by these two values, and the result is called a term symbol. The term symbol is usually found in the form seen in Expression (1).

$$\text{Term Symbol} = 2S+1L' \quad \begin{array}{l} \text{if } L = 0,1,2,3,4,5,6,\dots \\ \text{then } L' = S,P,D,F,G,H,I,\dots \end{array} \quad (1)$$

As an example, the  $\text{Pr}^{3+}$  ion has two electrons in the unfilled 4f sublevel (the vector sum of the  $\ell$  values and the vector sum of the  $s$  values in a filled sublevel are both zero). The  $\ell$  value of each of the electrons is 3 since they are in an f sublevel. The  $s$  value of each is  $1/2$ . The vector sum of the  $s$  values would be the integer values including and between  $(1/2 - 1/2)$  and  $(1/2 + 1/2)$  yielding  $S = 0$  and  $1$ , respectively. The vector sum of the  $\ell$  values yields  $L = 0, 1, 2, 3, 4, 5$ , and  $6$ . The sums obtained give all potential combinations of two electrons in an f sublevel and are listed in Table I (using the form seen in Expression 1).

TABLE I  
STATES RESULTING FROM TWO F-ORBITAL ELECTRONS

| $S = 0$                             | $S = 1$                             |
|-------------------------------------|-------------------------------------|
| $^1S, ^1P, ^1D, ^1F, ^1G, ^1H, ^1I$ | $^3S, ^3P, ^3D, ^3F, ^3G, ^3H, ^3I$ |

Some of the states listed in Table I violate the Pauli exclusion principle (both electrons have identical  $n$ ,  $\ell$ ,  $m_\ell$ , and  $m_s$  values) and will not be possible. The possible states can be determined through a microstate analysis in which all the possible configurations or microstates of the ion's electrons are found and  $M_L$  and  $M_S$  values are calculated by summing the  $m_\ell$  and  $m_s$  values. The total number of allowed microstates can be obtained through the use of Equation 2, where  $\ell$  = the quantum number of the unfilled level and  $m$  = the number of electrons in the unfilled sublevel (which in the case of the lanthanide ions  $\ell = f = 3$  and  $m$  = the number of electrons in the 4f sublevel).

$$\text{Number of Micro States} = \frac{4\ell+3-1}{1} \cdot \frac{4\ell+3-2}{2} \cdot \frac{4\ell+3-3}{3} \cdot \dots \cdot \frac{4\ell+3-m}{m} \quad (2)$$

Continuing the example of the  $\text{Pr}^{3+}$  ion, Equation (2) yields a total of 91 microstates. These microstates are listed in Table II.

TABLE II  
MICROSTATE ANALYSIS OF  $\text{Pr}^{3+}$

microstate = (first  $m_\ell$ , <sup>sign of first  $m_\ell$</sup> , second  $m_\ell$ , <sup>sign of second  $m_\ell$</sup> )

|          | $M_S=1$                                    | $M_S=0$                                                                                   | $M_S=-1$                                   |
|----------|--------------------------------------------|-------------------------------------------------------------------------------------------|--------------------------------------------|
| $M_L=6$  |                                            | $(3^+, 3^-)$                                                                              |                                            |
| $M_L=5$  | $(3^+, 2^+)$                               | $(3^+, 2^-) (2^+, 3^-)$                                                                   | $(3^-, 2^-)$                               |
| $M_L=4$  | $(3^+, 1^+)$                               | $(3^+, 1^-) (1^+, 3^-) (2^+, 2^-)$                                                        | $(3^-, 1^-)$                               |
| $M_L=3$  | $(3^+, 0^+) (2^+, 1^+)$                    | $(3^+, 0^-) (0^+, 3^-) (2^+, 1^-) (1^+, 2^-)$                                             | $(3^-, 0^-) (2^-, 1^-)$                    |
| $M_L=2$  | $(3^+, -1^+) (2^+, 0^+)$                   | $(3^+, -1^-) (-1^+, 3^-) (2^+, 0^-) (0^+, 2^-)$<br>$(1^+, 1^-)$                           | $(3^-, -1^-) (2^-, 0^-)$                   |
| $M_L=1$  | $(3^+, -2^+) (2^+, -1^+)$<br>$(1^+, 0^+)$  | $(3^+, -2^-) (-2^+, 3^-) (2^+, -1^-) (-1^+, 2^-)$<br>$(1^+, 0^-) (0^+, 1^-)$              | $(3^-, -2^-) (2^-, -1^-)$<br>$(1^-, 0^-)$  |
| $M_L=0$  | $(-3^+, 3^+) (-2^+, 2^+)$<br>$(-1^+, 1^+)$ | $(3^+, -3^-) (-3^+, 3^-) (2^+, -2^-) (-2^+, 2^-)$<br>$(1^+, -1^-) (-1^+, 1^-) (0^+, 0^-)$ | $(3^-, -3^-) (2^-, -2^-)$<br>$(1^-, -1^-)$ |
| $M_L=-1$ | $(-3^+, 2^+) (-2^+, 1^+)$<br>$(-1^+, 0^+)$ | $(-3^+, 2^-) (2^+, -3^-) (-2^+, 1^-) (1^+, -2^-)$<br>$(-1^+, 0^-) (0^+, -1^-)$            | $(-3^-, 2^-) (-2^-, 1^-)$<br>$(-1^-, 0^-)$ |
| $M_L=-2$ | $(-3^+, 1^+) (-2^+, 0^+)$                  | $(-3^+, 1^-) (1^+, -3^-) (0^+, -2^-) (-2^+, 0^-)$<br>$(1^+, 1^-)$                         | $(-3^-, 1^-) (-2^-, 0^-)$                  |
| $M_L=-3$ | $(-3^+, 0^+) (-2^+, -1^+)$                 | $(-3^+, 0^-) (0^+, -3^-) (-2^+, -1^-) (-1^+, -2^-)$                                       | $(-3^-, 0^-) (-2^-, -1^-)$                 |
| $M_L=-4$ | $(-3^+, -1^+)$                             | $(-3^+, -1^-) (-1^+, -3^-) (-2^+, -2^-)$                                                  | $(-3^-, -1^-)$                             |
| $M_L=-5$ | $(-3^+, -2^+)$                             | $(-3^+, -2^-) (-2^+, -3^-)$                                                               | $(-3^-, -2^-)$                             |
| $M_L=-6$ |                                            | $(-3^+, -3^-)$                                                                            |                                            |

The 91 microstates can then be accumulated into groups, each group representing an allowed state. This is done by working from the largest  $M_L$  and largest  $M_S$  values to the smallest of each. In this case, the greatest  $M_L$  value is 6 with its  $M_S$  value being 0. An  $M_L$  of 6 and  $M_S$  of 0 indicate that one possible state is the  $^1I$ . The full  $^1I$  level must include positive values and negative values of  $M_L$ , along with the integer values between 6 and -6 (6, 5, 4, 3, 2, 1, 0, -1, -2, -3, -4, -5, -6). Due to this requirement, the microstates with  $M_L = 6$  and  $M_L = -6$  are chosen as well as arbitrarily choosing one microstate of each  $M_L$  value between those two. The value of  $M_S$  for each of the chosen microstates is 0, since 0 to -0 and all integers between is only 0. For this example, the following will be chosen:  $(3^+, 3^-)$ ,  $(3^+, 2^-)$ ,  $(3^+, 1^-)$ ,  $(3^+, 0^-)$ ,  $(3^+, -1^-)$ ,  $(3^+, -2^-)$ ,  $(3^+, -3^-)$ ,  $(-3^+, 2^-)$ ,  $(-3^+, 1^-)$ ,  $(-3^+, 0^-)$ ,  $(-3^+, -1^-)$ ,  $(-3^+, -2^-)$ , and  $(-3^+, -3^-)$ . When these microstates are removed as those representing the  $^1I$  state, the next highest  $M_L$  is 5, with its highest  $M_S$  value of 1. Therefore microstates are chosen with  $M_L$  being each of 5, 4, 3, 2, 1, 0, -1, -2, -3, -4, and -5, and with  $M_S$  being each of 1, 0, and -1. The arbitrary selection could include the following: for  $M_S = 1$ ,  $(3^+, 2^+)$ ,  $(3^+, 1^+)$ ,  $(3^+, 0^+)$ ,  $(3^+, -1^+)$ ,  $(3^+, -2^+)$ ,  $(-3^+, 3^+)$ ,  $(-3^+, 2^+)$ ,  $(-3^+, 1^+)$ ,  $(-3^+, 0^+)$ ,  $(-3^+, -1^+)$ ,  $(-3^+, -2^+)$ ; for  $M_S = 0$ ,  $(2^+, 3^-)$ ,  $(1^+, 3^-)$ ,  $(0^+, 3^-)$ ,  $(-1^+, 3^-)$ ,  $(-2^+, 3^-)$ ,  $(-3^+, 3^-)$ ,  $(2^+, -3^-)$ ,  $(1^+, -3^-)$ ,  $(0^+, -3^-)$ ,  $(-1^+, -3^-)$ ,  $(-2^+, -3^-)$ ; for  $M_S = -1$ ,  $(3^-, 2^-)$ ,  $(3^-, 1^-)$ ,  $(3^-, 0^-)$ ,  $(3^-, -1^-)$ ,  $(3^-, -2^-)$ ,  $(-3^-, 3^-)$ ,  $(-3^-, 2^-)$ ,  $(-3^-, 1^-)$ ,  $(-3^-, 0^-)$ ,  $(-3^-, -1^-)$ ,  $(-3^-, -2^-)$ . These microstates make up the  $^3H$  state and are removed from the list. This process is repeated until all of the microstates are accounted for. For the  $Pr^{3+}$  ion this analysis results in the states listed in Table III.

TABLE III  
STATES OF  $\text{Pr}^{3+}$

| $S = 0$                                          | $S = 1$                              |
|--------------------------------------------------|--------------------------------------|
| $^1\text{S}, ^1\text{D}, ^1\text{G}, ^1\text{I}$ | $^3\text{P}, ^3\text{F}, ^3\text{H}$ |

To determine which of the states is the lowest or ground state one follows the rules determined by Hund. These state that the greater the S the greater the stability, and then the greater the L the greater the stability. Therefore, the  $^3\text{H}$  level would be the ground state of a  $\text{Pr}^{3+}$  ion, since  $S = 1$  and  $L = 5$ .

When the above manipulations are applied to the  $\text{Eu}^{3+}$  ion, a similar compilation can be made. There are six electrons in the unfilled 4f sublevel which would yield an L of 0 to 18 and an S of 0 to 3. The microstate analysis yields 3003 microstates which result in the states listed in Table IV. Observing Hund's rules the  $^7\text{F}$  state would be the ground state of the  $\text{Eu}^{3+}$  ion with  $S = 3$  and  $L = 3$ .

TABLE IV  
STATES OF  $\text{Eu}^{3+}$

| $S = 0$                                                                                                                                                                        | $S = 1$                                                                                                                                                          | $S = 2$                                                                                                                          | $S = 3$      |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|--------------|
| $4^*1\text{S}, ^1\text{P}, 6^*1\text{D}, 4^*1\text{F},$<br>$8^*1\text{G}, 4^*1\text{H}, 7^*1\text{I}, 3^*1\text{K},$<br>$4^*1\text{L}, 2^*1\text{M}, 2^*1\text{N}, ^1\text{Q}$ | $6^*3\text{P}, 5^*3\text{D}, 9^*3\text{F}, 7^*3\text{G},$<br>$9^*3\text{H}, 6^*3\text{I}, 6^*3\text{K}, 3^*3\text{L},$<br>$3^*3\text{M}, ^3\text{N}, ^3\text{O}$ | $^5\text{S}, ^5\text{P}, 3^*5\text{D}, 2^*5\text{F},$<br>$3^*5\text{G}, 2^*5\text{H}, 2^*5\text{I},$<br>$^5\text{K}, ^5\text{L}$ | $^7\text{F}$ |

### B. Coupling Schemes

The  $\ell$  and  $s$  quantum numbers discussed previously can couple with each other to give sublevels in each of the states. These sublevels are labeled J states and are determined by different methods depending upon the atom in question. The first method, that of Russell and Saunders, takes the vector sum of the  $\ell$  values to arrive at L, the vector sum of the  $s$  values to determine S, and the vector sum of the L and S values to

designate the coupling observed. The values so obtained are said to be an approximation of the total angular momentum and are labeled J. For example, the  ${}^7F$  ground state of the  $\text{Eu}^{3+}$  ion has  $S = 3$  and  $L = 3$ , therefore the possible J values would be 3-3 through 3+3, or the seven values 0 through 6. These sublevels or J states are designated by the addition of a subscript J value to the term symbol given in Expression (1). This new symbol is described by Expression (3).

$$\text{J STATE} = {}^{2S+1}L_J \quad \begin{array}{l} \text{if } L = 0,1,2,3,4,5,6,\dots \\ \text{then } L = S,P,D,F,G,H,I,\dots \end{array} \quad (3)$$

This gives  ${}^7F_0$ ,  ${}^7F_1$ ,  ${}^7F_2$ ,  ${}^7F_3$ ,  ${}^7F_4$ ,  ${}^7F_5$ , and  ${}^7F_6$  as the J states of  $\text{Eu}^{3+}$ 's  ${}^7F$  state.

The Russell-Saunders scheme of coupling more closely fits experimental observations when modeling atoms with low atomic numbers. In cases of atoms with large atomic numbers like the lanthanides, the results are better modeled by taking the vector sums of the initial quantum numbers  $\ell$  and  $s$  for each electron. This sum yields a total angular momentum ( $j$ ) per electron. The  $j$  values for each of the electrons can then be summed vectorially to obtain the total angular momentum J values. This model is described as  $j,j$  coupling. As an example, the  $\text{Pr}^{3+}$  ion has 2 electrons with  $\ell = 3$  and  $s = 1/2$  which yields values of  $j = 5/2$  and  $7/2$  for each electron. The vector sum of these values would be  $(7/2 + 7/2)$  through  $(7/2 - 7/2)$ ,  $(7/2 + 5/2)$  through  $(7/2 - 5/2)$ , and  $(5/2 + 5/2)$  through  $(5/2 - 5/2)$ . These values can then be analyzed much the same as the microstate analysis described above to give the allowed J-states. In the rest of this work the author will use the Russell-Saunders term symbol for convenience in identifying the individual electronic levels in the studied species, even though the theoretical model detailed by the Russell-Saunders description may not apply.

Relative energies of the J states will usually follow Hund's third rule. This rule states that (for lanthanide ions) the most stable J state will be the state with the lowest J

value for atoms in which the unfilled 4f sublevel contains seven or less electrons, but will be the state with the highest J for atoms in which the unfilled 4f sublevel contains eight or more electrons. Lanthanide ion examples of the first type would include  $\text{Ce}^{3+}$  through  $\text{Gd}^{3+}$ . Examples of the other type would include  $\text{Tb}^{3+}$  through  $\text{Lu}^{3+}$ . Therefore, europium's  ${}^7\text{F}$  state would have the  ${}^7\text{F}_0$  as its lowest J state and  ${}^7\text{F}_6$  as its highest. On the other hand, the ground state of  $\text{Tb}^{3+}$  (which is also a  ${}^7\text{F}$  state) would have  ${}^7\text{F}_6$  as its lowest J state and  ${}^7\text{F}_0$  as its highest energy J state.

### C. Group Theoretical Methods

When a field is applied to an atom, the J states discussed above split into levels depending upon their alignment in the field.<sup>4</sup> If the field is strong enough, the splitting of the J states will be dissolved and the splitting of the state will be determined by the alignment of  $M_L$  values to the field. In the case of the lanthanide ions, the field is generally weak because the electrons in the 4f sublevel (from which the studied transitions arise) are strongly shielded from the bonding orbitals (6s and above). The weak field splits the J slightly, into a maximum of  $2J+1$  levels. These levels are given the values of  $-J$  through  $J$ , and are labeled  $M_J$ . The number of spectral lines observed arising from a given J state will depend upon the strength and geometry of the applied field. This dependency upon the geometry or symmetry of the field allows for a group theoretical treatment of the splitting which is observed.

A molecule or molecular ion is said to have symmetry if it has more than one equivalent position. The symmetry of the molecule can be defined by the movements or operations needed to translate it from one equivalent position to another. A summary of symmetry operations is given in Table V.

TABLE V

## SYMMETRY OPERATIONS

| operation  |            | description                                                                                                                                           |
|------------|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| E          |            | This is the identity operation, in that if nothing is done to the molecule it is in an identical and therefore equivalent position.                   |
| $C_n$      |            | This is a rotation around an axis. The n equals the number of times an equivalent species occurs per complete rotation.                               |
| $\sigma$   | $\sigma_h$ | This is a reflection through a plane perpendicular to the C axis with the largest n.                                                                  |
|            | $\sigma_v$ | This is a reflection through a plane containing the C axis with the largest n and a second rotational axis.                                           |
|            | $\sigma_d$ | This is a reflection through the plane containing the C axis with the largest n but not containing any other rotational axis.                         |
| i          |            | This is an inversion through a point.                                                                                                                 |
| $S_n$      |            | This is a rotation around an axis followed by a reflection through a plane perpendicular to that axis. The n is the same as for the $C_n$ rotation.   |
| R          |            | This is a rotation by $360^\circ$ . <sup>a</sup>                                                                                                      |
| $C_n R$    |            | This is a rotation by $360^\circ$ , followed by a $C_n$ rotation. <sup>a</sup>                                                                        |
| $\sigma R$ |            | This is a rotation by $360^\circ$ , followed by a reflection through a mirror plane. <sup>a</sup>                                                     |
| iR         |            | This is a rotation by $360^\circ$ , followed by an inversion through a point. <sup>a</sup>                                                            |
| $S_n R$    |            | This is a rotation by $360^\circ$ , followed by a $C_n$ rotation and a reflection through a mirror plane perpendicular to rotation axis. <sup>a</sup> |

a. These are required only for double groups in which a rotation by  $360^\circ$  will not return the molecule to its identical orientation.

Each molecule can be labeled by the extent of its symmetry. As an example, water will give equivalent positions if nothing is done (E), if rotated  $180^\circ$  around an axis splitting the angle between the hydrogens ( $C_2$ ), if reflected through the plane containing the three atoms ( $\sigma_v$ ), and if reflected through the plane which splits the two hydrogens ( $\sigma_v$ ). The water molecule's symmetry is then labeled  $C_{2v}$  to designate its  $C_2$  axis and the v of its  $\sigma_v$ .

All molecules can be included in one of several groups (such as  $C_{2v}$ ) called point groups.

If the operations of a molecule's point group are performed upon the molecule, the results form a series of symmetry representations. These representations are collected to form what are called character tables, which can be employed in spectroscopy since each level can be designated by one of the representations. Continuing with the example of water, an E,  $C_2$ ,  $\sigma_v$ , and  $\sigma_v$  will have no effect upon the oxygen's s orbital. No effect for each operation is designated by 1, 1, 1, and 1. If applied to the oxygen's  $p_y$  orbital (taken as perpendicular to the plane containing the three atoms), E has no effect on it,  $C_2$  inverts it, one  $\sigma_v$  inverts it and the other has no effect. No effect, an inversion, an inversion, and no effect is designated as 1, -1, -1, and 1. Another stipulation laid upon these representations is that they be irreducible (one cannot equal the sum or difference of any number of the others). For the  $C_{2v}$  point group these manipulations result in Table VI. Once determined for one molecule, the character table will hold for any molecule of the group with that set of symmetry operations (which is called a point group).

TABLE VI  
CHARACTER TABLE OF THE  $C_{2v}$  POINT GROUP

| $C_{2v}$ | 1E | 1 $C_2$ | 1 $\sigma_v$ | 1 $\sigma_v$ | Electronic(x,y,z) and Magnetic<br>( $R_x$ , $R_y$ , $R_z$ ) dipole operators |
|----------|----|---------|--------------|--------------|------------------------------------------------------------------------------|
| A1       | 1  | 1       | 1            | 1            | z                                                                            |
| A2       | 1  | 1       | -1           | -1           | $R_z$                                                                        |
| B1       | 1  | -1      | 1            | -1           | x, $R_y$                                                                     |
| B2       | 1  | -1      | -1           | 1            | y, $R_x$                                                                     |

The number preceding the operation designation is the number of that particular operation that the molecule contains, and is called the order of that type of operation or class order.

The labels by which the irreducible representations are designated (A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, and B<sub>2</sub> in this case) relate the symmetry of the state to the operations of the point group. An A designation indicates a representation which is symmetric around the principal axis (rotation around the principle axis yields +1). A B designation denotes a representation which is antisymmetric around the principal axis (a rotation around the principal axis yields -1). Both the A and B labels indicate single irreducible representations and are called singly degenerate. Doubly and triply degenerate representations are also possible and are labeled E and T, respectively. The 1 and 2 designations denote symmetrical nature around a secondary axis; if no secondary axis is present, then they are used to indicate symmetry in relation to a mirror plane. When both a secondary rotation and a mirror plane are present, a prime (') and doubleprime (") designation is employed to signify the symmetry in relation to the mirror plane. If the compound contains an inversion center, two other labels (g and u) are used to signify the symmetry in relation to this operation. The g and u stand for gerade (German for even) and ungerade (German for odd), respectively.

#### D. Determination of Representations Making Up a J State

Given the J state of a specific ion and the symmetrical orientation of the surrounding environment, the representations which will make up that J state can be calculated. This calculation uses a series of formulas to determine a reducible representation<sup>3</sup> (the sum of one or more of the irreducible representations). The formulas required for this treatment are given in Table VII.

TABLE VII  
REDUCIBLE REPRESENTATION  
CHARACTER DETERMINATION FORMULAS

| Integer J      |                                                                                                                            |
|----------------|----------------------------------------------------------------------------------------------------------------------------|
| E              | Character = $2J + 1$                                                                                                       |
| $C_n$          | Character = $\frac{\text{Sin}(\text{angle rotated} \cdot (J + 1/2))}{\text{Sin}(\text{angle rotated}/2)}$                  |
| $\sigma$       | Character = $\text{Sin}(\pi \cdot (J + 1/2))$                                                                              |
| i              | Character = $2J + 1$                                                                                                       |
| $S_n$          | Character = $\frac{\text{Sin}((\text{angle rotated} + \pi) \cdot (J + 1/2))}{\text{Sin}((\text{angle rotated} + \pi)/2)}$  |
| Half Integer J |                                                                                                                            |
| R              | Character = $-(2J + 1)$                                                                                                    |
| $C_n R$        | Character = $-\frac{\text{Sin}(\text{angle rotated} \cdot (J + 1/2))}{\text{Sin}(\text{angle rotated}/2)}$                 |
| $\sigma R$     | Character = $-\text{Sin}(\pi \cdot (J + 1/2))$                                                                             |
| iR             | Character = $-(2J + 1)$                                                                                                    |
| $S_n R$        | Character = $-\frac{\text{Sin}((\text{angle rotated} + \pi) \cdot (J + 1/2))}{\text{Sin}((\text{angle rotated} + \pi)/2)}$ |

For the J state value of 2 for a molecule in the  $C_{2v}$  point group, the E character of the reducible representation equals 5, the  $C_2$  character is 1, and both  $\sigma_v$  operations are 1. This representation (5, 1, 1, 1) can be reduced by using Equation (4).

$$\text{Specific Irr. Rep.} = \frac{\sum_{\text{operations}} (\text{Chr}_{\text{Irr. Rep.}} \cdot \text{Chr}_{\text{Red. Rep.}} \cdot \text{Order}_{\text{oper.}})}{\text{total order of the point group}} \quad (4)$$

This equation yields a value of 2 for the number of A1 representations, and a value of 1 for each of the other representations. This result means that the J state of 2 is made up of two A1 type levels, an A2 type level, a B1 type level, and a B2 type level.

If one looks at a state in which  $J = 3$  in  $C_{2v}$  symmetry, the reducible representation which results is (7, -1, -1, -1). The reduction equation (4) yields 1 for number of A1 types, and 2 for each of the other types. A J state with  $J = 3$  will contain an A1 level, two A2 levels, two B1 levels, and two B2 levels.

### E. Lanthanide Emission

The intra-f orbital emission transitions for lanthanide compounds arise through one of three paths, electric dipole coupling, magnetic dipole coupling, or vibronic coupling. These paths are described by a set of several rules as to whether the occurrence of the transition will be allowed or forbidden. These rules include the symmetry selection rule, the parity selection rule, and several rules related to possible quantum number values.

The symmetry selection rule describes the electronic and magnetic coupling by asserting that a transition will be allowed along a given axis if the reducible representation formed by the triple product of the representation of the dipole operator for that axis and the representations of the upper and lower levels contains the totally symmetric representation (characters all ones). As an example, a transition from an A1 level to a B2 level in the  $C_{2v}$  point group gives a product for the two levels of (1\*1, 1\*(-1), 1\*(-1), 1\*1) or (1, -1, -1, 1). That product is then multiplied by each of the representations which function to represent a dipole operator (listed in the character table by x, y, and z for the electronic dipole and Rx, Ry, and Rz for the magnetic dipole). Upon looking back at Table V, these include A1 for the z axis electronically, A2 for the z axis magnetically, B1 for the x axis electronically and the y axis magnetically, and B2 for the x axis magnetically and the y axis electronically. When the representation (1, -1, -1, 1) is multiplied by the A1 representation (1, 1, 1, 1), the representation (1, -1, -1, 1) results, and the transition is forbidden electronically through the z axis because the A1 representation is not found in the product. The triple product with A2 and B1 gives (1, -1, 1, -1) and (1, 1, -1, -1), respectively, which also means forbidden character along those axes. The B2

representation, however, yields  $(1*1, -1*(-1), -1*(-1), 1*1)$  or the symmetrical form  $(1, 1, 1, 1)$ . Therefore this transition is allowed through the y axis electronically and x axis magnetically. This result implies that if polarized light is employed, alignment along the z axis will result in no transition, along the y axis will result in an electric dipole transition, and along the x axis will yield a magnetic dipole transition. If non-polarized light is used the transition will be allowed electronically and magnetically.

For the transition between an A2 level and a B2 level, the product of the two representations is  $(1, -1, 1, -1)$ . When multiplied by the representations of the electronic and the magnetic dipole axes, its product with the B1 representation (which contains the electronic dipole along the x axis and the magnetic dipole through the y axis) alone contains the A1 representation. Therefore the transition is allowed electronically through the x axis and magnetically through the y axis.

Vibronic coupling will be symmetry allowed if the totally symmetric representation is contained in the product of the representations of the excited electronic level, the final electronic level, the excited vibrational level, and the final vibrational level (the final vibrational level is always the totally symmetric representation and can be ignored since this amounts to multiplication by one). The vibrational operators are not usually listed as a part of the character table of a point group, as the electronic and magnetic dipole operators are, because they change depending upon the molecule in question. The determination of the vibrational operators can be accomplished through observing the action of the point group's operations upon the three axes of each atom in the molecule. The action of the operations yields a reducible representation from which can be found the representations of the translational (the x, y, and z representations), rotational (the  $R_x$ ,  $R_y$ , and  $R_z$  representations), and vibrational representations. The translational and

rotational representations can be subtracted off leaving the representations of the vibrational levels. For  $C_{2v}$  symmetry of water the operations yield the following. An E operation (shown in Figure 1) would leave all axes in their original position giving a value of 3 for the z axis, 3 for the x axis, and 3 for the y axis yielding a total of 9.

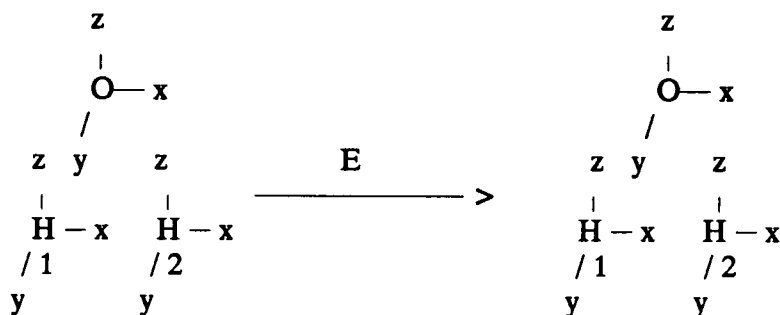


Figure 1. Result of E Operation on the Atomic Axes of Water

The  $C_2$  rotation (shown in Figure 2) moves the hydrogen atoms such that the first is where the second had been and the second is where the first had been. Therefore the value for each axis of a hydrogen is zero because none coincide with its previous position. The oxygen atom retains the same z axis and the x and y axes are inverted giving a total of  $1 + (-2) = -1$ .

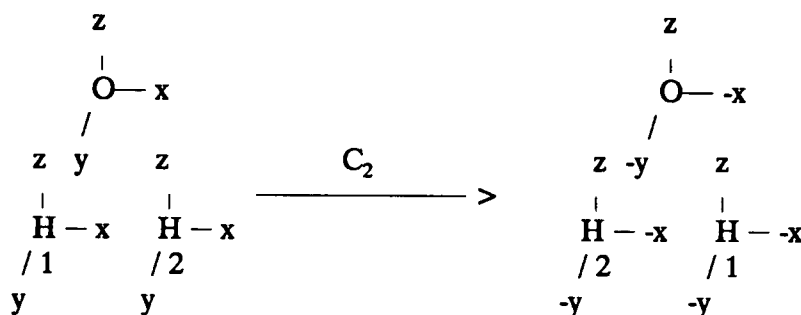


Figure 2. Result of a  $C_2$  Rotation on the Atomic Axes of Water

The first  $\sigma_v$  operations (that through the plane containing the atoms) keeps the x and z axes constant and inverts the y axis giving a value of  $6 + -3 = 3$ . The other  $\sigma_v$  (through the plane bisecting the angle of the hydrogens) moves the hydrogens yielding zero for their contribution and holds the z and y axes of the oxygen constant while inverting the x axis giving a total value of  $2 + -1 = 1$ . Thus the reducible representation (9, -1, 3, 1) is obtained which can be reduced as above to 3 A1, 1 A2, 3 B1, and 2 B2. From the irreducible representations just found, the representations listed in Table V for the translational and rotational operators are subtracted to obtain 2 A1 and 1 B1 as the vibrational representations for water.

Using the two vibrational levels derived previously it can be determined if an electronic transition will be allowed by vibronic coupling. For the A1 level to B2 level transition, the product of the two representations for the excited and final states is, as seen at the beginning of this section, (1, -1, -1, 1). If this representation is multiplied by the A1 vibrational representation, (1, -1, -1, 1) results. If the representation is multiplied by the B1 vibrational representation, (1, 1, -1, -1) results. Since neither product with the vibrational representation contains the (1, 1, 1, 1) representation, the A1 to B2 transition is forbidden vibronically.

The A2 to B2 transition yields (1, -1, 1, -1) as the product of the A2 and B2 representations. The triple product gives (1, -1, 1, -1) for the A1 vibrational representation and (1, 1, 1, 1) for the B1 vibrational representation. Therefore an A2 to B2 transition would be allowed vibronically.

It should be stated that a molecule containing a lanthanide ion (which has a coordination number of 8, 9, or 10) usually contains enough atoms that all representations become allowed as vibrational operators. If this is the case, all transitions will be allowed

through vibronic coupling. The relative intensity of a vibronically allowed line will be one to two orders of magnitude smaller than electronically or magnetically allowed transitions within the same manifold. In the rest of this work it will be assumed that all transitions will be allowed vibronically.

The parity rule deals only with those symmetries which have an inversion center, and asserts that an electronic transition will not occur between a gerade level and another gerade level or between an ungerade level and a second ungerade level. This gives rise to a problem with the lanthanides, because in the symmetry groups concerned, a specific lanthanide ion will have representations either all gerade (integer  $J$ ) or all ungerade (half integer  $J$ ). Because of this fact all electronic transitions will be forbidden in compounds with symmetry containing an inversion center.

The quantum number selection rules give the values of the quantum numbers for which meaningful answers result.<sup>5</sup> They arise from complicated mathematical formulas for the determination of intensities and involve the integral of the wave functions of the levels. Determination of the actual selection rules is often based upon experimental observation of transition intensities.

A first rule involves a change in  $L$  for all types of transitions and states that  $\Delta L$  must be  $+1$  or  $-1$ . There is also a similar rule,  $\Delta S$  must be zero, which lanthanide emission does not adhere to. The rules followed exclusively by electronic transitions are that  $\Delta J$  must be six or less and that the intensities of the electronic transitions will usually be largest for transitions for which  $\Delta J$  equals  $0$ ,  $\pm 2$ ,  $\pm 4$ , or  $\pm 6$ . Rules involving magnetic transitions are that  $\Delta J$  must equal  $-1$ ,  $0$ , or  $1$  for the transition to be allowed, and transitions from a level with  $J = 0$  to another level with  $J = 0$  are forbidden.

## F. Summary

The sum of the work described in this section is the determination of the electronic levels of a lanthanide ion and if transitions between those levels are possible. The general levels of the  $\text{Eu}^{3+}$  ion in  $C_{2v}$  symmetry are schematically presented in Figure 3.

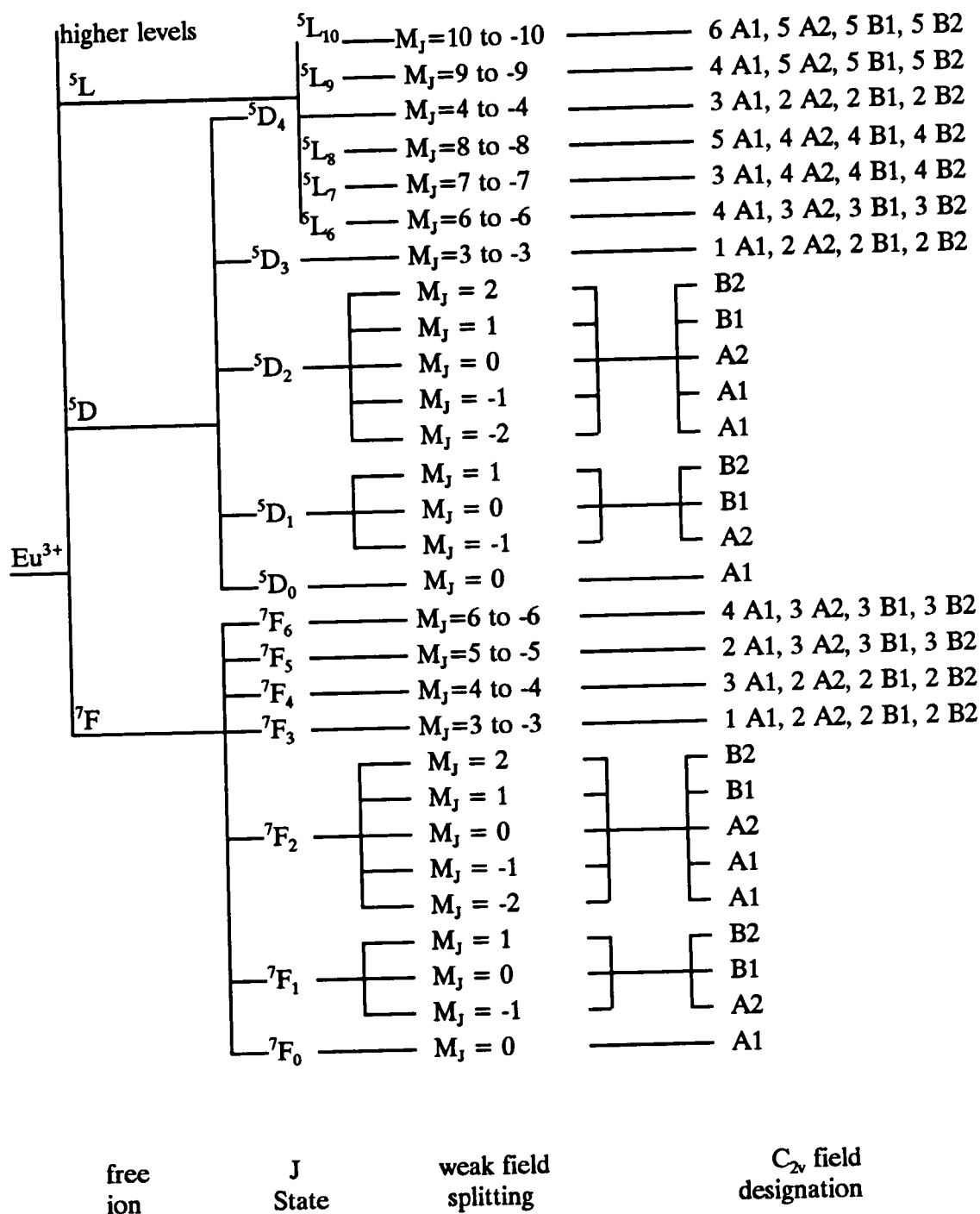


Figure 3. Diagram of  $\text{Eu}^{3+}$  Electronic Levels When Subjected to a  $C_{2v}$  Field

The calculations in this section are correct assuming that the symmetry of the lanthanide-containing compound is known. This is not usually the case. The ideal use of such calculations would be to determine the symmetry of a compound for which it is not known. The accomplishment of this objective would utilize a compilation of the allowed transitions for the various possible point groups. An abbreviated version of one such compilation (that for  $\text{Eu}^{3+}$  in an eight, nine, or ten coordinate site) is given as Table VIII. Similar tables are available in other works,<sup>6,7,8,9</sup> but care should be taken when using any of the published tables for site symmetry analysis, because errors have been found in some of the compilations.

TABLE VIII  
ALLOWED TRANSITIONS OF  
 $\text{Eu}^{3+}$  FOR SOME POSSIBLE POINT GROUPS

| Experimentally Observable Transitions |                                           |                                               |                                                 |                                                   | Site <sup>a</sup><br>Symmetry | Crystal <sup>b</sup><br>System | Geometric Polyhedron of Coordination <sup>c</sup>         |                                                                           |                                 |
|---------------------------------------|-------------------------------------------|-----------------------------------------------|-------------------------------------------------|---------------------------------------------------|-------------------------------|--------------------------------|-----------------------------------------------------------|---------------------------------------------------------------------------|---------------------------------|
| ${}^7F_0 - {}^5D_0$                   | ${}^7F_1 - {}^5D_0$                       | ${}^7F_2 - {}^5D_0$                           | ${}^7F_3 - {}^5D_0$                             | ${}^7F_4 - {}^5D_0$                               |                               |                                | CN = 8                                                    | CN = 9                                                                    | CN = 10                         |
| NONE*                                 | $A_1 - A_2$<br>$A_1 - E_1$                | NONE*                                         | $A_1 - E_1^*$                                   | $A_1 - B_2^*$<br>$A_1 - E_1^*$                    | $D_{4d}$                      | Tetragonal                     | Square<br>Antiprism                                       | NONE                                                                      | Bicapped<br>Square<br>Antiprism |
| $A_1 - A_1$                           | $A_1 - A_2$<br>$A_1 - E^2$                | $A_1 - A_1^*$<br>$A_1 - E^1$                  | $A_1 - 2 E^*$                                   | $A_1 - 2 A_1^*$<br>$A_1 - 2 E^1$                  | $C_{4v}$                      |                                |                                                           | Monocapped<br>Square<br>Antiprism                                         |                                 |
| NONE*                                 | $A_1 - A_2$<br>$A_1 - E$                  | $A_1 - E^*$                                   | $A_1 - A_2^*$<br>$A_1 - 2 E$                    | $A_1 - A_2^*$<br>$A_1 - 2 E$                      | $D_4$                         |                                |                                                           | NONE                                                                      |                                 |
| $A - A$                               | $A - A$<br>$A - E$                        | $A - A^*$<br>$A - E$                          | $A - A^*$<br>$A - 2 E$                          | $A - 3 A^*$<br>$A - 2 E$                          | $C_4$                         |                                |                                                           | Monocapped<br>Square<br>Antiprism                                         |                                 |
| NONE*                                 | $A_1 - A_2$<br>$A_1 - E^2$                | $A_1 - B_2^*$<br>$A_1 - E^1$                  | $A_1 - B_2^*$<br>$A_1 - 2 E^1$                  | $A_1 - B_2^*$<br>$A_1 - 2 E^1$                    | $D_{2d}$                      | Hexagonal                      | Triangulated<br>Dodecahedron                              | NONE                                                                      | NONE                            |
| NONE*                                 | $A_1' - A_2'$<br>$A_1' - E'$              | $A_1' - E'^*$                                 | $A_1' - A_2'^*$<br>$A_1' - E'^2$                | $A_1' - A_2'^*$<br>$A_1' - 2 E'^1$                | $D_{3h}$                      |                                |                                                           | Tricapped<br>Trigonal<br>Prism                                            |                                 |
| NONE*                                 | $A' - A'$<br>$A' - E'$                    | $A' - E'^*$                                   | $A' - 2 A'^*$<br>$A' - E'$                      | $A' - 2 A'^*$<br>$A' - 2 E'$                      | $C_{3h}$                      |                                |                                                           |                                                                           |                                 |
| $A_1 - A_1$                           | $A_1 - A_2$<br>$A_1 - E^2$                | $A_1 - A_1^*$<br>$A_1 - 2 E$                  | $A_1 - A_1^*$<br>$A_1 - 2 E$                    | $A_1 - 2 A_1^*$<br>$A_1 - 3 E$                    | $C_{3v}$                      | Trigonal                       | NONE                                                      |                                                                           |                                 |
| NONE*                                 | $A_1 - A_2$<br>$A_1 - E$                  | $A_1 - 2 E^*$                                 | $A_1 - 2 A_2^*$<br>$A_1 - 2 E^1$                | $A_1 - A_2^*$<br>$A_1 - 3 E$                      | $D_3$                         |                                |                                                           |                                                                           |                                 |
| $A - A$                               | $A - A$<br>$A - E$                        | $A - A^*$<br>$A - 2 E$                        | $A - 3 A^*$<br>$A - 2 E$                        | $A - 3 A^*$<br>$A - 3 E$                          | $C_3$                         |                                |                                                           |                                                                           |                                 |
| $A_1 - A_1$                           | $A_1 - A_2$<br>$A_1 - B_1$<br>$A_1 - B_2$ | $A_1 - 2 A_1^*$<br>$A_1 - B_1$<br>$A_1 - B_2$ | $A_1 - A_1^*$<br>$A_1 - 2 B_1$<br>$A_1 - 2 B_2$ | $A_1 - 3 A_1^*$<br>$A_1 - 2 B_1$<br>$A_1 - 2 B_2$ | $C_{2v}$                      | Rhombic                        | Square<br>Antiprism<br>or<br>Triangulated<br>Dodecahedron | Monocapped<br>Square<br>Antiprism<br>or<br>Tricapped<br>Trigonal<br>Prism | Bicapped<br>Square<br>Antiprism |
| None*                                 | $A - B_1$<br>$A - B_2$<br>$A - B_3$       | $A - B_1^*$<br>$A - B_2$<br>$A - B_3$         | $A - 2 B_1^*$<br>$A - 2 B_2$<br>$A - 2 B_3$     | $A - 2 B_1^*$<br>$A - 2 B_2$<br>$A - 2 B_3$       | $D_2$                         |                                |                                                           | NONE                                                                      |                                 |
| $A - A$                               | $A - A$<br>$A - 2 B$                      | $A - 3 A$<br>$A - 2 B$                        | $A - 3 A$<br>$A - 4 B$                          | $A - 5 A$<br>$A - 4 B$                            | $C_2$                         | Monoclinic                     | Triangulated<br>Dodecahedron                              | Monocapped<br>Square<br>Antiprism<br>or<br>Tricapped<br>Trigonal<br>Prism |                                 |
| $A' - A'$                             | $A - A'$<br>$A - 2 A''$                   | $A - 3 A'$<br>$A - 2 A''$                     | $A - 3 A'$<br>$A - 4 A''$                       | $A - 5 A'$<br>$A - 4 A''$                         | $C_s$                         |                                |                                                           |                                                                           |                                 |
| $A - A$                               | $A - 3 A$                                 | $A - 5 A$                                     | $A - 7 A$                                       | $A - 9 A$                                         | $C_1$                         |                                |                                                           | Triclinic                                                                 |                                 |

\* These manifolds contain other transitions which are vibronically allowed to varying degrees (10 to 100 times less in intensity than an electronic or magnetic dipole allowed transition).

<sup>a</sup> Site symmetry as determined by group theory.

<sup>b</sup> Crystal system as given by Hüfner.<sup>4</sup>

<sup>c</sup> Geometric polyhedra as determined by ligand substitution and chelate bridging.

## CHAPTER III

### EXPERIMENTAL PROCEDURES

#### A. Instrumental Apparatus

The spectroscopic studies included in this work were carried out using several forms of a simple spectroscopic arrangement.<sup>10</sup> A block diagram of this type of instrument is given in Figure 4.

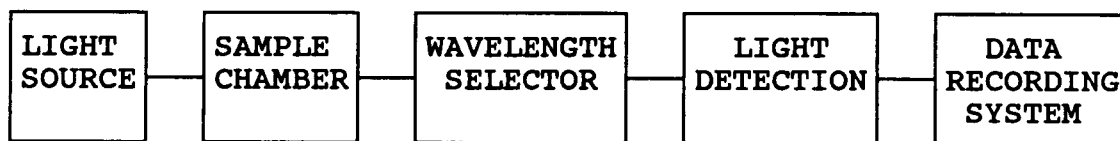


Figure 4. Block Diagram of Instrumental Apparatus

#### 1. Sources Used

As light sources for this work, the author made use of various systems depending upon experimental conditions and instrumental availability. The simplest source employed was a small, hand-held, four-watt mercury-arc lamp (Shortwave Hand Lamp, Fisher Scientific, model number UVS-11 UVP). This lamp was used as a ready and mobile source for the excitation of chelate compounds through absorption of the energy by the ligand and transfer of the energy to the lanthanide ion. The author also made use of the source unit of a semi-defunct fluorometer (AMINCO-BOWMAN Spectrophotofluorometer, American Instruments Company, model number D223-62155).

This 500-watt xenon arc lamp provided a wider range of wavelengths and direct excitation of the europium ion. When high-power excitation was required, the author made use of a six-watt argon-ion laser (Coherent Radiation, model number Innova 300), which was a part of a Raman spectroscopic facility at the Oak Ridge National Laboratory.

## 2. Sample Chamber

The solid and liquid samples were usually enclosed within a capillary tube or 1-dram vial. The tube or vial was attached to a glass rod and positioned in the light beam exiting from the light source. If cold samples were required, the sample was immersed in a clear glass or quartz (depending upon the excitation wavelength) Dewar vacuum bottle filled with liquid nitrogen (other methods were attempted, but proved less reliable or less convenient than immersion). The emitted light was collected at an angle less than or equal to ninety degrees with respect to the exciting light path either by the slit of the wavelength selector or by a liquid light guide (Oriel Corporation, part number 77556) which delivered the light to the wavelength selector.

## 3. Wavelength Selection

Three different monochromators were used during the course of this work. The first was a 1/3-meter instrument (Scanning Monochromator Module, GCA/McPherson, model number EU-700-32) used in the initial studies. Upon completion of the preliminary investigations, a 3/4-meter monochromator (Czerny-Turner Scanning Spectrometer, SPEX industries, model number SPEX 1702) was employed. The third instrument was a part of the Raman spectroscopic system which included the argon-ion laser described above. The

wavelength selection of this system was accomplished by a 1-meter double monochromator (Ramanor Spectrophotometer, Jobin Yvon-Instruments SA, model number HG.2S). The resolution of these instruments is on the order of 0.5 to 2.0 wavenumbers at 514 nm.

#### 4. Light Detection and Data Recording

In all instrumental setups employed (the 1/3 or 3/4-meter single-pass monochromator with various sources and the Raman spectrophotometer), low light levels were expected. The method of choice and that used for low light detection was a photon counting system. A system of this type is shown schematically in Figure 5.

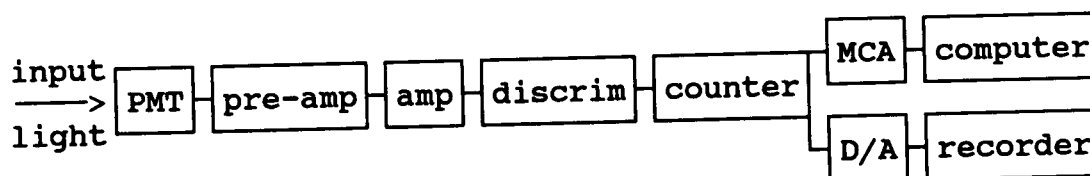


Figure 5. Schematic Diagram of the Photon Counting System

The light entering the detector was converted to an electronic pulse by the Photomultiplier Tube (PMT). The pulse was then amplified as soon as possible by a fast pre-amplifier. The enlarged and shaped pulse was further amplified and then sorted by height (the energy of the pulse) by the discriminator module. The discrimination was designed to remove low-energy thermal noise and high-energy "spike" noise. The pulses which were passed through the discriminator were then counted by a pulse-counting system. The digital output of the counter was subsequently sent into a recorder through a digital-to-analog (D/A) converter or stored in a multichannel analyzer (MCA) system. The multichannel analyzer gave output to a personal computer system employing "Spectra Calc" software (Galactic Industries Corp.) from which hard copy of the results could be

obtained.

### B. Compound Synthesis

The compounds studied were usually synthesized by allowing or forcing crystallization of the europium salt or europium-chelate salt. In the synthesis of these compounds, an unnoticed slight change in experimental conditions often meant the difference between obtaining a spectroscopically pure compound or an material which exhibited emission from multiple  $\text{Eu}^{3+}$  ion site symmetries. The required conditions also tended to vary slightly by ligand and counterion. An initial synthetic procedure was first found,<sup>11</sup> then altered to fit the given ligand. The best method for the repetition of a synthesis was determined by the author by trial and error. A general synthetic procedure will be given later in each of the sections devoted to a specific compound.

Solutions of  $\text{Eu}^{3+}$  salts were made by the addition of the appropriate acid to europium(III) oxide or freshly precipitated europium(III) hydroxide. If an acid was not available, an ion exchange type of reaction was employed to replace the anionic species. The europium used was obtained in the form of the trivalent oxide with at least 99.9% purity from Johnson Matthey/ALFA Products. The inorganic acids and ligands used were obtained from Mallinckrodt Incorporated and Fisher Scientific Company. The inorganic bases used were diluted to 1 M solutions from starting materials obtained from Johnson Matthey/ALFA Products and the Aldrich Chemical Company. The organic compounds used as acids, bases, and ligands were obtained for the most part from the Aldrich Chemical Company. These commercial materials were used as supplied by the vendor.

### C. Studied Compounds

Only those compounds (Table IX, Row 1) for which moderate spectral purity was obtained and for which the author was the primary researcher will be discussed. A multitude of other compounds were studied and are listed in Table IX. Several of these compounds (Table IX, Row 2) were studied as background material and to aid the research of other workers.<sup>12,13,14,15</sup> Other compounds (Table IX, Row 3) proved difficult to synthesize by the means employed in this research or showed promise in only a single case of a series.

TABLE IX  
A COMPILATION OF THE COMPOUNDS WHICH WERE STUDIED

|                                                                                                        | Cationic $\text{Eu}^{3+}$ Complexes<br>Of:                                                                                            | Anionic $\text{Eu}^{3+}$ Complexes<br>Of:                                                                                                                                                                                                                                    | Neutral $\text{Eu}^{3+}$ Compounds<br>Of:                                       |
|--------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| 1. Successful Preparation as<br>Primary Researcher                                                     | Dipyridine,<br>Triphenyl-Phosphine-Oxide                                                                                              | 2,6-Pyridinedicarboxylate,<br>2-Pyridinecarboxylate-N-Oxide,<br>Acetate, Malonate                                                                                                                                                                                            | Sulphate, Phosphate,<br>Formate, Acetate,<br>Malonate,<br>2-Pyridinecarboxylate |
| 2. Successful Preparation as<br>Secondary Researcher                                                   | Phenanthroline                                                                                                                        | Benzoylacetate,<br>Ethylenediaminetetraacetate,<br>Oxydiacetate                                                                                                                                                                                                              | Hydroxide, Oxide,<br>Chloride, Oxychloride                                      |
| 3. Unsuccessful Preparation<br>of a Spectrally Pure<br>Compound by Simple<br>Synthetic Routes Employed | Trioctyl-Phosphine-Oxide,<br>Phenanthrolinedicarboxylate,<br>Pyridine-N-Oxide,<br>Triethylenetetraamine,<br>Polyvinylpyridine-N-Oxide | Dibenzoylmethane,<br>Thenoyltrifluoroacetate,<br>Carbonate, Sulphate, Oxalate,<br>Phosphate, Formate,<br>Phthalate, Phenylmalonate,<br>Salicylate,<br>2-Pyridinecarboxylate,<br>Benzoylformate,<br>Acetoacetate,<br>Allylacetate,<br>Nitrilotriacetate,<br>Polyvinylbenzoate | Benzoate, Carbonate,<br>Oxalate,<br>Various Cation Exchange<br>Resins           |

The means which were attempted for the synthesis of the third group included many variations. One such variation was that of the solvent employed in the synthesis, which was used to control the adsorption of solvent molecules by the compound and to promote the crystallization of a single species. These solvents included pure solutions and mixtures of water, methanol, ethanol, propanol, butanol, acetone, ether, carbon tetrachloride, chloroform, formaldehyde, tetrahydrofuran, dimethylsulfoxide, and dimethoxypropane. Another variation was in the ligand:metal concentration ratio, which gave some control of the species formed. This was especially helpful in cases in which the most stable ligand:metal ratio was not that of the preferred compound. Various methods of drying or storing a sample under a solvent system were also tried. These methods were used to control changes in the compound following synthesis and to promote the conversion of a sample exhibiting multiple crystal forms to one exhibiting a single form.

## CHAPTER IV

### SALTS OF THE TRIS (2,6-PYRIDINEDICARBOXYLATE) COMPLEX

The emission spectra of the tris(2,6-pyridinedicarboxylate) [dipicolinate or  $\text{DPA}^{2-}$ ] chelate complexes have been well studied because of the ease of their synthesis and well-behaved emission characteristics. However, until recently,<sup>8,16</sup> studies of the corresponding crystalline salts were carried out at such low resolution or dealt with such a few electronic transitions that any conclusions reached about the  $\text{Eu}^{3+}$  site symmetry were questionable at best.

In this chapter the author presents the results of the study of such a series of compounds. The research included the observation of observed shifts in the emission spectra caused by distant moieties (the cationic counterions), the ion exchange of cationic counter ions, and the effects of synthetic procedures, especially solvents, on the compounds' emission spectra.

#### A. Typical Spectral Characteristics

The trilithium salt of the europium chelate ( $\text{Li}_3\text{Eu}(\text{DPA})_3$ ) will be employed in this work to describe the emission characteristics of the series of compounds which were synthesized for this study. All the monovalent cations appear to show a similar emission spectrum. Previously<sup>8</sup> the anhydrous trisodium salt was assigned a trigonal  $\text{D}_3$  site symmetry from analysis of four transition manifolds in the europium emission spectrum.

However, discrepancies and errors in the method of interpretation and in the determination of symmetry-allowed transitions have led to questions about the validity of this assignment.

### 1. Spectral Characteristics

The 465.8 nm excitation source falls coincidentally upon the  ${}^7F_0$  to  ${}^5D_2$  absorption feature of  $\text{Eu}^{3+}$  compounds. The observed emission from a single-photon absorption should arise from the  ${}^5D_2$  level and from the  ${}^5D_1$  and  ${}^5D_0$  levels following a non-radiative transition. The observed transitions from these levels to the  ${}^7F$  levels are shown in Figures 6, 7, and 8. The sequential absorption of two photons allows transitions from higher levels to be observed. Such emissions observed in the present work included those transitions arising from the  ${}^5D_3$  electronic level and falling to several of the  ${}^7F$  levels; they are shown in Figure 9.

The energies of the electronic levels in the  $\text{Eu}^{3+}$  ion, relative to the ground state, can be determined from the energies ( $\text{cm}^{-1}$ ) of the observed transitions. In some instances these relative energies can be determined from more than one observable transition. This determination of energy levels by several transitions allows for greater certainty in the assignment of transitions to a given manifold and J-state. A compilation of the observed transitions and the calculated relative electronic energy levels for the trillithium compound are given in Table X.

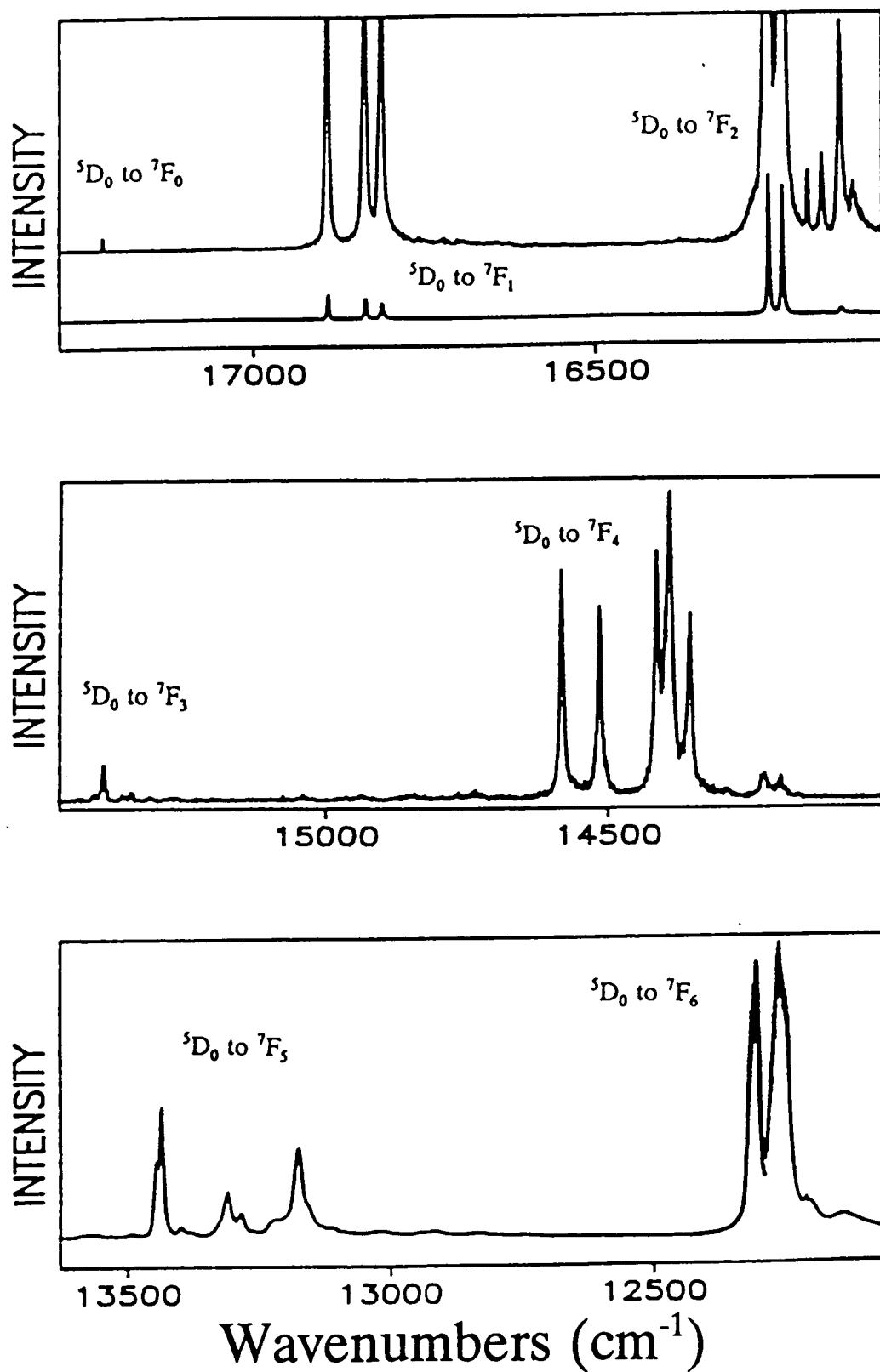


Figure 6. Emission Spectrum of  $\text{Li}_3\text{Eu}(\text{DPA})_3$  Arising From the  $^5\text{D}_0$  Level

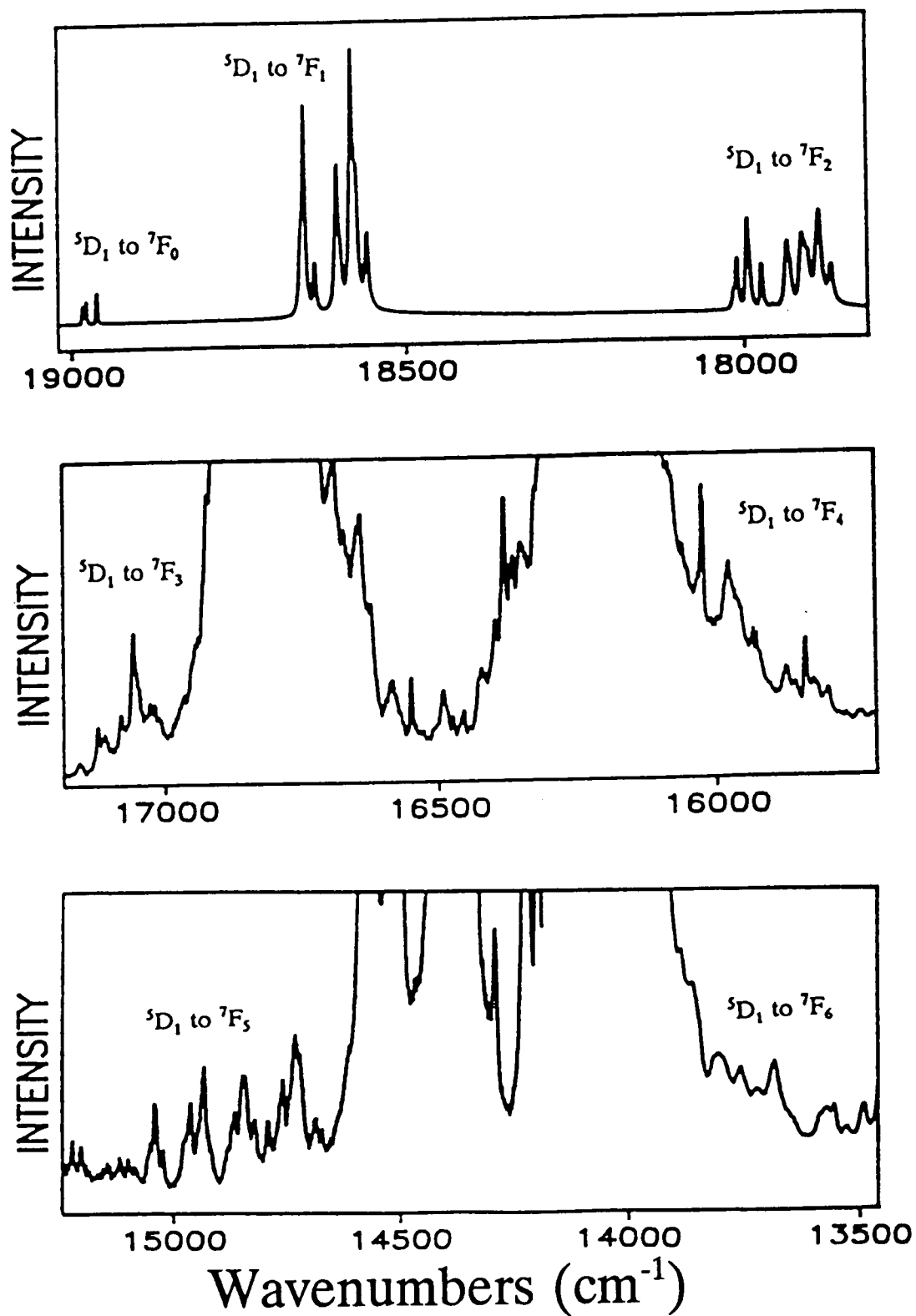


Figure 7. Emission Spectrum of  $\text{Li}_3\text{Eu}(\text{DPA})_3$  Arising From the  $^5\text{D}_1$  Level

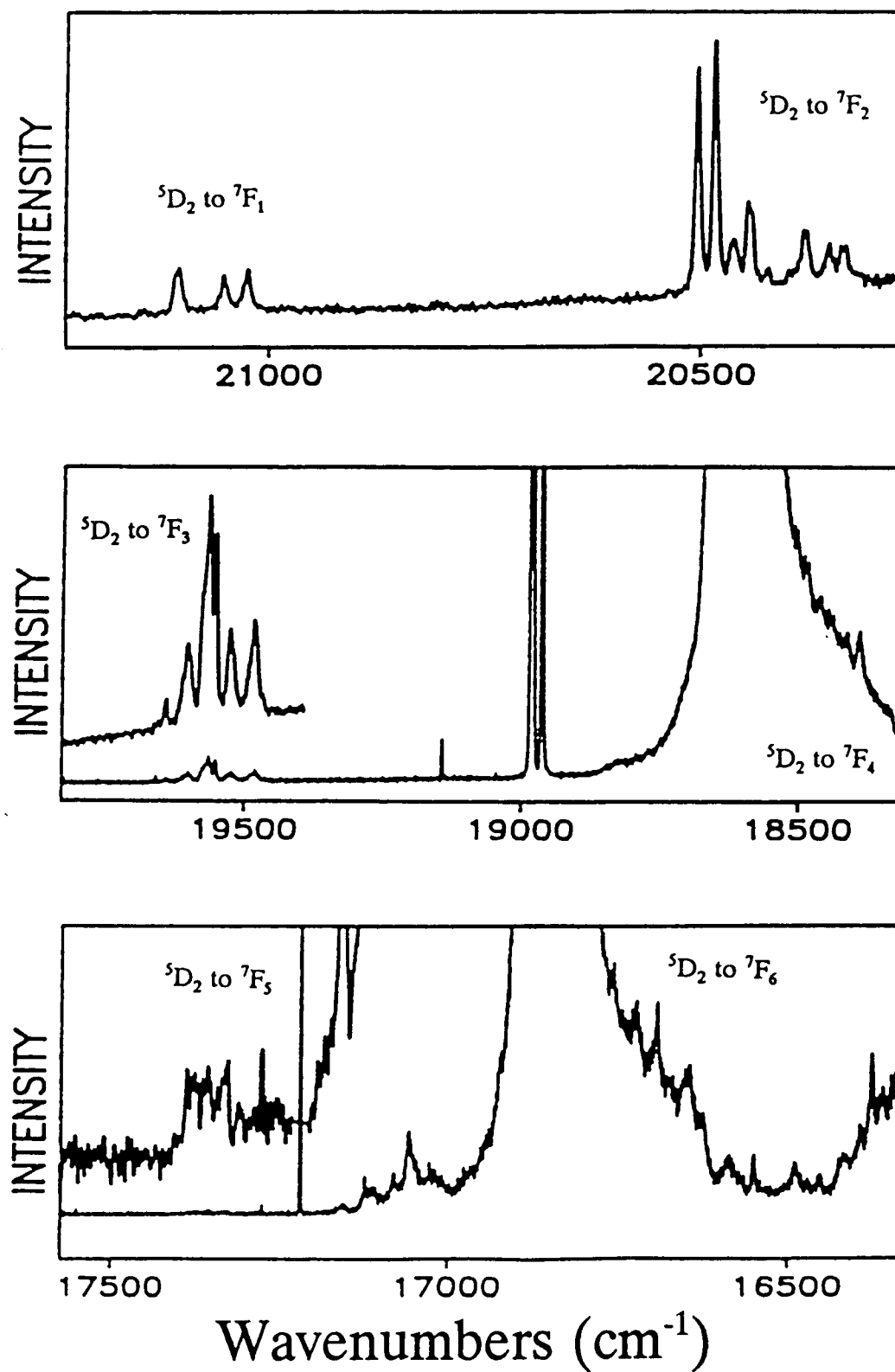


Figure 8. Emission Spectrum of  $\text{Li}_3\text{Eu}(\text{DPA})_3$  Arising From the  $^5\text{D}_2$  Level

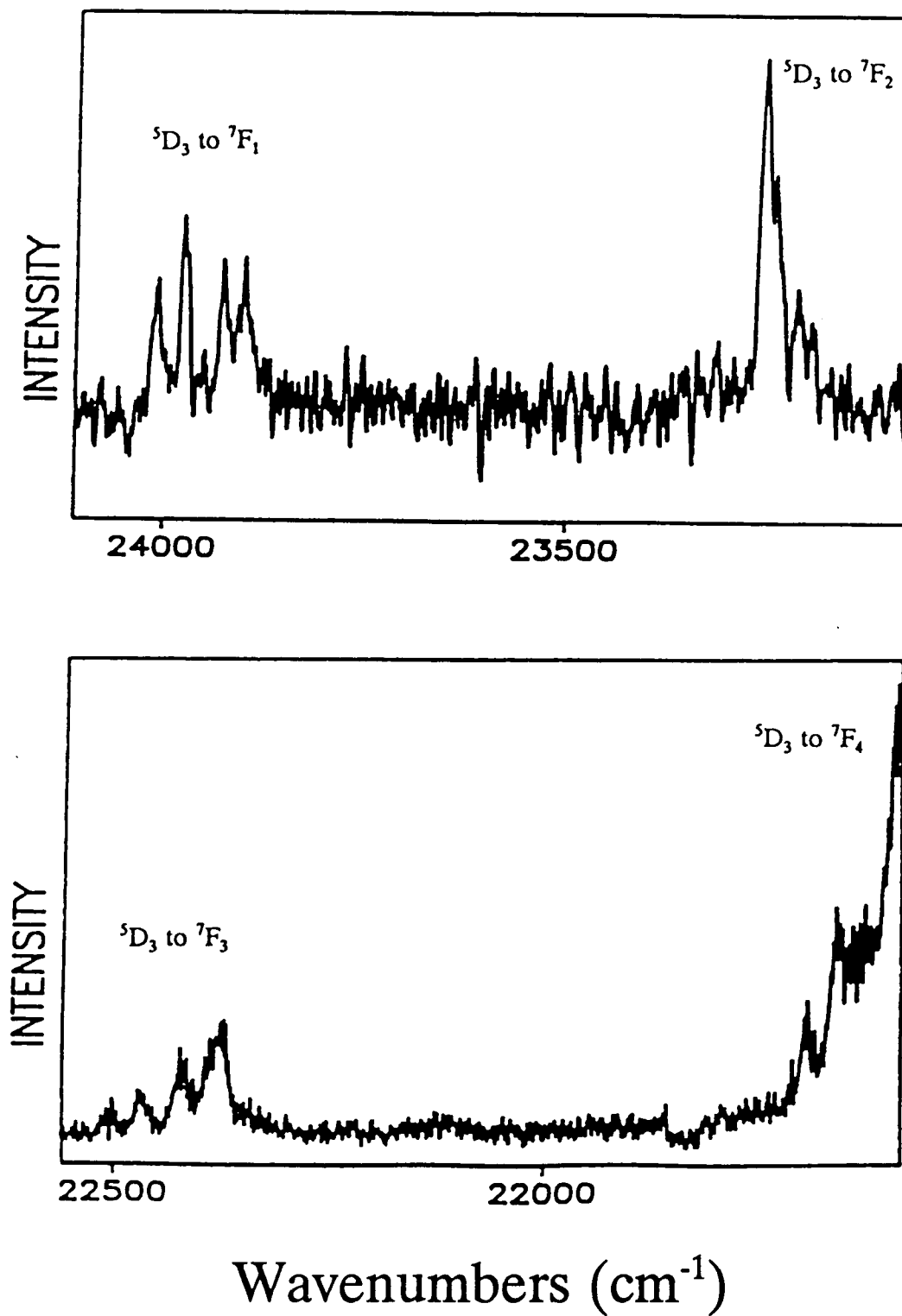


Figure 9. Emission Spectrum of  $\text{Li}_3\text{Eu}(\text{DPA})_3$  Arising From the  $^5\text{D}_3$  Level

TABLE X

OBSERVED TRANSITION ENERGIES AND CALCULATED RELATIVE ENERGIES OF  $\text{Li}_3\text{Eu}(\text{DPA})_3$ 

| Relative Energies (cm <sup>-1</sup> )   | <sup>5</sup> D <sub>0</sub> | <sup>5</sup> D <sub>1</sub> |                                                                    |       | <sup>5</sup> D <sub>2</sub> |                                                                    |       |       |       | <sup>5</sup> D <sub>3</sub> |                       |       |       |       |       |       |       |
|-----------------------------------------|-----------------------------|-----------------------------|--------------------------------------------------------------------|-------|-----------------------------|--------------------------------------------------------------------|-------|-------|-------|-----------------------------|-----------------------|-------|-------|-------|-------|-------|-------|
|                                         | 17214                       | 18961                       | 18977                                                              | 18983 | 21426                       | 21430                                                              | 21435 | 21470 | 21505 | 24273                       | 24281                 | 24298 | 24301 | 24325 | 24333 | 24337 |       |
| Transition Energies (cm <sup>-1</sup> ) |                             |                             |                                                                    |       |                             |                                                                    |       |       |       |                             |                       |       |       |       |       |       |       |
| <sup>7</sup> F <sub>4</sub>             | 3050±2                      |                             |                                                                    | 15927 | 15933                       | 18383                                                              | 18387 | 18391 | 18422 | 18459                       | Rayleigh Line overlap |       |       |       |       |       |       |
|                                         | 3021±2                      | 14193                       |                                                                    | 15955 | 15964                       | 18405                                                              | 18410 |       |       | 18483                       |                       |       |       |       |       |       |       |
|                                         | 2991±1                      | 14223                       |                                                                    | 16051 | 16058                       | 18436                                                              | 18439 | 18445 | 18480 |                             |                       |       |       |       |       |       |       |
|                                         | 2859                        | 14355                       | <sup>5</sup> D <sub>0</sub> to <sup>7</sup> F <sub>2</sub> overlap |       |                             | <sup>5</sup> D <sub>1</sub> to <sup>7</sup> F <sub>1</sub> overlap |       |       |       |                             |                       |       |       |       |       |       |       |
|                                         | 2825                        | 14389                       |                                                                    |       |                             |                                                                    |       |       |       |                             |                       |       |       |       |       |       |       |
|                                         | 2802±1                      | 14412                       |                                                                    |       |                             |                                                                    |       |       | 18672 | 18704                       |                       |       |       |       |       |       |       |
|                                         | 2701±2                      | 14513                       |                                                                    |       |                             |                                                                    |       |       | 18770 |                             |                       | 21581 | 21597 | 21602 | 21624 |       |       |
|                                         | 2661±2                      |                             |                                                                    |       | 16322                       | 18766                                                              | 18770 |       | 18807 | 18845                       |                       |       | 21635 | 21639 | 21666 | 21671 | 21676 |
|                                         | 2635±3                      | 14579                       |                                                                    | 16342 | 16347                       | 18790                                                              | 18798 |       |       |                             | 21639                 | 21604 | 21664 | 21666 | 21691 | 21700 | 21703 |
| <sup>7</sup> F <sub>3</sub>             | 1952±2                      | 15262                       | 17010                                                              | 17025 |                             | 19474                                                              | 19479 | 19485 | 19519 | 19553                       |                       | 22329 | 22348 | 22348 | 22371 | 22382 | 22385 |
|                                         | 1944±3                      | 15270                       | 17017                                                              |       | 17039                       | 19479                                                              | 19485 | 19489 | 19525 | 19561                       | 22329                 | 22340 |       | 22360 | 22382 | 22388 | 22393 |
|                                         | 1904±3                      | 15310                       | 17055                                                              | 17073 | 17077                       | 19523                                                              | 19525 | 19530 | 19565 | 19602                       | 22369                 | 22376 | 22394 | 22394 | 22423 | 22429 |       |
|                                         | 1874±2                      | 15340                       | 17087                                                              | 17102 | 17108                       | 19553                                                              | 19555 | 19561 | 19577 |                             | 22401                 | 22407 | 22423 | 22429 | 22449 | 22459 | 22464 |
|                                         | 1864±3                      | 15350                       | 17097                                                              | 17113 |                             | 19561                                                              | 19565 | 19569 | 19604 | 19643                       | 22412                 | 22416 |       |       | 22459 | 22469 | 22474 |
|                                         | 1856±2                      | 15358                       |                                                                    | 17121 |                             | 19569                                                              | 19573 | 19579 | 19613 | 19648                       | 22416                 | 22423 |       |       | 22469 | 22479 | 22482 |
|                                         | 1825±3                      | 15389                       |                                                                    | 17154 |                             | 19602                                                              | 19604 | 19611 | 19645 |                             | 22449                 | 22455 | 22474 | 22479 | 22500 | 22506 | 22513 |
| <sup>7</sup> F <sub>2</sub>             | 1092±3                      | 16122                       | 17869                                                              | 17887 | 17890                       | 20333                                                              | 20337 |       | 20379 |                             |                       | 23192 | 23211 | 23211 | 23231 | 23238 | 23247 |
|                                         | 1073±4                      | 16141                       | 17890                                                              | 17904 | 17908                       | 20352                                                              | 20358 |       | 20397 | 20433                       | 23204                 | 23211 |       |       | 23252 |       |       |
|                                         | 1048±3                      | 16167                       | 17912                                                              | 17930 | 17935                       | 20379                                                              | 20379 | 20388 | 20423 | 20460                       |                       | 23231 | 23252 | 23255 |       |       |       |
|                                         | 988±2                       | 16226                       | 17973                                                              | 17989 | 17993                       | 20437                                                              | 20440 | 20446 | 20482 | 20517                       |                       |       |       |       |       |       |       |
|                                         | 968±2                       | 16246                       | 18993                                                              | 18008 | 18015                       | 20456                                                              | 20461 | 20465 | 20502 | 20537                       |                       |       |       |       |       |       |       |
| <sup>7</sup> F <sub>1</sub>             | 403±4                       | 16811                       | 18557                                                              | 18574 | 18581                       | 21023                                                              | 21028 | 21034 |       | 21098                       | 23868                 | 23877 | 23893 | 23900 | 23923 | 23926 |       |
|                                         | 380±2                       | 16834                       | 18581                                                              | 18598 | 18603                       | 21048                                                              | 21051 | 21058 | 21090 |                             | 23893                 | 23900 | 23919 | 23923 | 23947 | 23949 | 23958 |
|                                         | 325±3                       | 16889                       | 18635                                                              | 18652 | 18657                       | 21098                                                              | 21105 | 21109 | 21146 |                             | 23949                 | 23958 | 23972 | 23977 |       | 24007 | 24015 |
| <sup>7</sup> F <sub>0</sub>             | 0                           | 17214                       | 18961                                                              | 18977 | 18983                       | Rayleigh Line overlap                                              |       |       |       |                             |                       |       |       |       |       |       |       |

## 2. Discussion of Site Symmetry Assignment

It shall be seen from the discussion below that only a small number (just five of the 24 observed) of the transition manifolds are required to evaluate the site symmetry of this compound. This required set includes the manifolds resulting from the transitions arising from the  $^5D_0$  to  $^7F_{0,1,2}$  and 4 and from the  $^5D_1$  to  $^7F_2$  electronic levels.

For the analysis of this compound, it must be assumed that doubly-degenerate transitions can be split by slight distortions of the metal's geometric polyhedron. This requirement is best exemplified by the two singly-degenerate transitions observed in the  $^5D_0$  to  $^7F_2$  manifold (Figure 6), and the lack of a point group which would allow two singly-degenerate transitions in this manifold (Table VIII). The two mentioned transitions must be singly-degenerate, since transitions resulting from three other electronic levels can be seen as low intensity lines at slightly lower energies than the two allowed transitions (Figure 6). This set of five electronic levels is further verified by the transitions observed resulting from drop-ins from the three  $^5D_1$ , the five  $^5D_2$ , and the seven  $^5D_3$  electronic levels to the five  $^7F_2$  levels. In the previous analysis<sup>8</sup> of the trisodium compound, the two singly-degenerate transitions mentioned above were mistakenly evaluated as two doubly-degenerate transitions. Assuming that the above reasoning is correct, the  $^5D_0$  to  $^7F_2$  manifold should be evaluated as containing a single, allowed, doubly-degenerate transition. According to Table VIII, three possible site symmetries agree with this assignment. These include the point groups  $D_4$ ,  $D_{3h}$ , and  $C_{3h}$ .

Five transitions are observed in the  $^5D_0$  to  $^7F_4$  manifold (Figure 6). It will be assumed that a doubly-degenerate transition in this manifold will be split in a similar manner as that in the  $^5D_0$  to  $^7F_2$  manifold described above. If two doubly-degenerate

transitions are present, it will be assumed that both will show similar splittings and intensity patterns. The inspection of the five allowed transitions shows two pairs which meet this criterion, including the pair at higher energy and the outer two of the set of three at lower energy. Therefore, the manifold will be interpreted as containing one singly-degenerate transition and two doubly-degenerate transitions. This evaluation agrees with splitting patterns for the  $D_4$  and  $D_{3h}$  site symmetries.

A  $D_4$  site symmetry is not a viable assignment for a nine coordinate complex in a tricapped trigonal prismatic polyhedron as described for the analogous compound in the X-ray work.<sup>17,18,19,20</sup> This is most easily seen in the lack of a  $C_4$  rotational axis. The X-ray work also showed no tetragonal structure which would be indicated by a  $D_4$  point group. We will, therefore, tentatively assign a distorted form of the  $D_{3h}$  site symmetry to the Eu(III) ion in this compound. This implies a hexagonal crystal structure for the compound similar to that which was observed by Albertsson<sup>17,18,19,20</sup> for the trisodium chelate salts of the heavier lanthanides. The  $D_{3h}$  site symmetry is indicative of a tricapped trigonal prismatic geometry. The coordinating nitrogens would fill the capping or equatorial sites, while the coordinating oxygens would be in the sites making up the trigonal prism.

The observed distortion is not great enough to affect the symmetry-dictated allowed and forbidden natures of the emission transitions. However, the distortion is large enough to dissolve the degeneracies of the doubly-degenerate electronic levels. The observability and similarity of intensities seen for the disallowed transitions indicate that the distortion of the compound is toward lower symmetry, probably  $C_2$  or lower. However, in our judgment, the much greater intensity of the allowed transitions means  $D_{3h}$

symmetry must be assigned to the Eu(III) ion.

### B. Possible Impurities

In the synthesis of the tris salts of europium dipicolinate, several fluorescent impurities can be formed which can give rise to spurious emission characteristics. Because of this possibility, the author synthesized and studied the emission of several compounds which might be formed when synthesizing the desired compound. These compounds included the monoprotic ( $\text{HEu}(\text{DPA})_2$ ) and triprotic ( $\text{H}_3\text{Eu}(\text{DPA})_3$ ) acid forms, and the ionized solution form.

#### 1. The Monoprotic Acid Chelate Compound

The monoprotic acid chelate  $\text{HEu}(\text{DPA})_2$  was synthesized by mixing 0.07 g of the ligand acid with  $2.8 \times 10^{-4}$  mole of freshly precipitated europium(III) hydroxide (precipitated with 1 M NaOH and washed three times with deionized water) in 5 mL deionized water. The suspension, upon mixing and gentle heating, appeared to begin to clear, but then clouded to yield a suspension of finely divided fluorescent solid in an acidic solution (pH  $\sim 1$ ). The precipitate was collected and sealed in a glass capillary under a solution of the mother liquor.

The emission spectrum of the monoprotic acid species (shown in Figure 10) is interpreted to include an allowed  $^5\text{D}_0$  to  $^7\text{F}_0$  transition (a singlet), three allowed  $^5\text{D}_0$  to  $^7\text{F}_1$  transitions (a singlet and a split doublet), three allowed  $^5\text{D}_0$  to  $^7\text{F}_2$  transitions (a singlet and a split doublet), and seven allowed  $^5\text{D}_0$  to  $^7\text{F}_4$  transitions (three singlets and two split doublets). This type of splitting implies a tetragonal site symmetry of  $\text{C}_{4v}$  for the Eu(III) ion as seen in Table VIII.

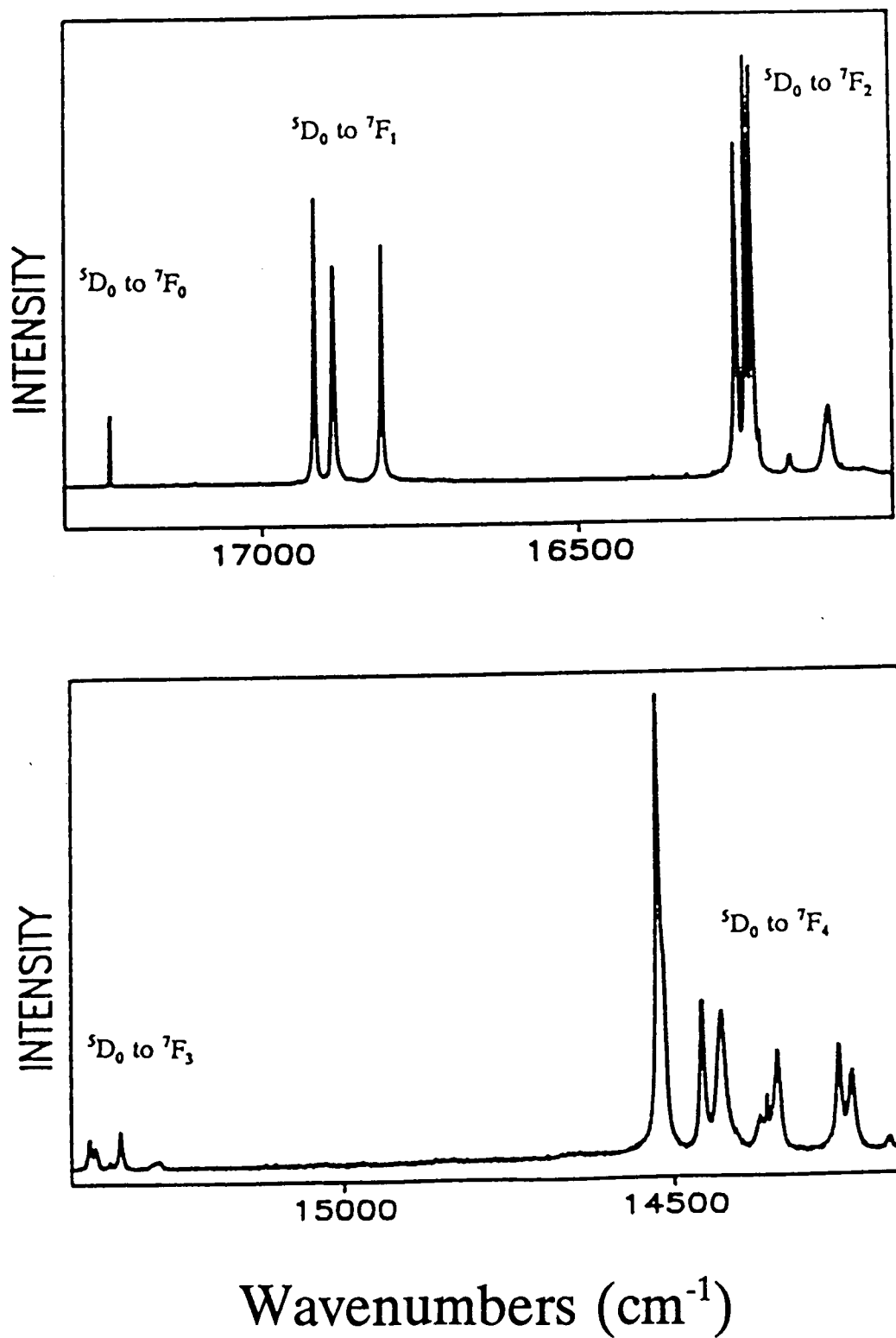


Figure 10. Emission Spectrum of  $\text{HEu}(\text{DPA})_2$

Given the result of this evaluation and the low pH of the solution, it would appear that the nitrogen of both dipicolinate molecules is not complexed and is probably protonated. This assumption arises from the inability to locate a  $C_4$  axis for the coordination sphere if it contains two complexed nitrogen atoms (if the nitrogens are on the poles of the axis, only a  $C_2$  axis is found due to the attached carboxylate oxygens). This hypothesis is corroborated by the  $pK_a$  of a similar deprotonation, that of the nitrogen in picolinic acid. The  $pK_a$  of 1.31 for the reaction  $H_2(pic)^+ \rightarrow H(pic) + H^+$  is enough above the experimental solution pH of  $\sim 1$  to allow protonation of some of the nitrogen in the mixture.<sup>21</sup>

This compound was detected by its emission spectrum in the syntheses of the tris compounds as a solid formed upon the addition of three mole equivalents of the acid to one mole equivalent of freshly precipitated  $Eu(OH)_3$ . Upon the addition of the counterion's hydroxide or oxide, this compound dissolved to form the solution species of the tris compound.

## 2. The Tris Solution Species

The tris chelate salts  $M_3Eu(DPA)_3$  all appeared to have a moderate solubility in polar solvents and were all stored in some fashion under a solution to prevent changes due to drying. To form the solution species  $Eu(DPA)_3^{3-}$  of the complex, a small amount of the solid trisodium salt was dissolved in an appropriate solvent (the other tricationic salts were also studied, but yielded the same emission spectrum). This was done with water and methanol as solvents in that they were preferentially used as solvents in the synthesis of the tris compounds. The solutions were sealed in glass capillaries and studied as frozen glasses immersed in liquid nitrogen.

The resulting spectra of the two solutions are shown in Figure 11. The most

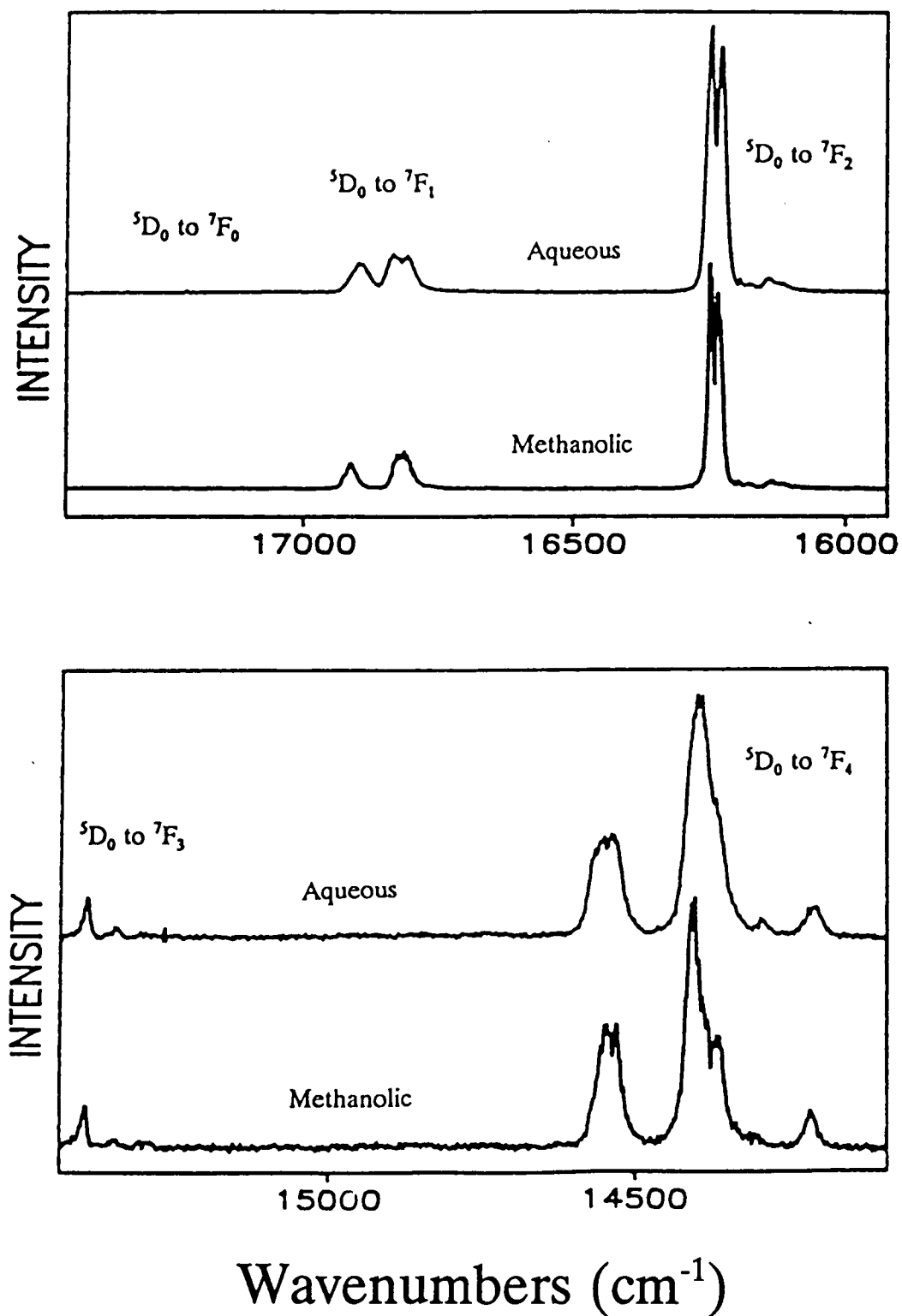


Figure 11. Emission Spectra of Aqueous and Methanolic  $\text{Eu}(\text{DPA})_3^{3+}$

visible characteristic is the broadening of the emission frequencies; however, the splitting which is observed is still consistent with the  $D_{3h}$  site symmetry tentatively assigned to the solid compounds (disallowed  $^5D_0$  to  $^7F_0$  manifold, a singlet and a doublet in the  $^5D_0$  to  $^7F_1$  manifold, a doublet in the  $^5D_0$  to  $^7F_2$  manifold, and a singlet and two doublets in the  $^5D_0$  to  $^7F_4$  manifold).

### 3. The Triprotic Acid Form

The triprotic acid form of the chelate  $H_3Eu(DPA)_3$  was synthesized by mixing 0.21 g of DPA with  $2.8 \times 10^{-4}$  mole of freshly precipitated europium(III) hydroxide in 5 mL of deionized water. 1 M NaOH was then added with stirring until the solution reached a pH greater than 11 (the solution cleared). This was followed by the addition of concentrated HCl until the solution pH was less than 1 (the solution remained clear). The resulting solution was then heated at 95°C for approximately one hour, after which a crystalline precipitate was collected and sealed in a glass capillary under a small amount of the solution.

The emission spectrum of the triprotic acid form (shown in Figure 12) appeared to show at least two crystal sites for the europium(III) ion, neither of which can be attributed to the monoprotic form addressed above. The principal Eu(III) site appears to be  $D_{3h}$ ; however, a truly valid assignment is not possible from these data.

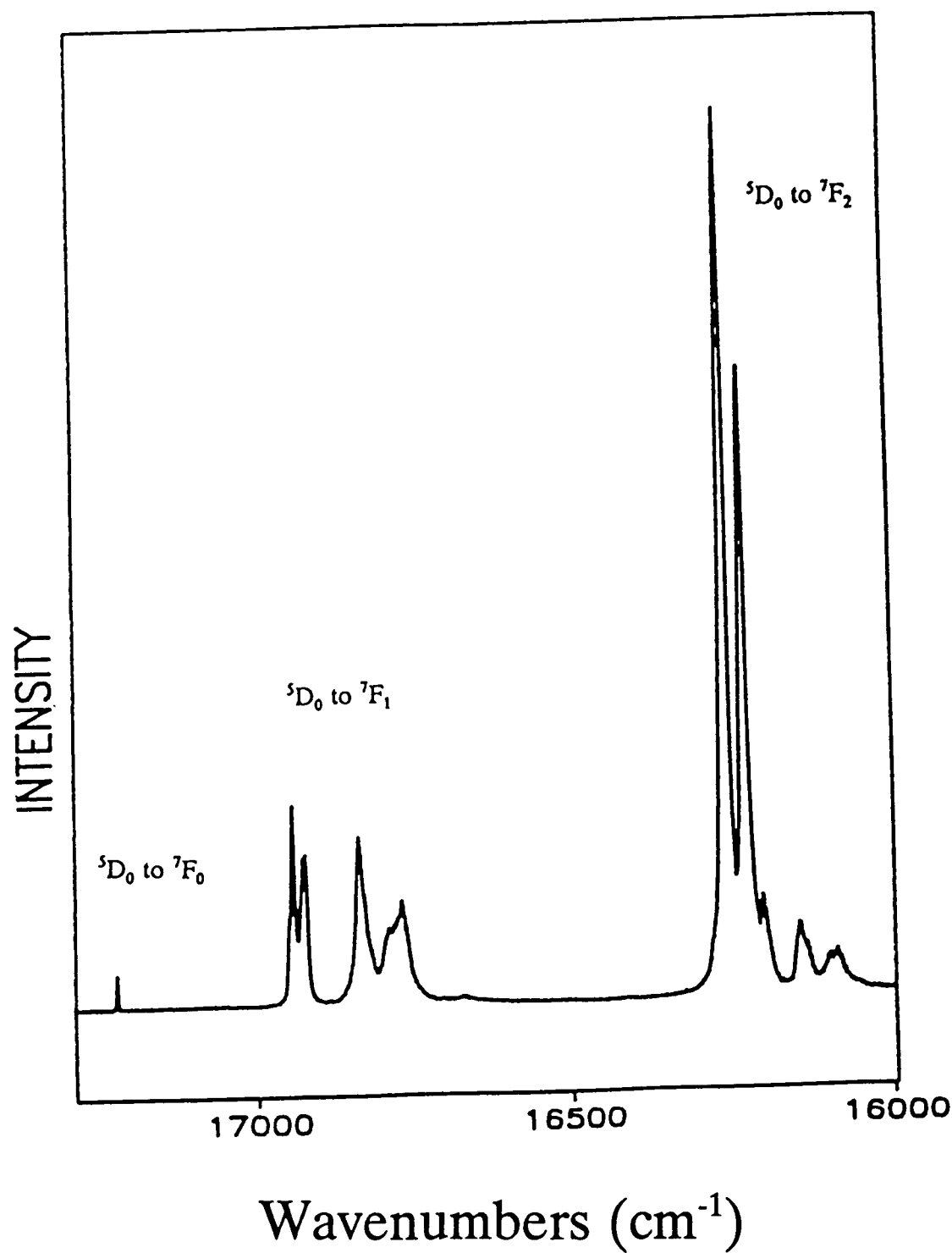


Figure 12. Emission Spectrum of  $\text{H}_3\text{Eu}(\text{DPA})_3$

#### 4. The Effects of pH

Considering the above set of possible impurities (especially the problem of protonation and deprotonation of the carboxylic acids), a short study of the effects of pH on the emission spectrum of the solution compound was needed. The study entailed the synthesis of the sodium compound described above. However, during the process of raising the pH with NaOH, the solution pH was monitored and two-drop aliquots of the solution were collected at various points during the elevation of the pH. The samples were then sealed in capillaries, immersed in liquid nitrogen, and the emission spectrum recorded for each.

The titration curve resulting from this study is shown in Figure 13. It appears to show two equivalence points. As the pH was raised, the europium(III) emission spectra of the solutions (Figure 14) showed a distinct change in transition energies preceding the first equivalence point. However, once the first proton was removed, no detectable change in the emission spectrum was observed. This appears to indicate that once the europium's geometrical environment is formed, it is maintained through the final deprotonation of the compound.

#### C. Perturbations Due to Changes of Counterion

As a general rule the shifts in the electronic spectra of europium-containing molecules which are attributable to the change in cationic counterion are usually small in that the counterions are not complexing and do not force a large change in the coordination sphere. This is the case with the dipicolinates, since most retain a distorted  $D_{3h}$  symmetry with slight shifts of less than 25 wavenumbers.

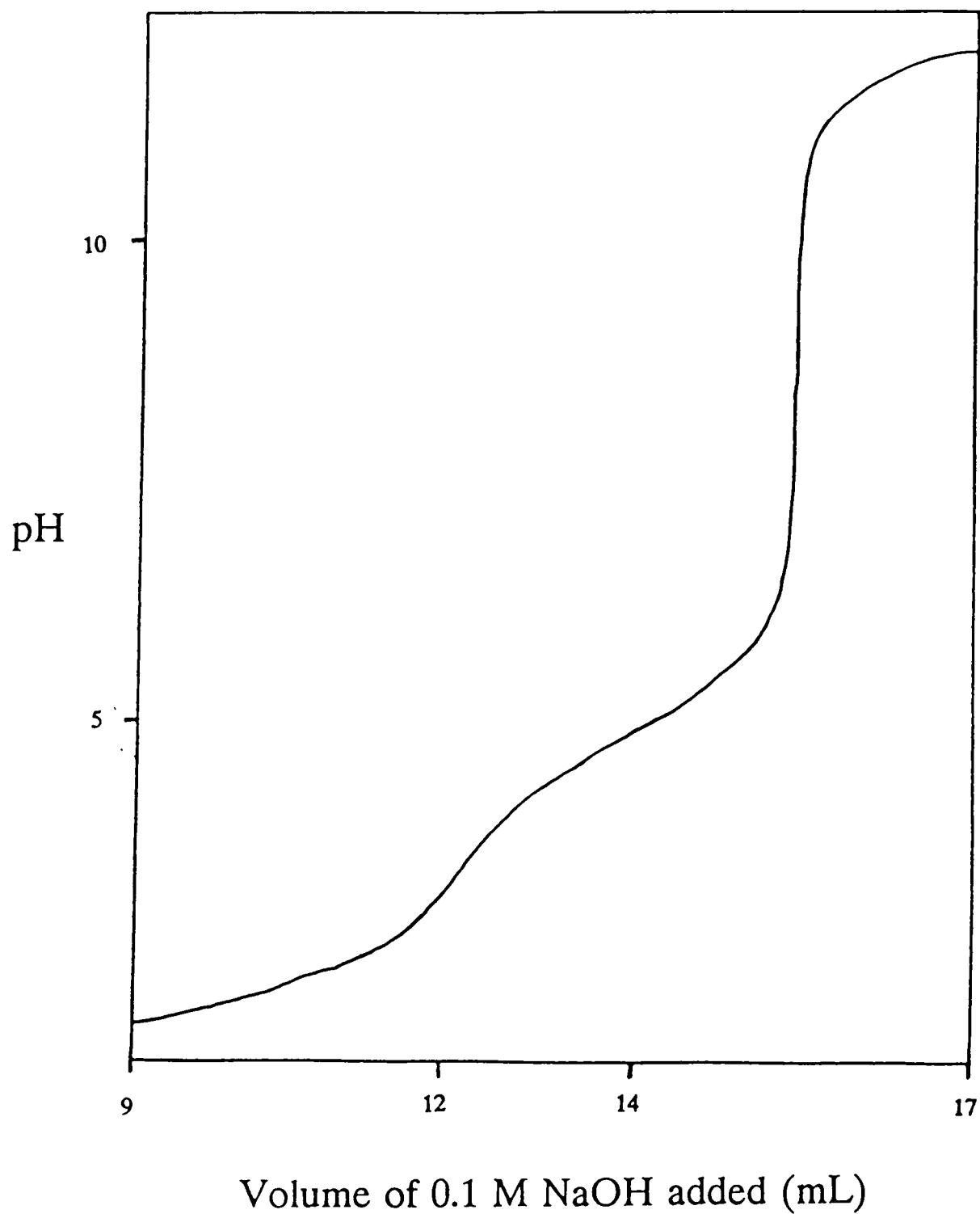


Figure 13. Titration Curve for the Neutralization of  $\text{H}_3\text{Eu}(\text{DPA})_3$

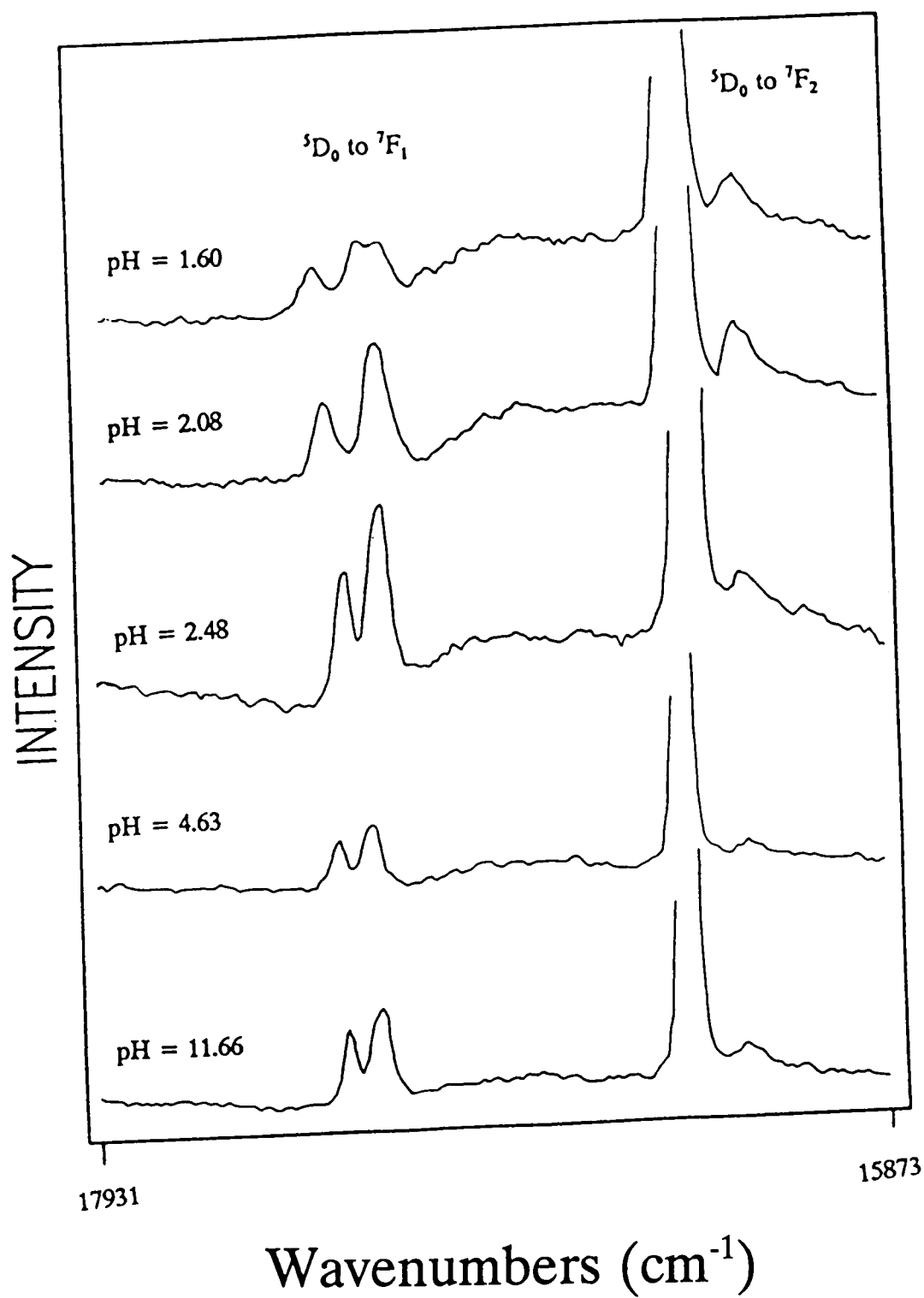


Figure 14. Emission Spectra of the Solutions During the Neutralization of  $\text{H}_3\text{Eu}(\text{DPA})_3$

### 1. Monovalent Counterions, $M_3Eu(DPA)_3$

Approximately 2 mL of the appropriate metal(I) hydroxide or aqueous amine solution was added to 1 mL of the europium stock solution. The precipitated hydroxide was then washed three times with 5 mL aliquots of deionized water. 0.15 g of the solid ligand ( $H_2DPA$ ) was mixed with the europium hydroxide, diluted to about 5 mL, and heated to a gentle boil. The metal(I) hydroxide or aqueous amine was then added dropwise to the boiling solution until a solution pH of about 11 was reached. The materials dissolved to produce a strongly luminescent solution, which upon concentration yielded clear luminescent crystals except in the case of the pyridinium compound in which an air dried sample was used (the sample required concentration almost to the point of dryness before precipitation in the form of a white powder occurred). A small amount of the precipitate along with a small amount of the saturated solution was sealed in a glass capillary.

The lithium compound's spectrum has been described in detail in the previous section (Chapter IV, section A) devoted to the typical characteristics of the dipicolinates' spectra. It should also be noted that the emission spectrum of the lithium compound (Figures 6, 7, 8, and 9) showed a single europium site with most line widths (full width at half maximum) on the order of 1.5 to 4 wavenumbers. The single europium site was tentatively assigned a  $D_{3h}$  symmetry as discussed previously.

The sodium and potassium compounds, when crystallized out of water, give rise to spectra (Figure 15) which show multiple sites. For the sodium compound this is consistent with the results reported by others,<sup>8</sup> who attributed the multiple sites to various forms of hydration. The included spectra show the cleanest (meaning those most nearly single site) compounds which were synthesized. The splitting of the predominant emission lines in both compounds are indicative of the  $D_{3h}$  symmetry assigned previously to the lithium compound.

Two other salts with monovalent cations, ammonium and pyridinium, were included in this work. The spectra are shown in Figure 16. The recognizable  $D_{3h}$

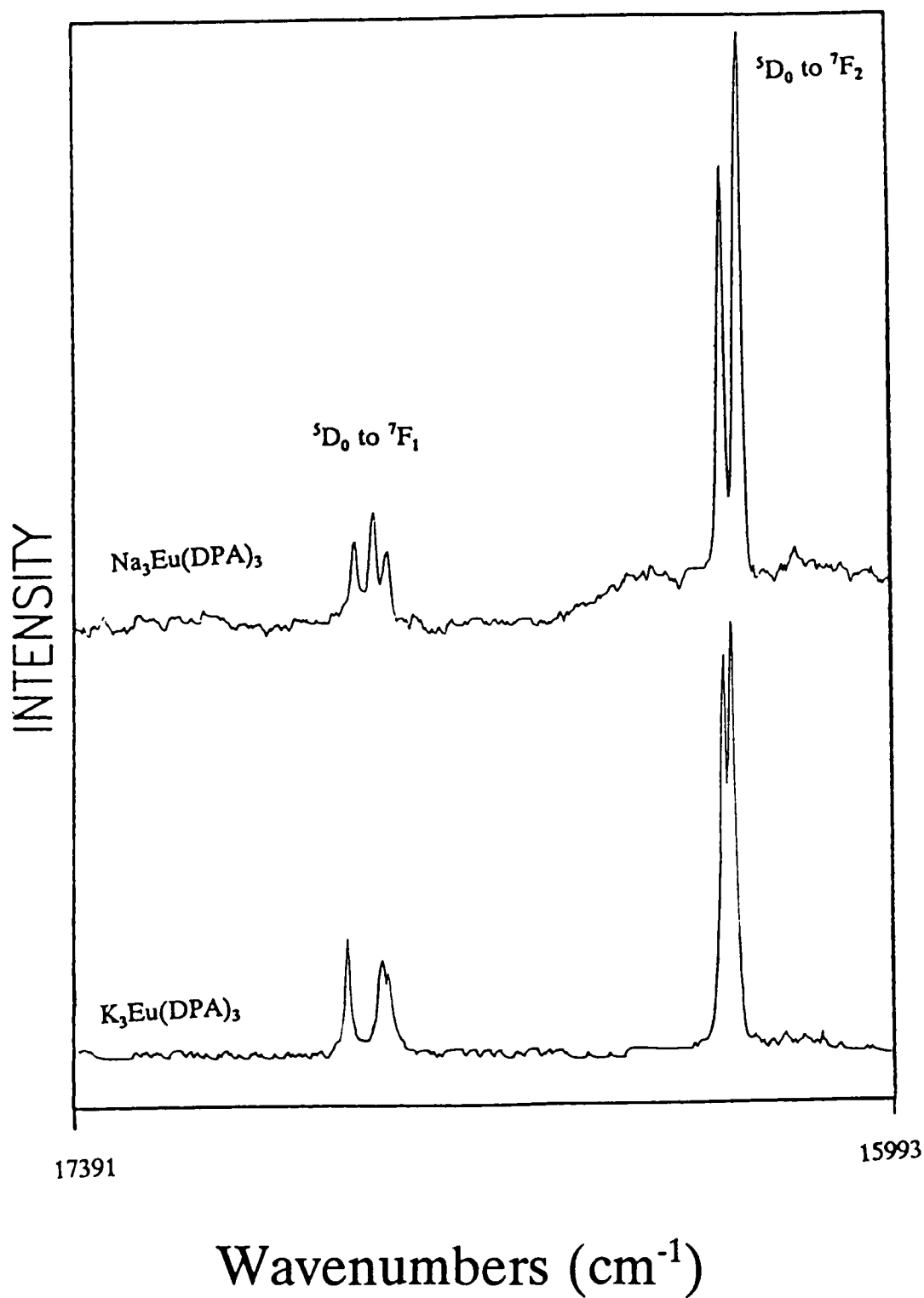


Figure 15. Emission Spectra of Hydrated  $\text{Na}_3\text{Eu}(\text{DPA})_3$  and  $\text{K}_3\text{Eu}(\text{DPA})_3$

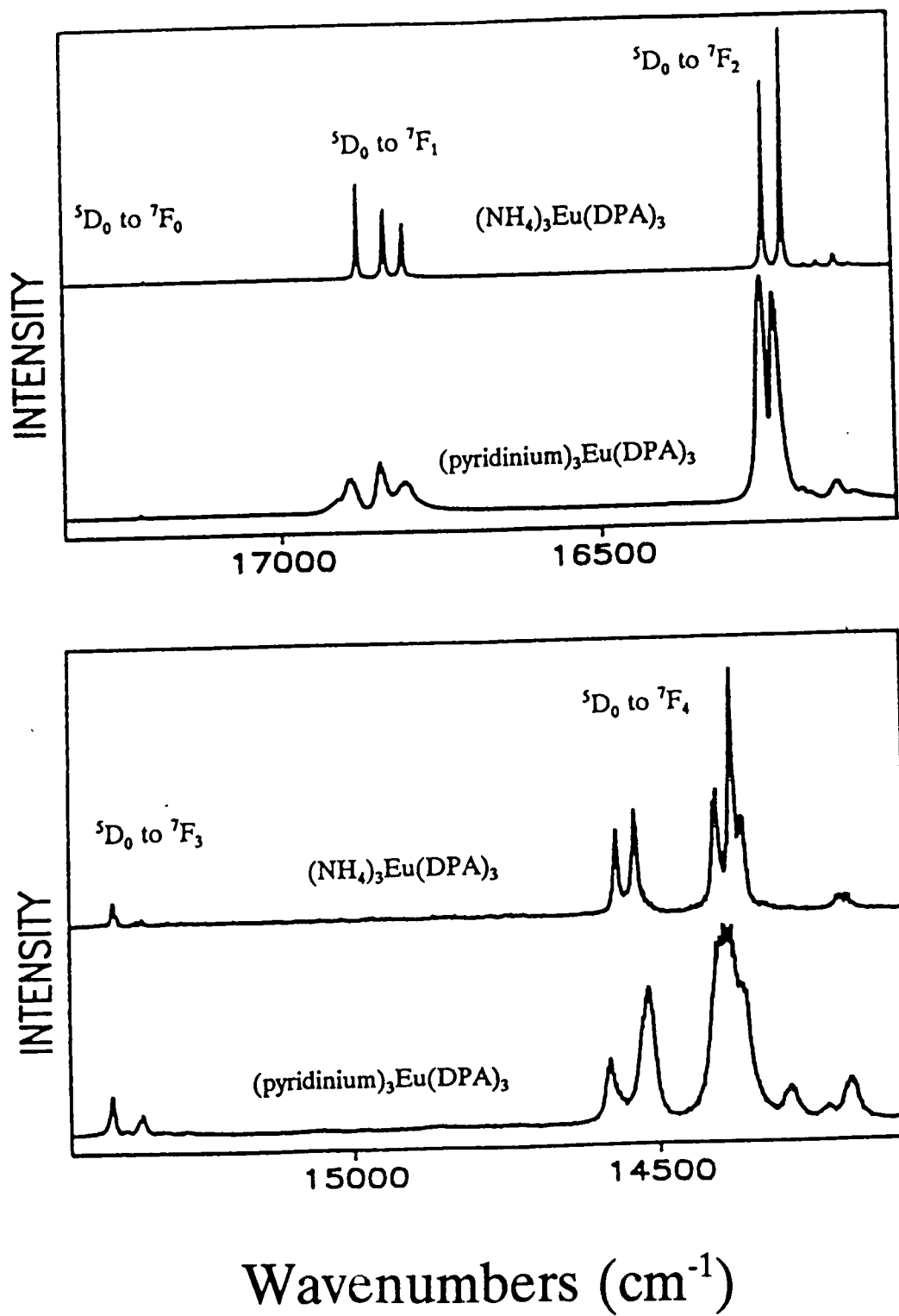


Figure 16. Emission Spectra of Hydrated  $(\text{NH}_4)_3\text{Eu}(\text{DPA})_3$  and  $(\text{pyridinium})_3\text{Eu}(\text{DPA})_3$

splitting pattern is found in both. While the ammonium salt appears to be a single site, the pyridinium salt appears to contain multiple sites, because its spectrum exhibits line widths (FWHM) of around 10 to 15 wavenumbers.

## 2. Divalent Counterions

Salts of the alkaline earth metals were synthesized using the same methods employed previously for the monovalent counterions, using calcium and magnesium hydroxides to raise the pH. Upon concentration of the solvent, these solutions gave fluorescent rectangular crystals about 0.5 mm in length.

The zinc salt was synthesized using methods similar to those used for monovalent counterions. Approximately 2 mL of 1 M sodium hydroxide solution was added to 1 mL of the europium stock solution. The precipitated hydroxide was then washed three times with 5 mL aliquots of deionized water. 0.15 g of the solid acid ( $\text{H}_2\text{DPA}$ ) was mixed with the europium hydroxide, diluted to about 5 mL, and heated to a gentle boil. A suspension of hydrated zinc hydroxide (freshly precipitated with 1 M NaOH and washed three times with deionized water) was added dropwise until a solution pH between 5 and 6 was reached. The solid hydroxide would not completely dissolve, therefore the mixture was centrifuged and the supernatant decanted. The resulting luminescent solution was concentrated until a precipitate formed.

The magnesium salt appeared to be predominantly of a single site nature. A second site can be seen but appears to be present in a smaller concentration than the first. The spectrum exhibited by the magnesium salt is shown in Figure 17. The calcium salt's spectrum indicated two distinct sites were present, with both having about equal intensities (Figure 17). The spectrum of the zinc salt was remarkable in its simplicity (Figure 18). Although the widths of the observed transitions indicate the presence of multiple sites, the

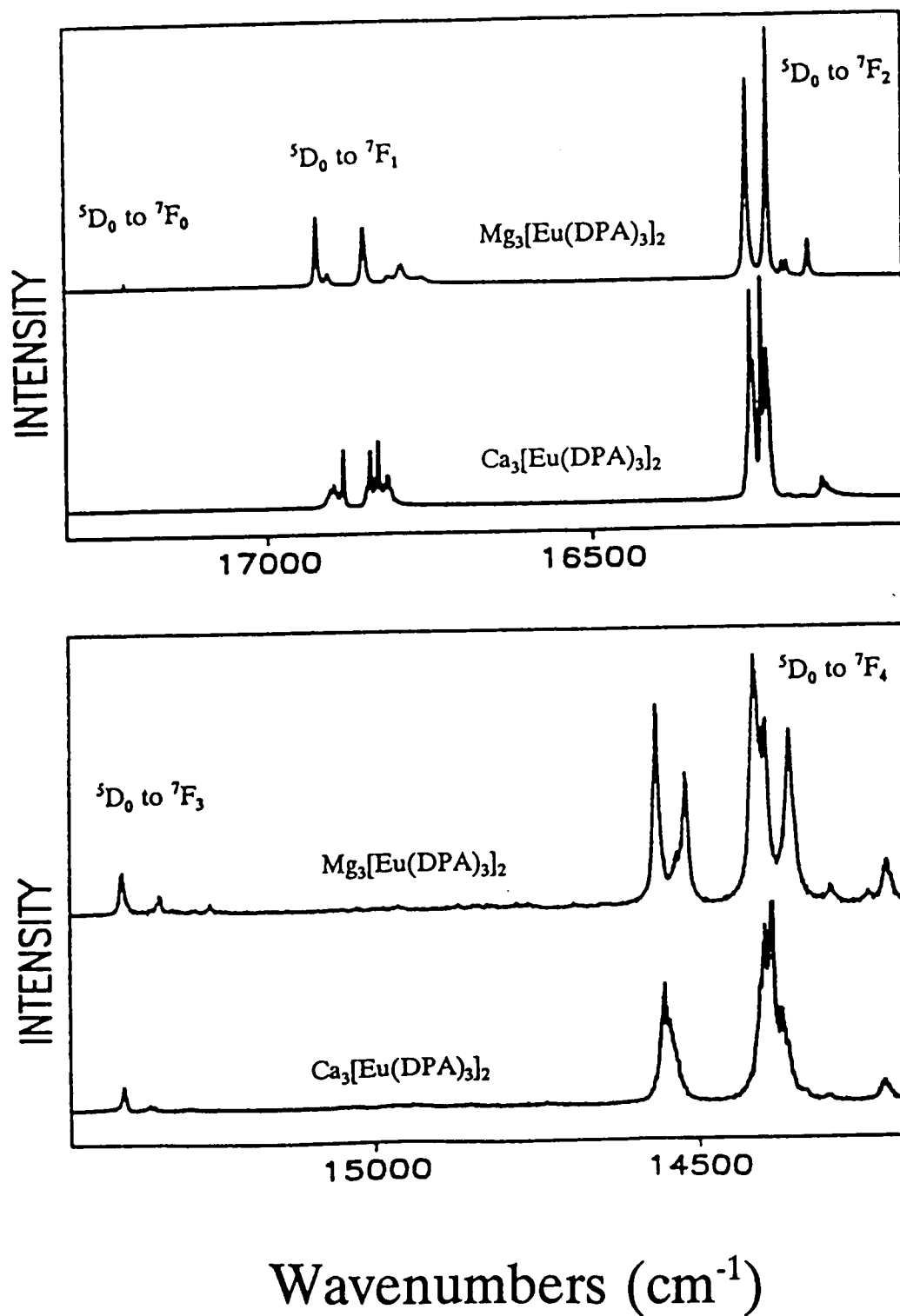


Figure 17. Emission Spectra of Hydrated  $\text{Mg}_3[\text{Eu}(\text{DPA})_3]_2$  and  $\text{Ca}_3[\text{Eu}(\text{DPA})_3]_2$

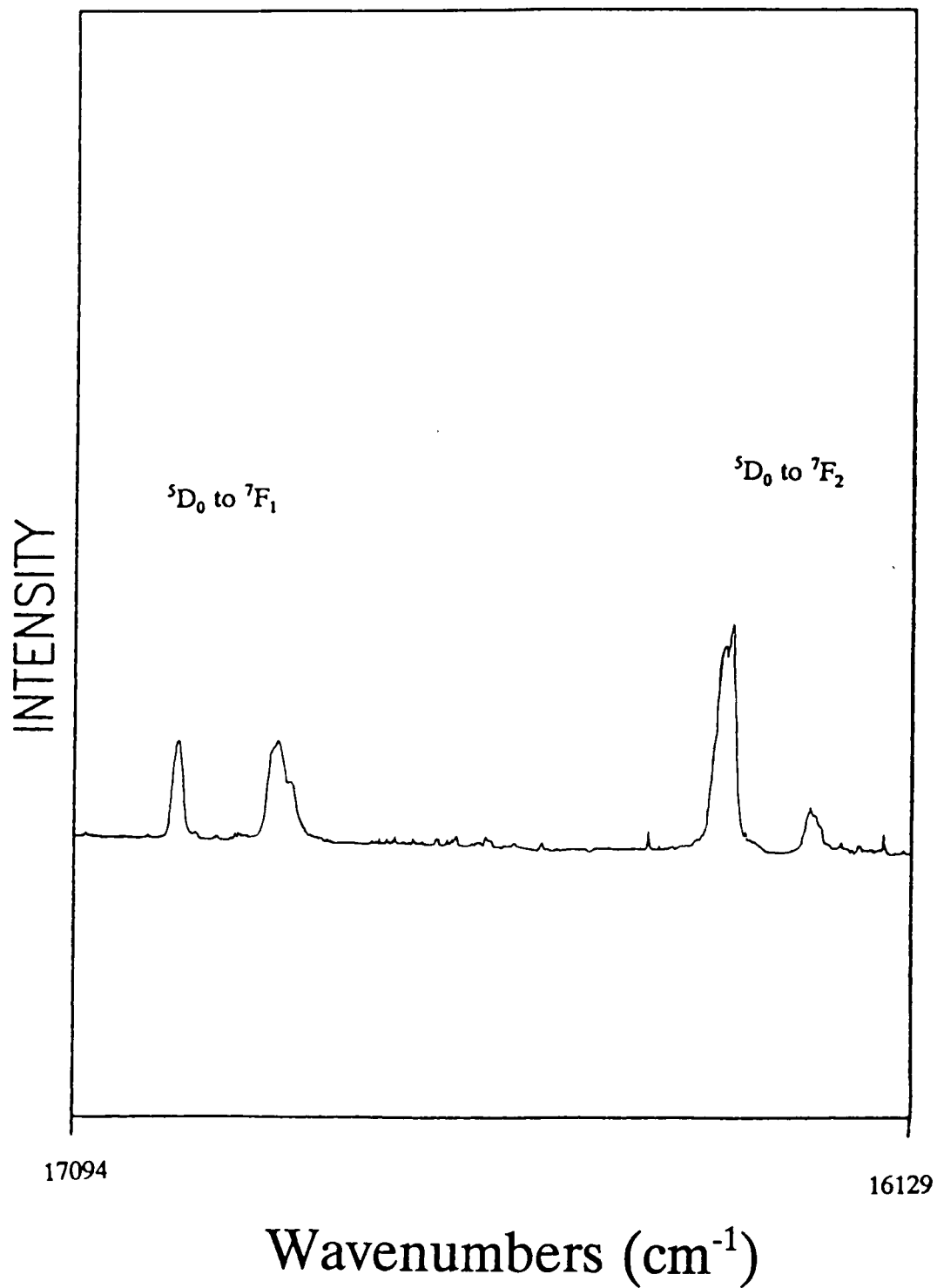


Figure 18. Emission Spectrum of Hydrated  $Zn_3[Eu(DPA)_3]_2$

spectrum still appears simple enough for interpretation. The spectra of all three of the salts appear to follow the now familiar pattern of  $D_{3h}$  symmetry. In the case of calcium both sites appear to be in a distorted  $D_{3h}$  configuration.

### 3. Summation and Discussion

The main conclusion obtainable from this work is that the counterion, while shifting the peak positions slightly, does not distort the crystal structure enough to change the overall symmetry about the Eu(III) ion. This appears to be the case for both monovalent and divalent counterions. The slight shift of the transition energies, which is attributable to the change in counterion, is believed to be due to minor distortions in the placement of the ligands caused by the different sizes and electrical structures of the counterions.

#### D. Exchange of Counterions

The ability to exchange counterions on a chelate salt can allow for the synthesis of compounds which cannot be synthesized through the hydroxide method described previously. There has also been a proposed method of inorganic ion determination through the use of lanthanide chelates<sup>12</sup> which would require the exchange of an analyte ion for a known ion, thus allowing for qualitative and quantitative determination of the ion through fluorescence.

A small piece of filter paper was wet with a solution of the trisodium salt, dried in air, then immersed in a saturated methanolic solution of a nitrate salt of the exchanging ion and allowed to equilibrate several hours. The paper was removed from the solution, dried under a heat lamp for about 20 minutes, and then sealed into a glass capillary. The spectra of the samples were collected at room temperature.

The resulting emission spectra are shown in Figure 19. The transition line widths of 5 to 15 wavenumbers, while indicative of multiple sites, were typical for samples and

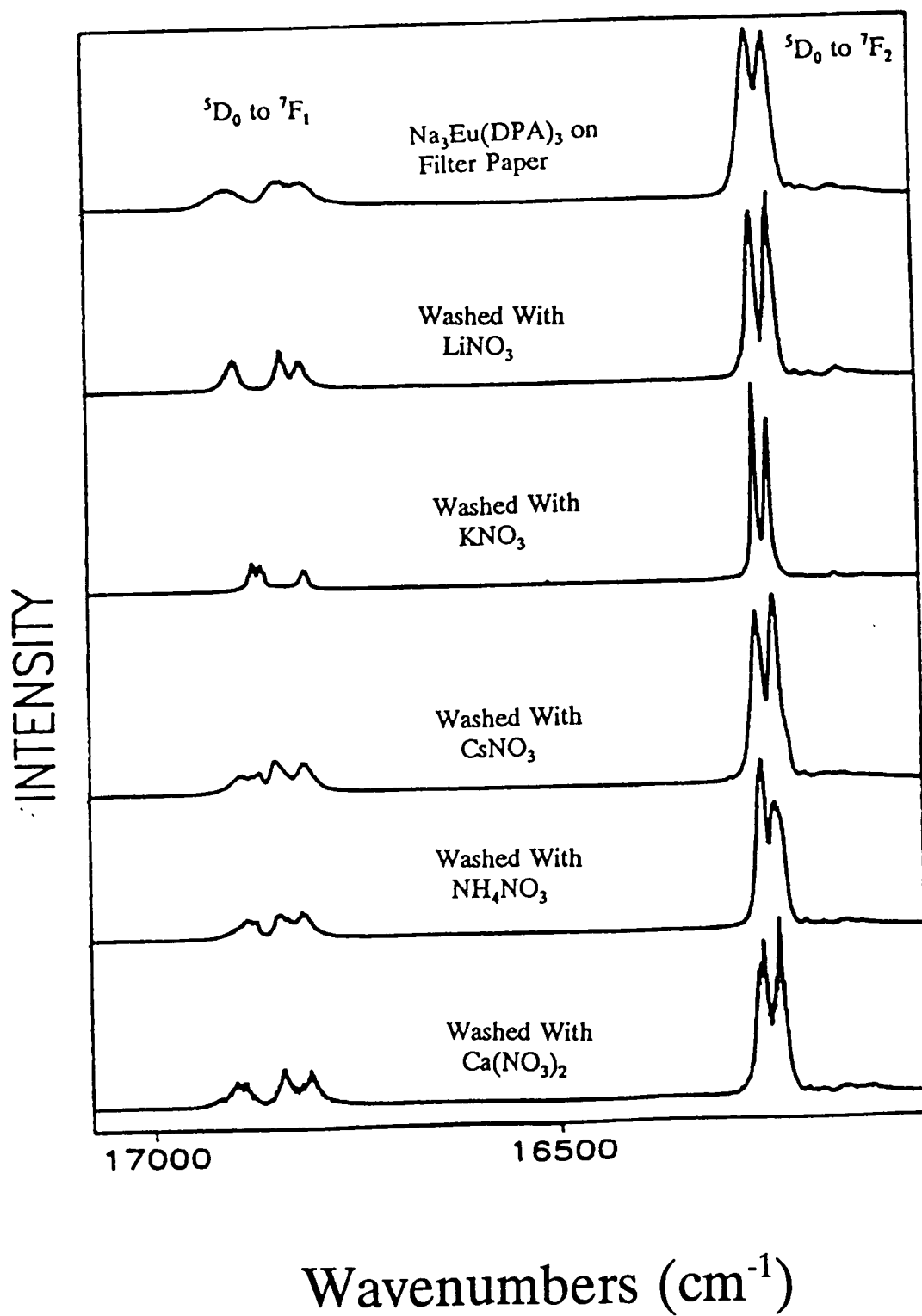


Figure 19. Emission Spectra of  $\text{M}_3[\text{Eu}(\text{DPA})_3]$  Following Ion Exchange

probably arose from the effects of the adsorption of the compound onto the filter paper and its effects upon the molecule's emission spectrum. The spectra showed definite shifts in the position of the emission features, especially those making up the  $^5D_0$  to  $^7F_1$  manifold. Due to the observed shifts, it is believed that ion exchange did occur, but further work is required to enhance the methods employed.

### E. The Effects of Solvent

Solvents can affect the emission spectra in much the same ways that substitution of different counterions shifts the spectra. The crystallization of the solid salt is usually heavily dependent upon the solvent used. If the solvent can be complexed to the metal, then the whole coordination polyhedron, and thus the symmetry, might be shifted. If the solvent does not complex strongly, then it may extract another type of solvent molecule from the complex (i.e., placement of a hydrated sample in anhydrous methanol, which may extract the water molecules from the complex leaving an anhydrous form).

In this experiment hydrated samples were synthesized using the methods discussed previously. A small amount of the compound was then either refluxed with a nonaqueous solvent or sealed in a 1-dram vial with a solvent and heated at 100°C. A small amount of the solid was then sealed in a capillary under some of the solution or dried at ambient temperature and pressure.

#### 1. The Sodium Compound

Previous work on the sodium compound has observed a hydrated and an anhydrous form depending upon the solvent (water or methanol, respectively) used in its

synthesis. Similar results have been seen by the author following the heating of crystals of the hydrated salt in anhydrous methanol which resulted in a fluorescent powder which showed the same emission characteristics as those reported for the anhydrous compound. A third form of the compound was seen to form as large crystals upon the heating of either the anhydrous or hydrated salt in an aliquot of a one-to-one mixture of methanol/water. This salt appears to be an intermediate hydrate form and was very dependent upon the methanol/water ratio for site purity. Other solvents, including acetone and dimethylsulfoxide, were also examined. The emission spectra of the trisodium compound refluxed in the five solvents mentioned above are shown in Figure 20.

## 2. The Potassium Compound

Several solvents including methanol, ethanol, and acetone were employed to study the effects of solvent upon the potassium compound. In the case of methanol and ethanol, a sample of the hydrated salt, crystallized from water, was heated with the second solvent. The experiment with acetone made use of some of the salt which had been refluxed with methanol preceding the addition of acetone. It was attempted to dry the hydrated potassium salt at room temperature and pressure. This yielded several other forms of the compound, but the unpredictable nature of the loss of adsorbed water meant that controlled synthesis of a given compound was not possible. The salt formed from the reflux of the compound in methanol was dried in air at 110°C to yield a different compound, however the same problems listed above, as well as sample decomposition, hampered progress beyond that completed. The spectra resulting from these studies are shown in Figure 21.

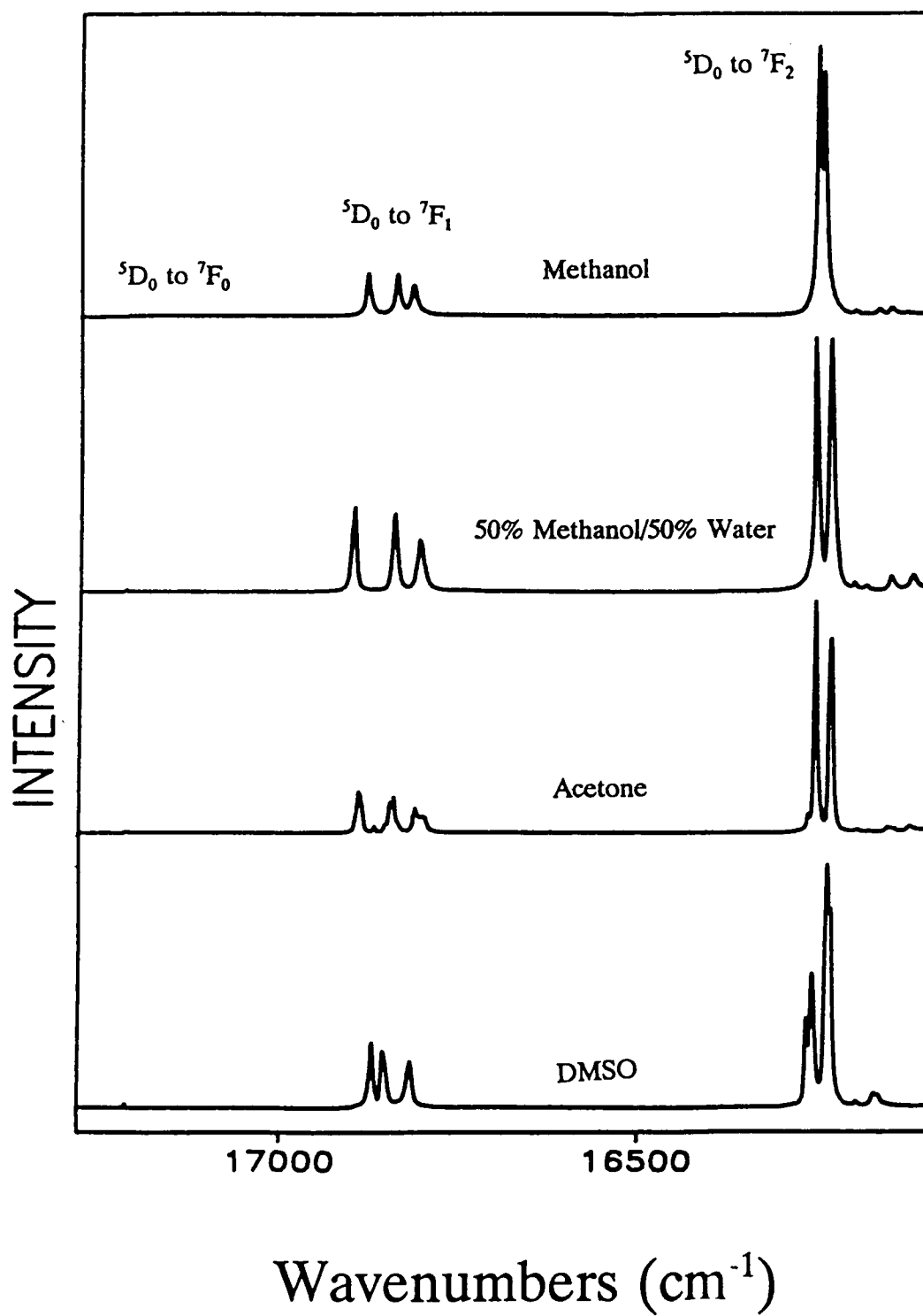


Figure 20. Emission Spectra of  $\text{Na}_3[\text{Eu}(\text{DPA})_3]$  Following Reflux in Various Solvents

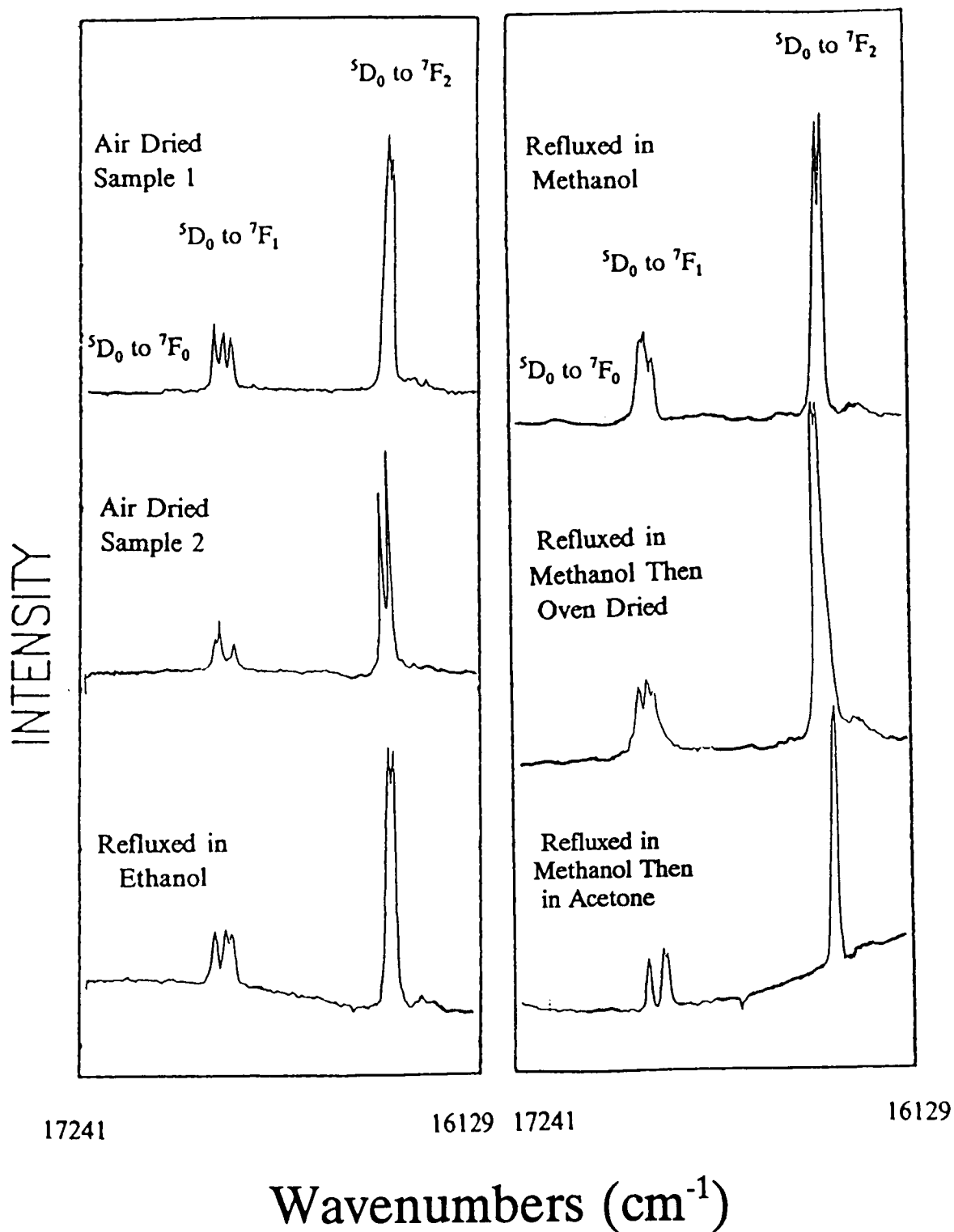


Figure 21. Emission Spectra of  $K_3[Eu(DPA)_3]$  Following Reflux in Various Solvents

### 3. Conclusions

In both cases (the sodium and the potassium), all of the emission spectra still appear to show the pattern of the  $D_{3h}$  site symmetry. This retention of the same symmetry is believed to indicate that the three ligands coordinatively saturate the europium ion such that none of the solvent molecules is within the first coordination sphere of the europium(III) ion. The slight shifts in the spectra that arise with the change of solvent are showing minor distortions of the positioning of the complexing oxygen and nitrogen atoms due to slight changes in the positions of the ligands and counterions.

## CHAPTER V

## VARIOUS COMPLEXES WITH COORDINATED CARBOXYLATE OXYGENS

A. Salts of the Tetrakis  
(2-Pyridinecarboxylate-N-Oxide) Complex

Very little work has been done concerning the synthesis and emission spectroscopy of the tetrakis(2-pyridinecarboxylate-N-oxide) [picolinate n-oxide or PiaNO] complex of europium. A study of the synthesis of the potassium salts of the chelate with several lanthanide ions has been completed and published,<sup>22,23</sup> but no emission work was attempted and europium was not studied. In the following section the author presents the results of a study of the emission spectra from the tetrakis(PiaNO) salts of  $\text{Eu}^{3+}$  with various counterions.

## 1. Synthetic Procedure

In the current study the tetrakis(PiaNO) compounds,  $\text{M}^n+[\text{Eu}(\text{PiaNO})_4]_n$ , were found to have extremely high solubilities in water, which did not facilitate the separation of the compounds from excess reaction materials and other impurities by forcing precipitation through concentration of the aqueous solvent. Because of this, several organic solvents were employed to attempt to force precipitation of the preferred compound. However, great care was required in this method to extract the compound preferentially over other impurities which might also be insoluble in the organic solvent. Such impurities (noncomplexed PiaNO salts and other excess reaction material) should have no effect on the emission spectrum of the europium ion but may be observable in methods for the determination of purity such as IR spectroscopy or elemental analysis.

The synthesis of the various compounds involved the addition of 0.20 g picolinic

acid N-oxide to  $2.8 \times 10^{-4}$  mole of freshly precipitated  $\text{Eu}(\text{OH})_3$  suspended in about 25 mL of deionized water. This mixture was heated to  $100^\circ\text{C}$  and the counterion's hydroxide or oxide was added slowly until a solution pH of 5 to 7 was obtained. In the case of the  $\text{Ba}^{2+}$  and  $\text{Al}^{3+}$  counterions, the hydroxide was freshly precipitated with dilute sodium hydroxide followed by several washings with deionized water. As was the case seen previously in the synthesis of the zinc salt of the tris(dipicolinate) salt, often the solid hydroxide did not completely dissolve upon mixing with the acidic ligand. In such cases the solution was centrifuged and only the supernatant was employed. The resulting fluorescent solution was concentrated by evaporation as far as possible, then added to a larger quantity of the organic solvent being used to attempt to force the precipitation. The solids formed were usually collected as white, feathery powders.

## 2. The Typically Observed Spectra

Two obviously different groups of spectra were obtained from the tetrakis(PiaNO) compounds. The deciding factor appears to be related to the size of the counterion. The smaller counterions exhibited spectra similar to the sodium salt's spectrum shown in Figure 22. The larger counterions exhibited spectrum similar to the potassium salt's spectrum shown in Figure 23.

In the first group the  $^5\text{D}_0$  to  $^7\text{F}_0$  transition is of such low intensity that it shall be deemed disallowed. Three transitions are observed in the  $^5\text{D}_0$  to  $^7\text{F}_1$  transition region (as stated in the chapter about the dipicolinate chelate salts, all eight, nine, or ten coordinate  $\text{Eu}^{3+}$  symmetries can allow three peaks in this manifold). The  $^5\text{D}_0$  to  $^7\text{F}_2$  manifold is interpreted to contain two strongly allowed transitions, one moderately allowed transition, and two vibronically allowed transitions (the relative energies of all five  $^7\text{F}_2$  levels being determined from transitions arising from both the  $^5\text{D}_0$  and  $^5\text{D}_1$  levels). Six peaks are

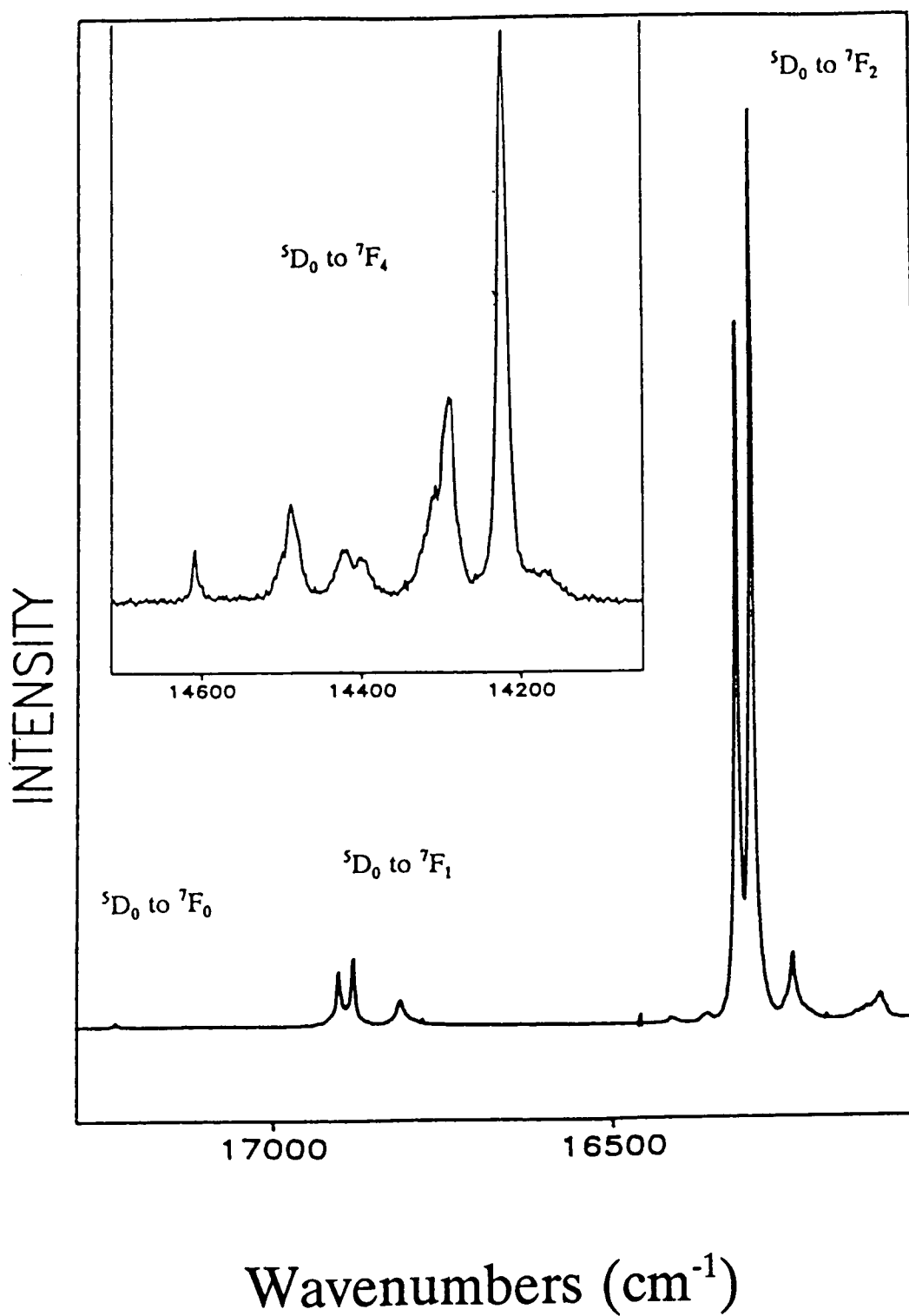


Figure 22. Emission Spectrum of  $\text{NaEu(PiaNO)}_4$

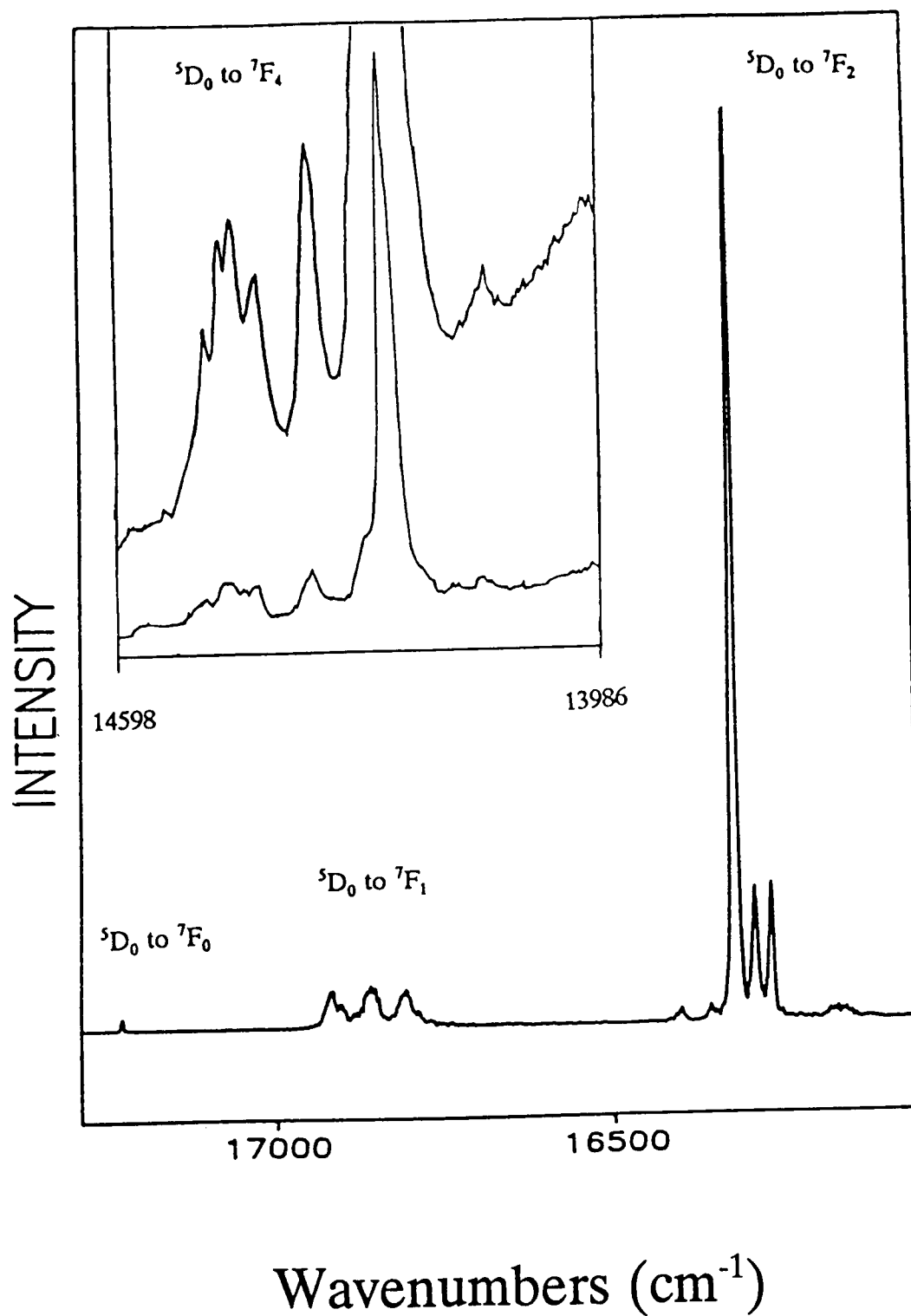
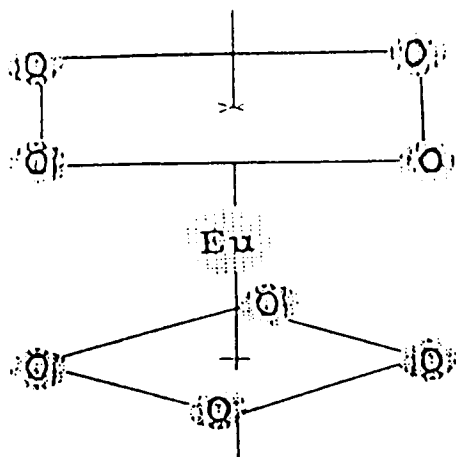


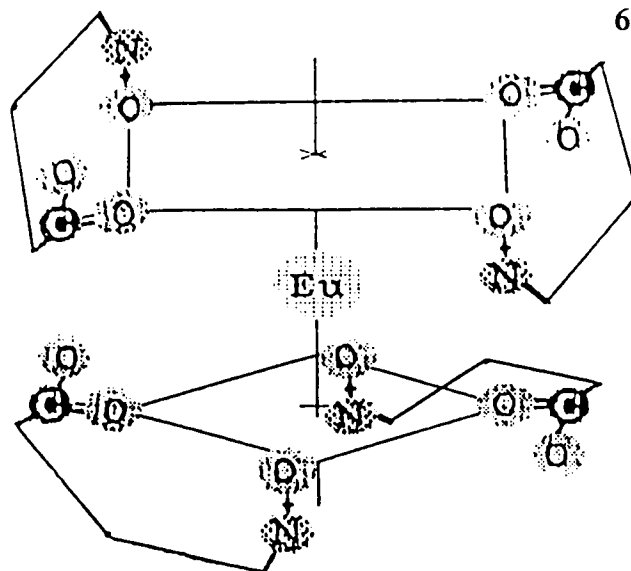
Figure 23. Emission Spectrum of  $\text{KEu(PiaNO)}_4$

judged to be allowed in both the  $^5D_0$  to  $^7F_3$  and the  $^5D_0$  to  $^7F_4$  manifolds. This splitting pattern is indicative of a  $D_2$  site symmetry as seen in Table VIII. The symmetry appears to be nearing  $D_4$ , as seen in the moderately forbidden nature of the third  $^5D_0$  to  $^7F_2$  transition, and by inspection of the relative intensities of the six peaks observed in the  $^5D_0$  to  $^7F_4$  manifold. This site symmetry assignment is consistent with a square antiprismatic geometry with the four bidentate ligands attached to the eight corners. The drop from  $D_4$  to  $D_2$  symmetry might be assigned to a difference between the coordination of a carboxylate oxygen and an N-oxide oxygen (as depicted in Figure 24).

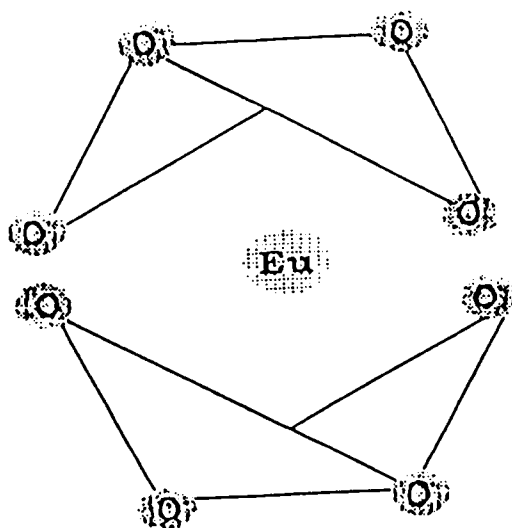
The second group of spectra appeared to exhibit a disallowed  $^5D_0$  to  $^7F_0$  transition which seemed to have a slightly greater allowed nature than that seen in the first group. The  $^5D_0$  to  $^7F_1$  manifold was judged to contain three observably allowed transitions. The  $^5D_0$  to  $^7F_2$  manifold was interpreted to show one strongly allowed transition, two moderately allowed transitions, and probably two disallowed transitions. The  $^5D_0$  to  $^7F_3$  and  $^7F_4$  manifolds both appeared to show six allowed transitions. This is again indicative of a  $D_2$  site symmetry. However, the line intensities and splittings appear to show the compound nearing  $D_{2d}$  symmetry. The  $D_{2d}$  symmetry would include one singly and one doubly-degenerate transition in the  $^5D_0$  to  $^7F_2$  manifold and one singly and two doubly-degenerate transitions in the  $^5D_0$  to  $^7F_4$  manifold. This  $D_{2d}$  site symmetry would indicate a triangulated dodecahedral geometry, with the drop in symmetry possibly being an effect of the difference in the coordination of the two types of oxygens (as depicted in Figure 24).



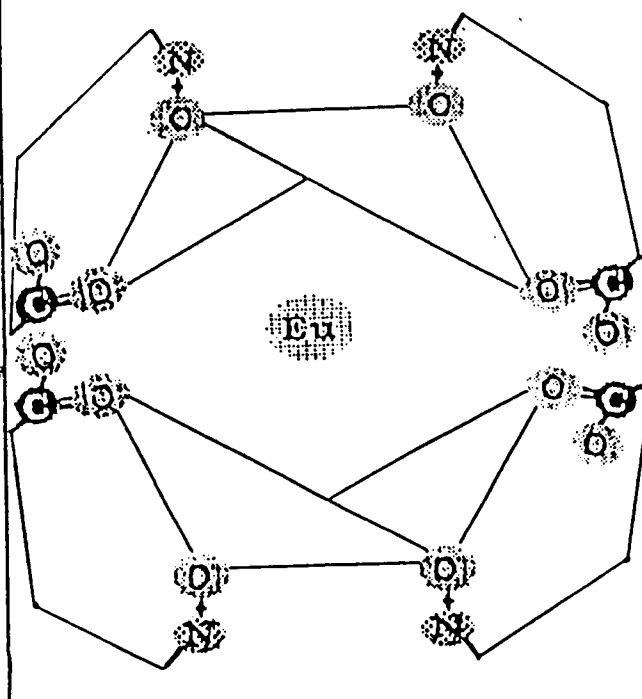
$D_{4d}$   $\text{Eu}^{3+}$  site symmetry  
in a square antiprism  
geometry



$D_2$   $\text{Eu}^{3+}$  site symmetry  
in a square antiprism  
geometry



$D_{2d}$   $\text{Eu}^{3+}$  site symmetry  
in a tricapped trigonal  
prism geometry



$D_2$   $\text{Eu}^{3+}$  site symmetry  
in a tricapped trigonal  
prism geometry

Figure 24. Suspected First Coordination Spheres of Europium  
in the Tetrakis(PiaNO) Complex

### 3. Precipitation From Water

Two of the compounds which were studied, the sodium and ammonium salts, were collected following the concentration of their aqueous solvents. The emission spectra which were obtained from these compounds are shown in Figure 25. As can be seen in Figure 25, the sodium compound's emission is representative of the first group of spectra mentioned earlier. In contrast the ammonium compound exhibits a spectrum typical of the second group of spectra.

### 4. Precipitation Forced by Acetone

Six compounds were synthesized through a procedure using acetone as the solvent which forced precipitation. These included the lithium, sodium, potassium, rubidium, cesium, and ammonium salts. The spectra exhibited by these compounds are shown in Figure 26. The lithium and sodium salts both show patterns indicative of the first group of spectra, while the remaining salts exhibit spectra of the second group.

### 5. Salts of the Alkaline Earth Cations and Aluminum

Salts of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ , and  $Al^{3+}$  were synthesized by the same method using a 10:1 butanol/methanol solution to force precipitation of the compound. The collected compounds were then washed with an aliquot of acetone. The resulting spectra are presented in Figure 27. The spectra appear to follow the relationship seen before in that the smaller counterion, magnesium, exhibits a spectrum representative of the first group of spectra. The larger divalent counterions, calcium and barium, and aluminum show spectra typical for the second group of spectra.

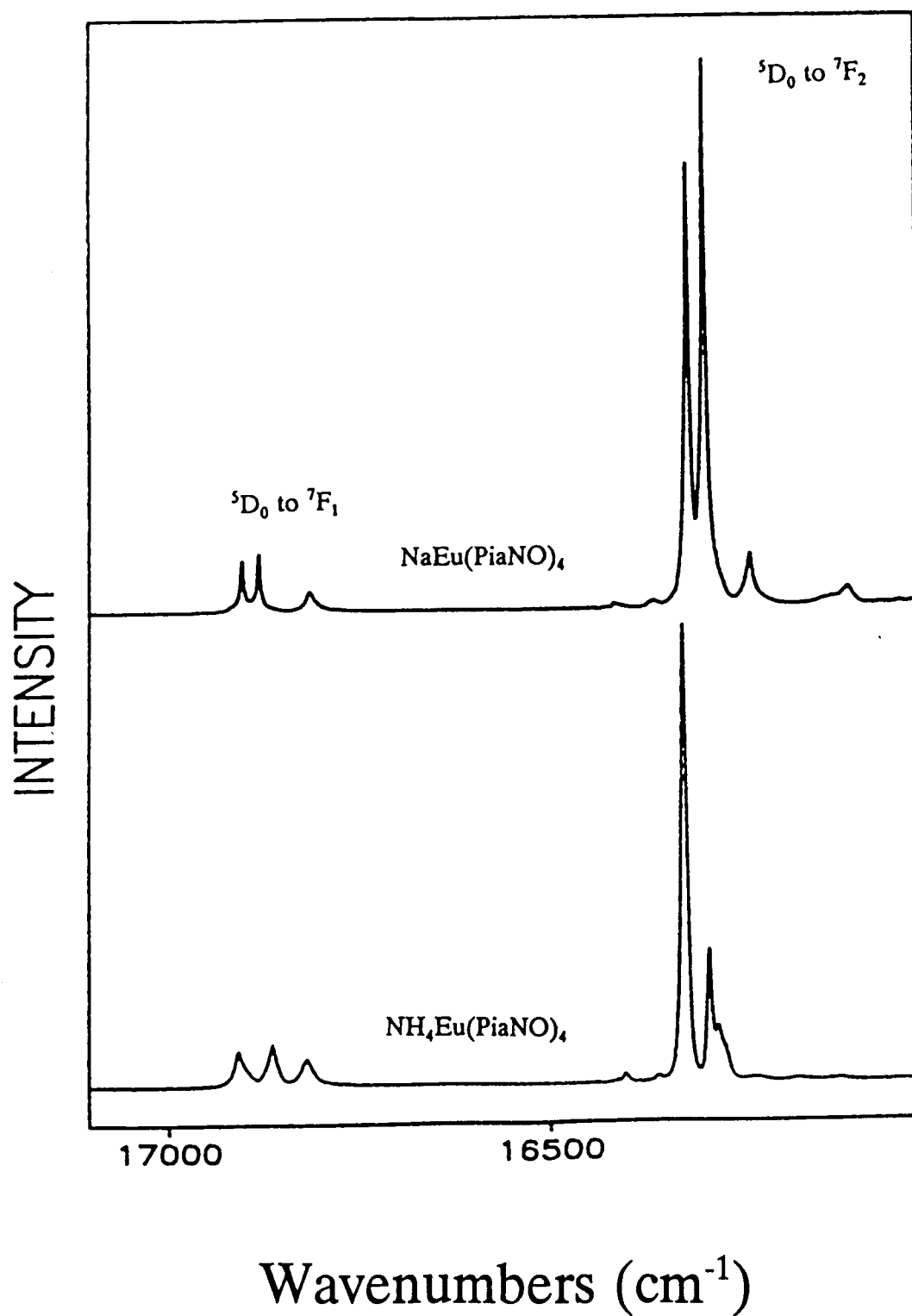


Figure 25. Emission Spectra of NaEu(PiaNO)<sub>4</sub> and NH<sub>4</sub>Eu(PiaNO)<sub>4</sub>

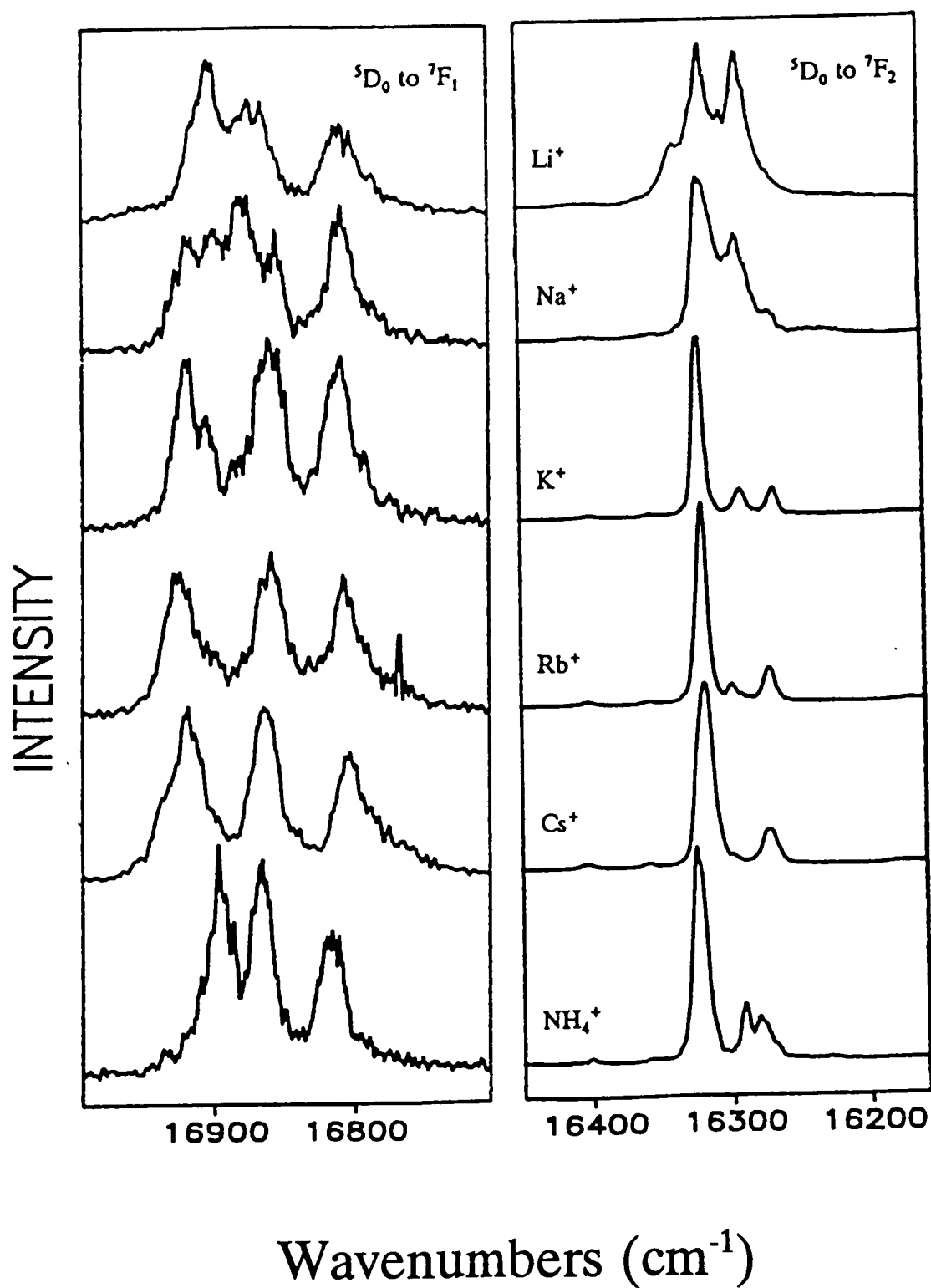


Figure 26. Emission Spectra of Several Acetone Refluxed  $\text{MEu(PiaNO)}_4$  Salts ( $\text{M} = \text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ , and  $\text{NH}_4^+$ )

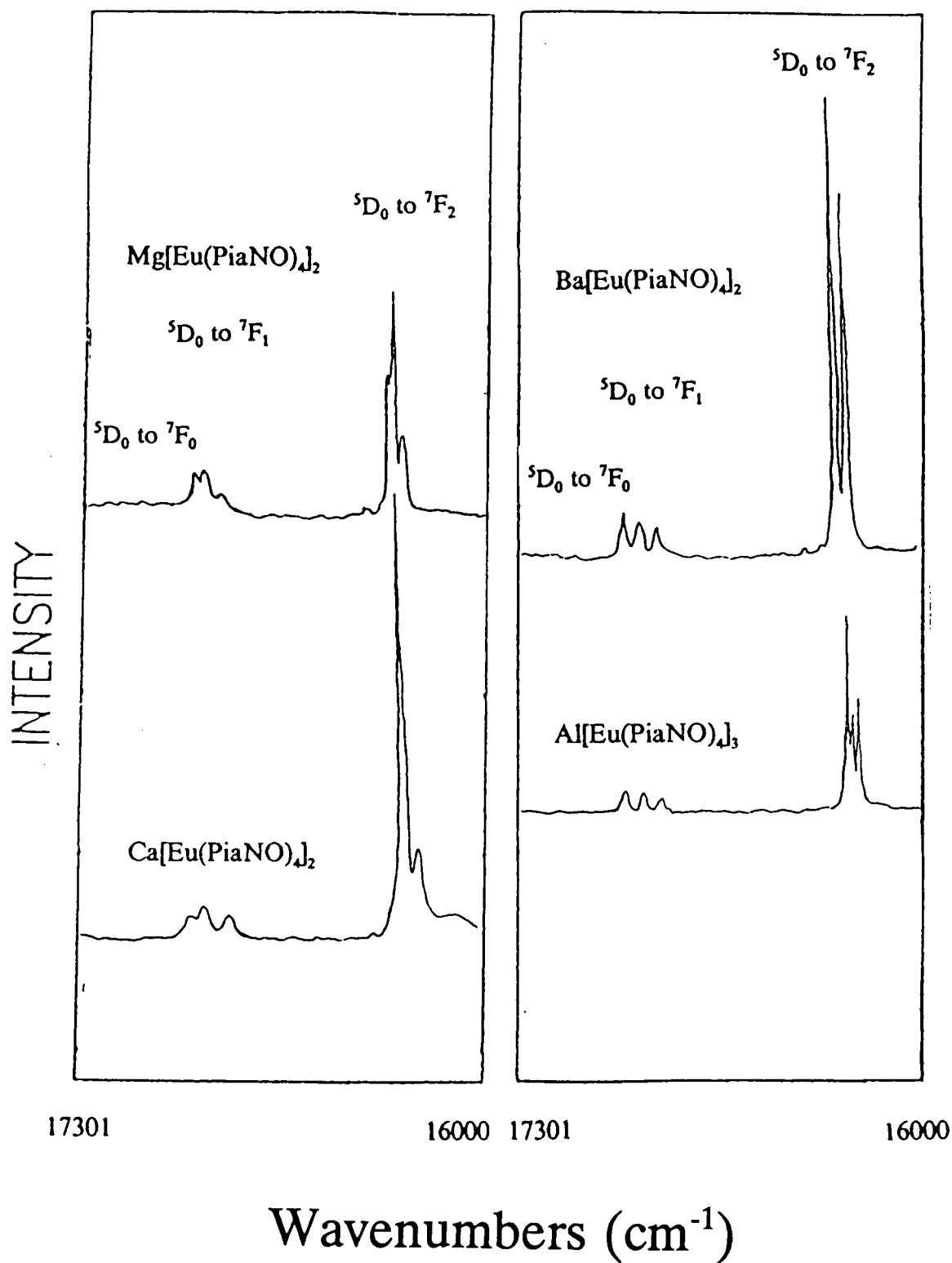


Figure 27. Emission Spectra of Several Acetone Refluxed  $M[\text{Eu}(\text{PiaNO})_4]_{2,3}$  Salts ( $M = \text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Al}^{3+}$ )

## 6. Conclusions

The symmetries of the tetrakis(PiaNO) compounds appear to be fairly sensitive to the size and charge of the counterion. The ionic size at which the change occurs falls between the sodium [ionic radius(102 pm) x charge(1) = 102] and potassium [138 pm x 1 = 138] ions, between the magnesium [72 pm x 2 = 144] and calcium [100 pm x 2 = 200] ions, and is smaller than the aluminum [53 pm x 3 = 159] ion. Thus, the critical ionic size x charge of the counterion falls in the range 130 to 150.

### B. The Tris(2-Pyridinecarboxylate) Compound

The ionic tetrakis(2-pyridinecarboxylate or picolinate) compounds,  $M^{n+}[\text{Eu}(\text{picolinate})_4]_n$ , proved extremely difficult to synthesize due to the weakness of lanthanide coordination by a fourth molecule of this chelate. However, the nonionic tris form,  $\text{Eu}(\text{picolinate})_3$  was easily synthesized. This was done by the addition of five mole equivalents of 2-pyridinecarboxylic acid to one mole equivalent of freshly precipitated europium hydroxide. The pH of the solution was then raised to about 6 with 1 M sodium hydroxide.

The spectra obtained from the nonionic tris compound upon precipitation from water and upon annealing of the solid compound at 100°C are shown in Figure 28. Although not enough of either of the spectra was collected for the assignment of specific site symmetries, some generalizations and observations can be made. The first is that the compound upon crystallization from water contains more than a single europium site. This can be seen from the observation of seven strong transitions in the  $^5D_0$  to  $^7F_2$  manifold in which a maximum of five transitions is permitted for a single  $\text{Eu}^{3+}$  site. Upon annealing of the compound, these seven transitions are replaced by three strong transitions and two, moderately strong transitions.

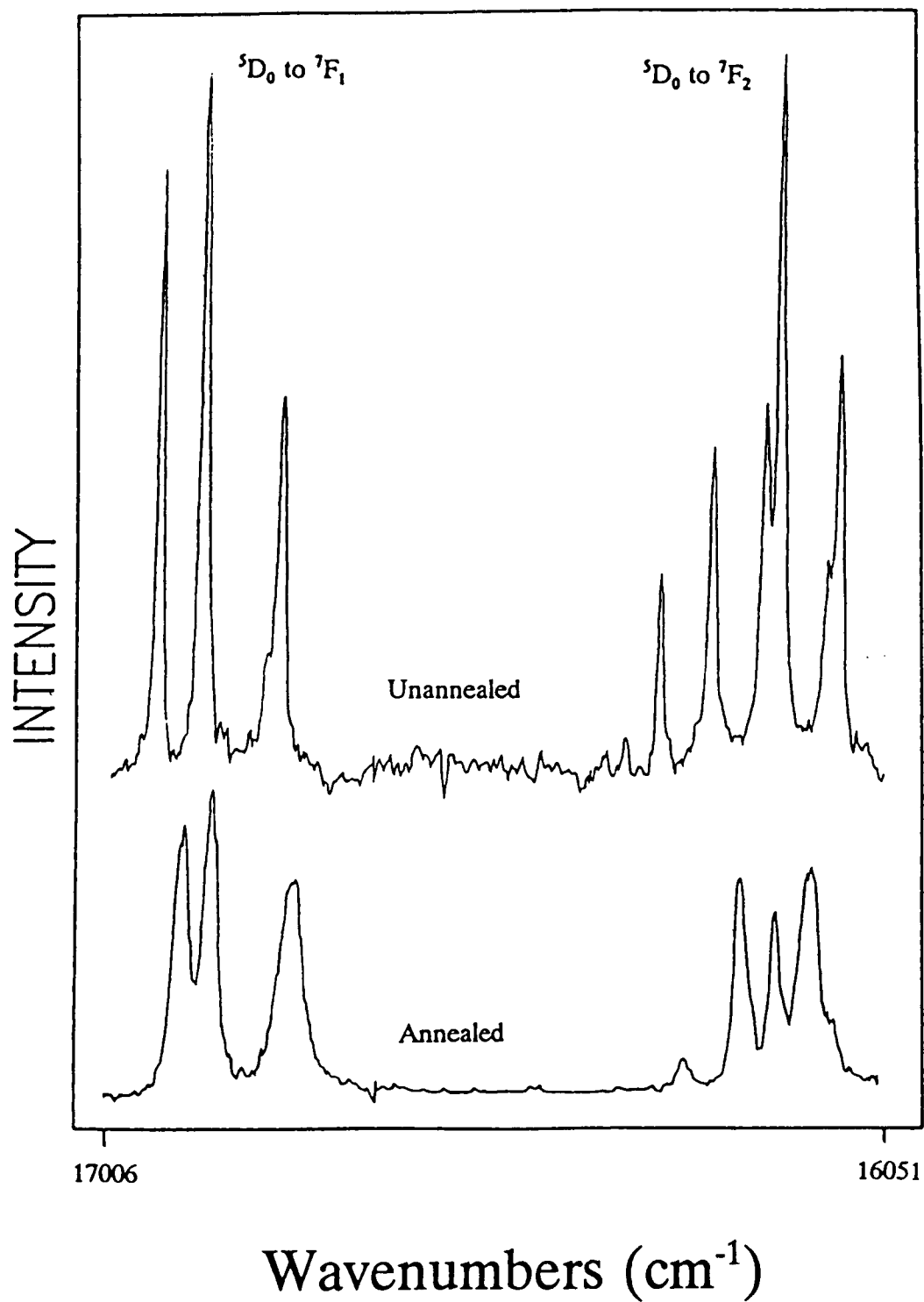


Figure 28. Emission Spectra of Annealed and Unannealed  $\text{Eu}(\text{picolate})_3$

### C. The Tris(Formate) Compound

The tris(formate) compound,  $\text{Eu}(\text{formate})_3$ , was synthesized by the addition of  $2.8 \times 10^{-4}$  mole of freshly precipitated europium hydroxide to 2 mL of 85% formic acid. The solution was then added to about 50 mL of acetone which forced the precipitation of the tris compound. The spectrum which was exhibited by this compound is shown in Figure 29. The studies performed on this nonionic tris(formate) compound have shown that it may be an exceptionally good candidate for a probe study of the structural characteristics of the other lanthanide formates. This conclusion is based upon the narrowness and simplicity of the emission spectrum.

### D. Compounds of Europium Acetate

A preliminary investigation of the acetate salts was also initiated. It was found that two tetrakis salts,  $\text{M}^+\text{Eu}(\text{acetate})_4$ , could be synthesized, one with potassium and the other with cesium as the counterion, as well as the nonionic tris form,  $\text{Eu}(\text{acetate})_3$ . The nonionic tris form was synthesized by dissolving one mole equivalent of europium oxide with four mole equivalents of glacial acetic acid yielding a clear solution. The solution was then mixed with 95% ethanol (1 mL clear solution:10 mL ethanol) which forced precipitation of the tris compound. The tetrakis forms were synthesized by the addition of ten mole equivalents of the acetate salt of the counterion to 1 mole equivalent of the tris compound in aqueous solution. The solution was then concentrated by evaporation at room temperature to yield the tetrakis form.

The emission spectra of the tris and the two tetrakis compounds were collected in the  ${}^5\text{D}_0$  to  ${}^7\text{F}_2$  region and are shown in Figure 30. In that only a small portion of the electronic spectrum of each compound was recorded, nothing can be said about the symmetry of the compound except that all three have  $\text{Eu}^{3+}$  ion site symmetries greater than  $\text{C}_2$  and that the symmetry of the tris compound differs from that of the tetrakis compounds.

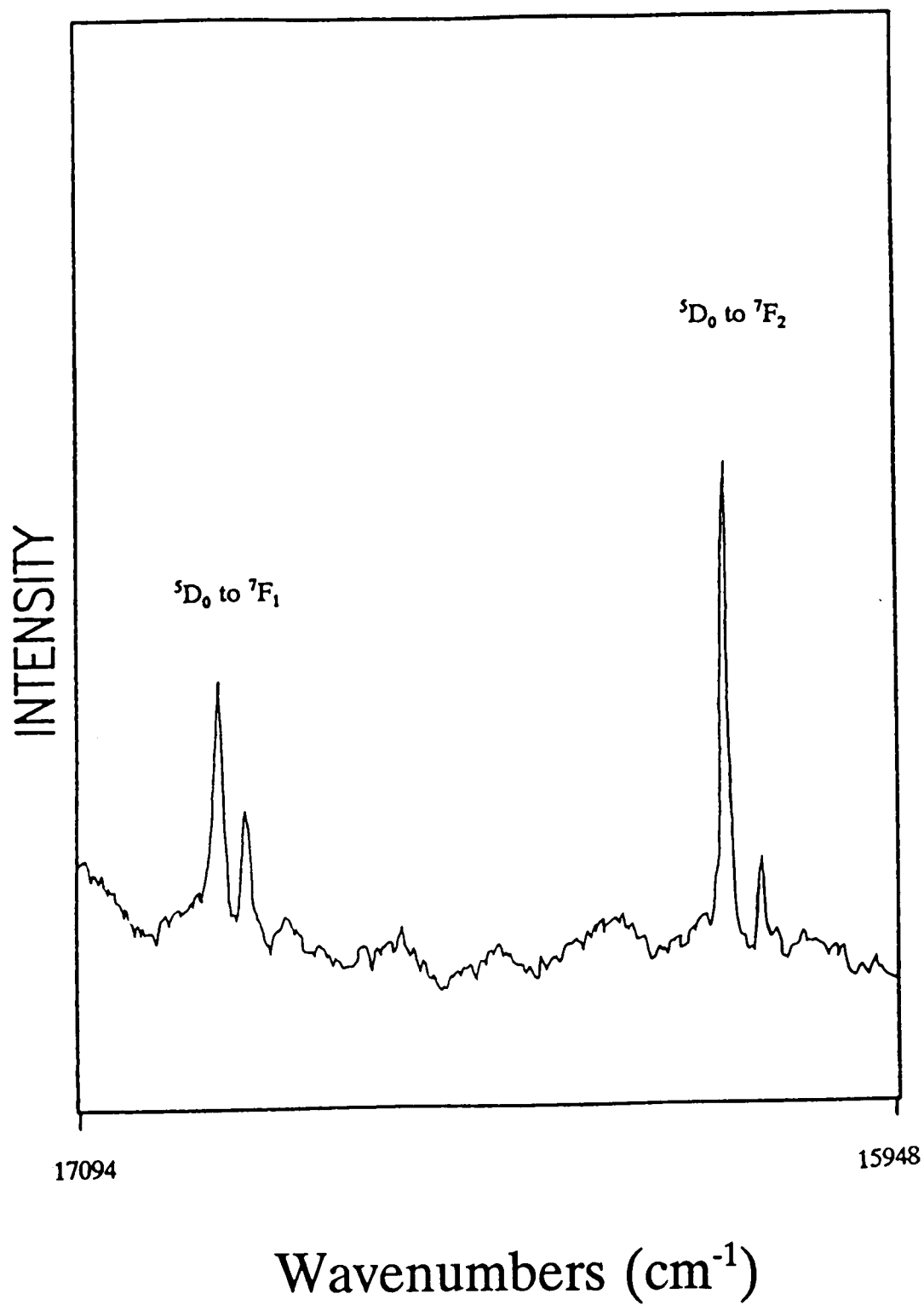


Figure 29. Emission Spectrum of  $\text{Eu}(\text{formate})_3$

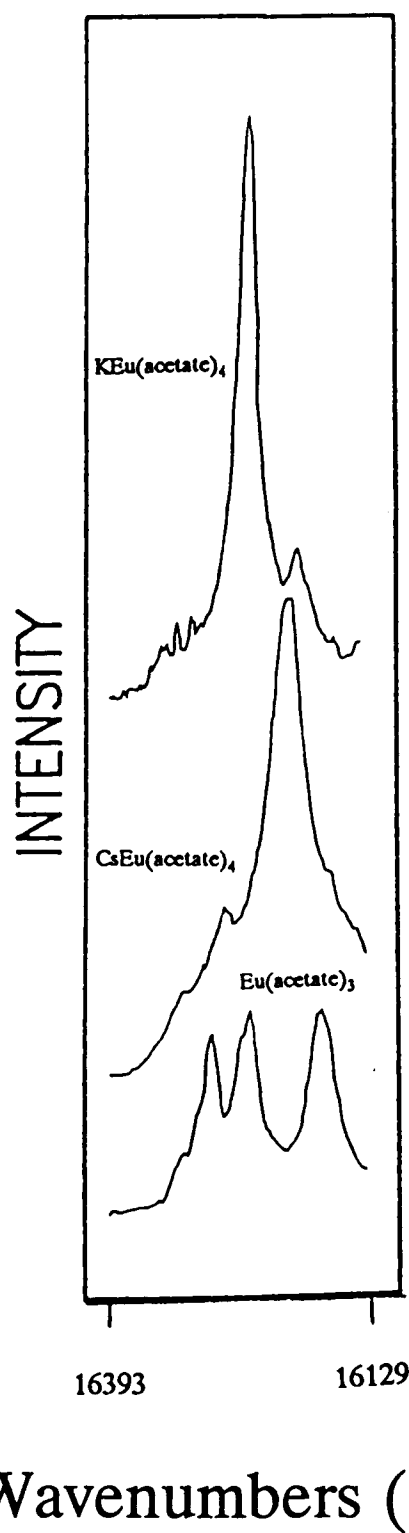


Figure 30. Emission Spectra of  $\text{Eu}(\text{acetate})_3$ ,  $\text{KEu}(\text{acetate})_4$ , and  $\text{CsEu}(\text{acetate})_4$

### E. Compounds of Europium Malonate

Sodium and hydrogen europium bis(malonate) salts,  $\text{NaEu}(\text{malonate})_2$  and  $\text{HEu}(\text{malonate})_2$ , were also synthesized. The syntheses involved the neutralization of freshly precipitated  $2.8 \times 10^{-4}$  mole europium hydroxide with 0.1 g of malonic acid in 25 mL deionized water. The solution pH was raised with 1 M sodium hydroxide. At a low pH the acid form precipitated, and a sample was collected. The acid form redissolved upon further addition of the sodium hydroxide. The resulting solution was concentrated by evaporation at room temperature until clear rectangular crystals of the sodium compound formed and were collected.

The spectra exhibited by the two malonate compounds are shown in Figure 31. That of the nonionic form is deemed to contain an allowed  $^5D_0$  to  $^7F_0$  transition, three allowed  $^5D_0$  to  $^7F_1$  transitions, and one singlet and one doublet  $^5D_0$  to  $^7F_2$  transition. This pattern is indicative of  $C_4$  or  $C_{4v}$  site symmetry. The sodium salt's spectrum is interpreted as containing a disallowed  $^5D_0$  to  $^7F_0$  transition, one singlet and one doublet  $^5D_0$  to  $^7F_1$  transition, and one singlet and one doublet  $^5D_0$  to  $^7F_2$  transition. This pattern suggests a  $D_{2d}$  symmetry about the  $\text{Eu}^{3+}$  ion. The possible symmetries assigned to the hydrogen compound are both indicative of a square antiprismatic geometry while that suggested for the sodium compound implies a triangulated dodecahedral geometry.

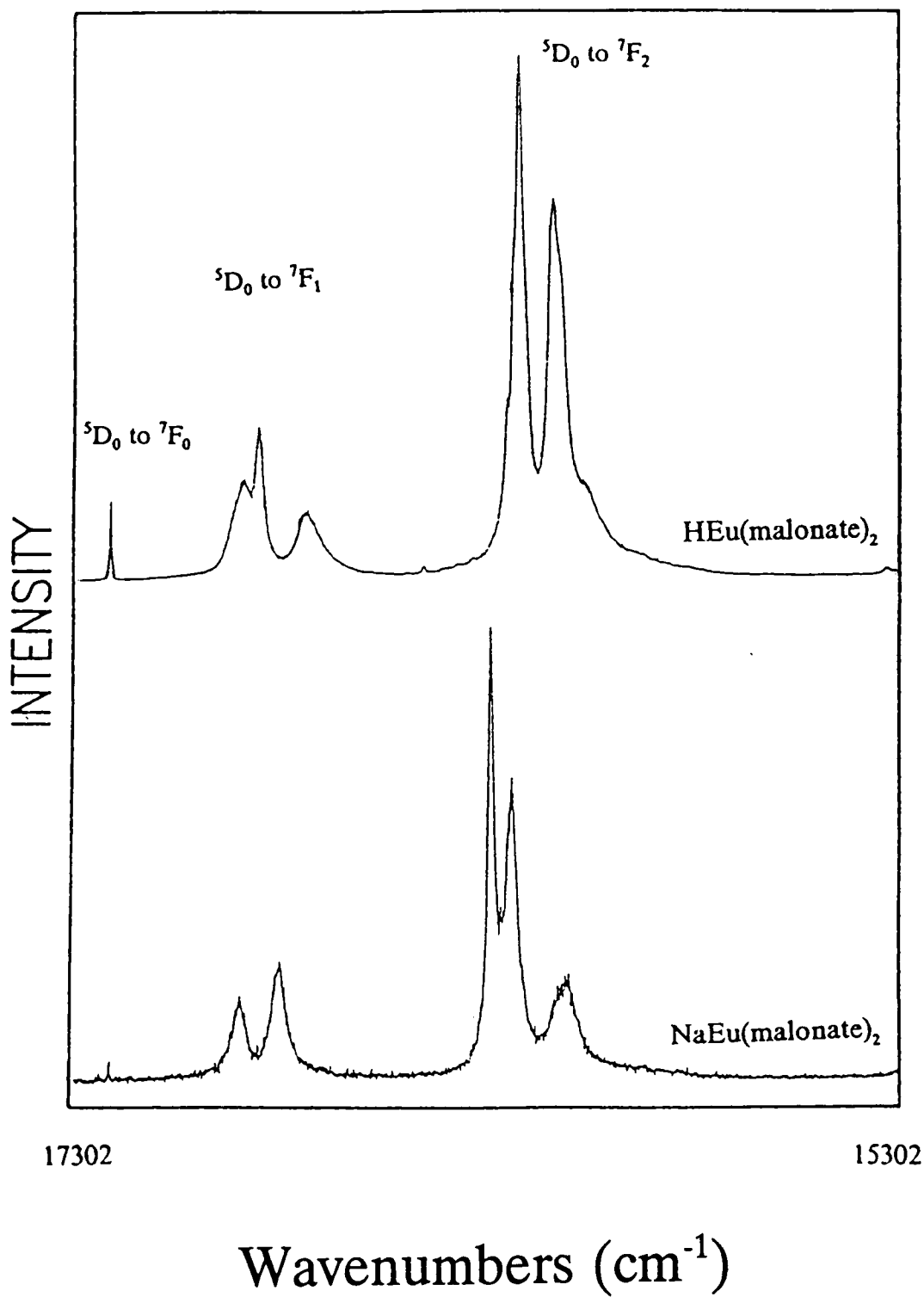


Figure 31. Emission Spectra of HEu(malonate)<sub>2</sub> and NaEu(malonate)<sub>2</sub>

## CHAPTER VI

## SALTS OF DIPYRIDINE AND TRIPHENYLPHOSPHINE-OXIDE COMPLEXES

## A. Salts of Dipyridine

Several salts of the triply-charged cationic  $\text{Eu}(\text{dipyridine})_x^{3+}$  complex ( $x=1,2$ ) have been synthesized to allow for a study of shifts in the emission characteristics of  $\text{Eu}^{3+}$  caused by a change in anionic counterions. Unlike changes in cationic counterions, shifts arising from a change in anionic counterion can be very dramatic. This is usually considered to be a result of the complexation of the metal by the counterion and of the strength with which the counterion is held by the emitting  $\text{Eu}^{3+}$ .

## 1. The Nitrate Salt

The nitrate salt was synthesized through the method described by Hart and Laming<sup>24</sup> for the synthesis of  $\text{Eu}^{3+}$  phenanthroline compounds. Two mole equivalents of dipyridine in methanol were added to one mole equivalent of the hydrated  $\text{Eu}(\text{NO}_3)_3$  in methanol. The luminescent solution was concentrated by evaporation at room temperature until a precipitate formed. The solid was collected, then dried and stored in a vacuum desiccator.

The emission spectrum of the resulting compound is shown in Figure 32 and resulted from the excitation of the ligand with a mercury-arc lamp and subsequent energy transfer to the metal ion. Upon inspection of the emission characteristics, the spectrum was judged to show no  $^5\text{D}_0$  to  $^7\text{F}_0$  transition, three  $^5\text{D}_0$  to  $^7\text{F}_1$  transitions, and one strongly allowed  $^5\text{D}_0$  to  $^7\text{F}_2$  doubly degenerate transition. This pattern can be indicative of  $\text{D}_4$ ,  $\text{D}_{3h}$ , and  $\text{C}_{3h}$  site symmetries. Elemental analysis of this compound (Desert Analytics) revealed a composition of 1.5 ligand to 1 europium. A ligand bridged dinuclear compound does

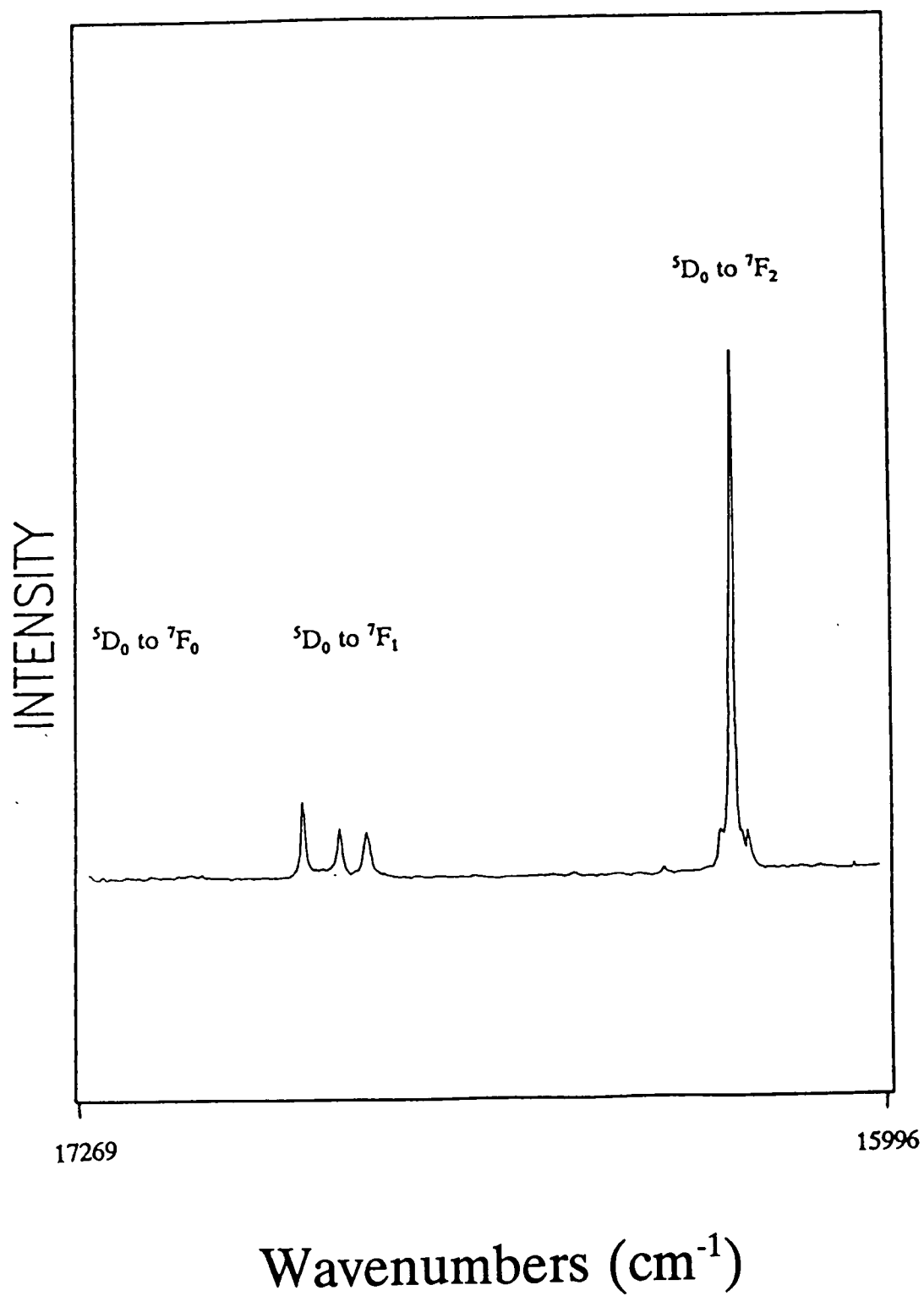


Figure 32. Emission Spectrum of  $\text{Eu}(\text{dipyridine})_2(\text{NO}_3)_3$

not appear likely, therefore the solid is probably a mixture of the monokis and bis forms. It will be assumed that the bis compound gives the strongest emission characteristics resulting from ultraviolet excitation because the fluorescence should be enhanced through photon absorption by two dipyridines rather than one. Of the three symmetries listed above, only the  $D_4$  site symmetry could arise from the bis form (a  $C_3$  axis is not possible given that the symmetry should be dictated by two bidentate ligands). From the above logic, a site symmetry of  $D_4$  will be tentatively assigned to the most intensely emitting  $\text{Eu}^{3+}$  ion, which appears to be from the bis(dipyridine) salt.

## 2. The Chloride Salt

The chloride salt was synthesized by the same method described above. However, the final product tended to be more easily decomposed and required great care in its collection and storage. The emission spectrum of the chloride salt (Figure 33) is interpreted as showing an allowed  $^5D_0$  to  $^7F_0$  transition, three allowed  $^5D_0$  to  $^7F_1$  transitions, and three allowed  $^5D_0$  to  $^7F_2$  transitions. This pattern is indicative of a  $C_4$  or  $C_{4v}$  site symmetry, which is also likely to arise from a bis(dipyridine) salt.

## 3. The Acetate Salt

The synthesis of the acetate salt was carried out in the same way as that of the first two salts except that tetrahydrofuran was employed as the solvent. This alteration appeared to induce better crystallization and purity of the final product. The emission spectrum of the acetate salt (Figure 34) is interpreted as an allowed  $^5D_0$  to  $^7F_0$  transition, three allowed  $^5D_0$  to  $^7F_1$  transitions, and four allowed  $^5D_0$  to  $^7F_2$  transitions. This splitting pattern is indicative of a  $C_{2v}$  site symmetry which could arise from monokis, bis, or tris compounds of the salt.

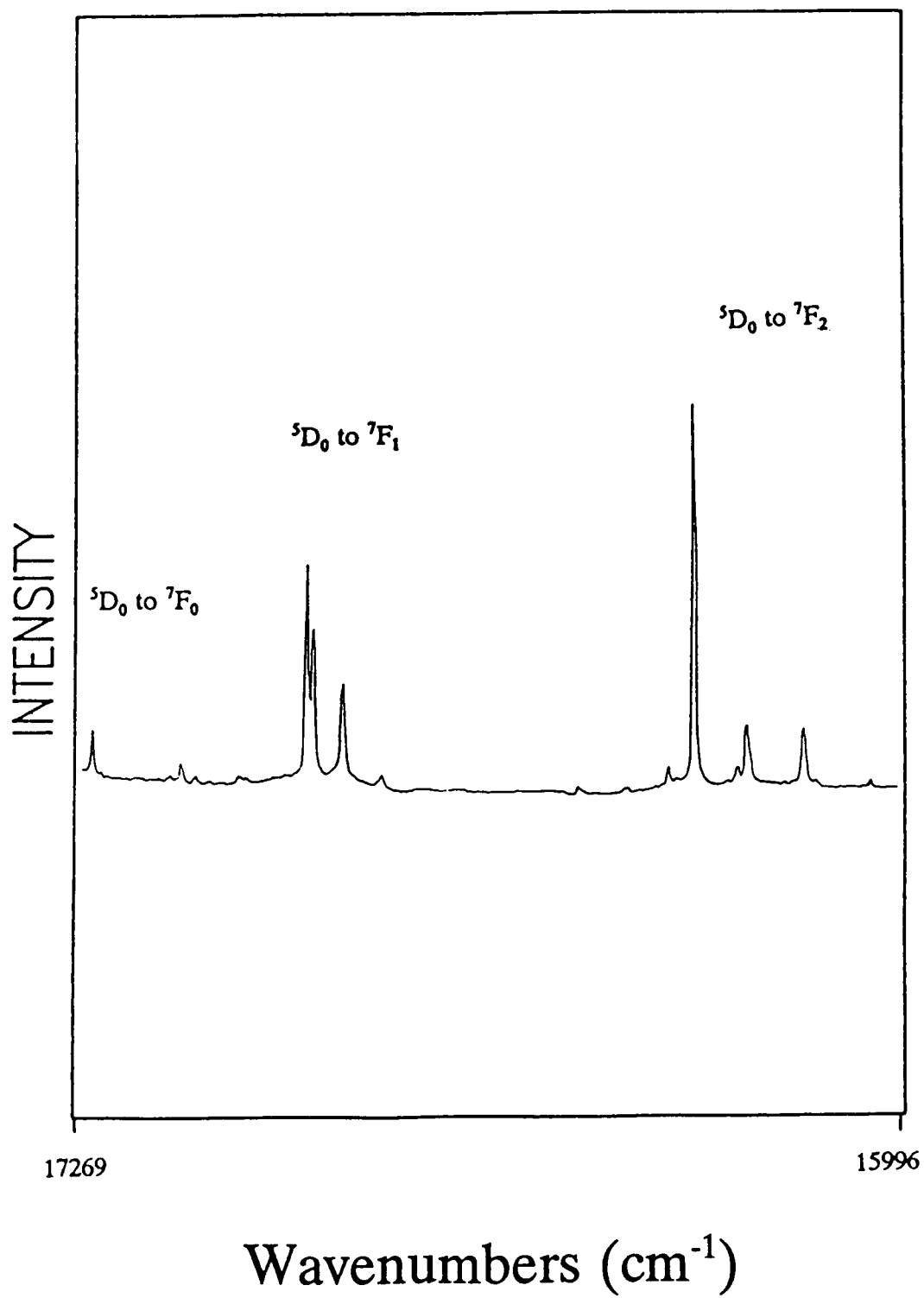


Figure 33. Emission Spectrum of  $\text{Eu}(\text{dipyridine})_2\text{Cl}_3$

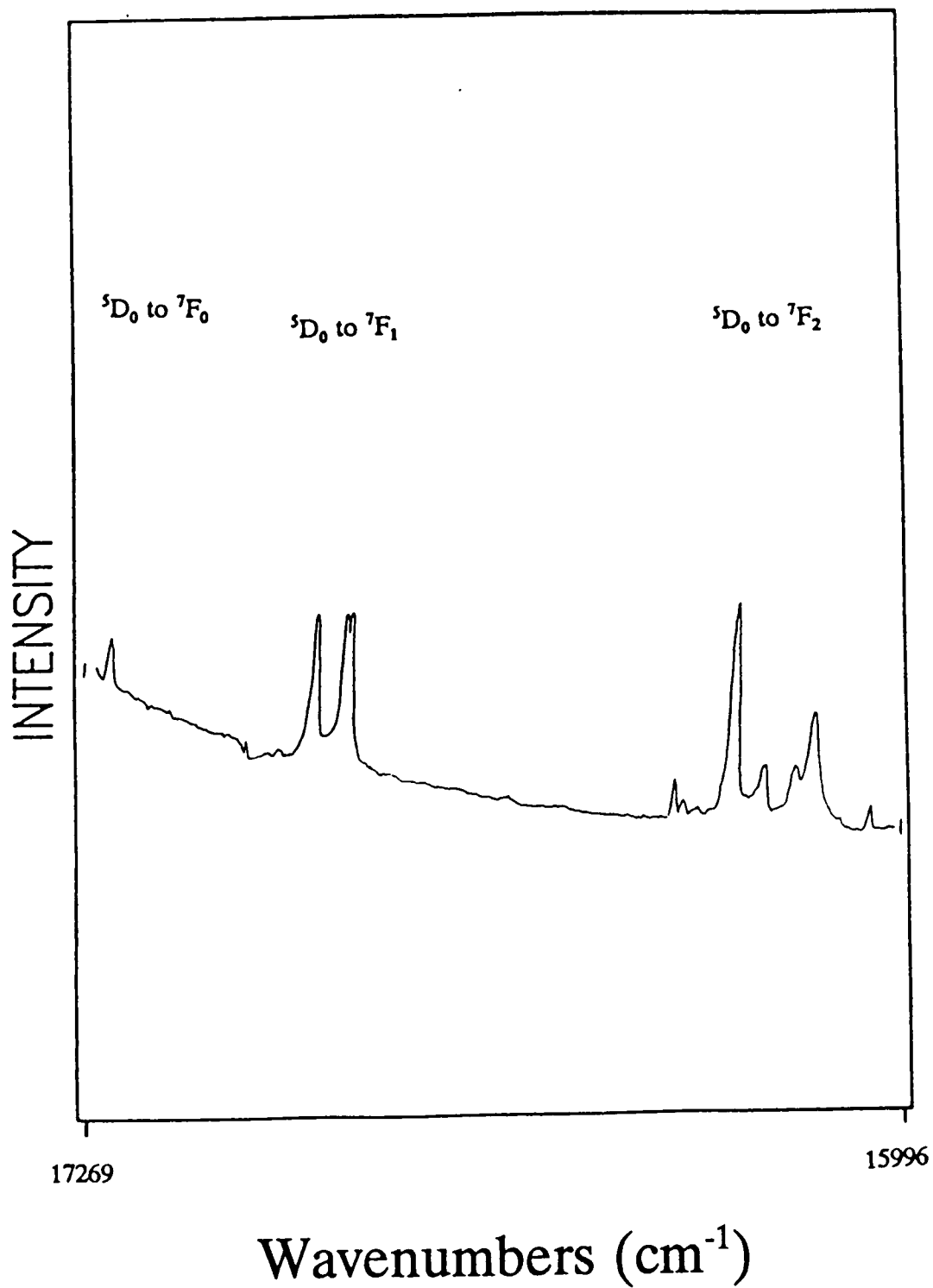


Figure 34. Emission Spectrum of  $\text{Eu}(\text{dipyridine})_x(\text{acetate})_3$  ( $x = 1, 2$ , or  $3$ )

#### 4. The Benzoate Salt

The benzoate salt was synthesized using the same procedure as that used for the acetate salt. However, the tetrahydrofuran solvent did not appear to give a pure form in terms of a single site. The most predominant transitions appear to indicate a site symmetry which is  $C_n$  or  $C_{nv}$  in that a strongly allowed  $^5D_0$  to  $^7F_0$  transition is observable, and the five strong transitions in the  $^5D_0$  to  $^7F_2$  region would further limit the options to those less than  $C_{3v}$ . The emission spectrum of the benzoate salt is shown in Figure 35.

#### 5. Conclusions

The most stable form of the dipyrindine complex appears to be the bis compound. However, the other forms will be present in various concentrations possibly nearing that of the more stable form. This problem of multiple forms, and therefore multiple sites, is further compounded by the strength of solvent complexation to the point of competition with the dipyrindine chelate. This is believed to be the major stumbling block in the synthesis of these and other dipyrindine complexes.

A study should be commenced upon the separation and spectral characterization of the multiple forms. This would probably best be realized by the use of anhydrous methods including inert atmosphere synthesis which was not readily available for the present work.

#### B. Salts of Triphenylphosphine-Oxide

Most of the salts of triphenylphosphine-oxide (TPPO) with  $Eu^{3+}$  were synthesized in a manner similar to that used for the dipyrindine complexes.<sup>24,25,26</sup> An ethanol solution of two mole equivalents of the ligand was added to a ethanolic solution of one mole equivalent of the  $Eu^{3+}$  salt. The solution was then concentrated by evaporation to

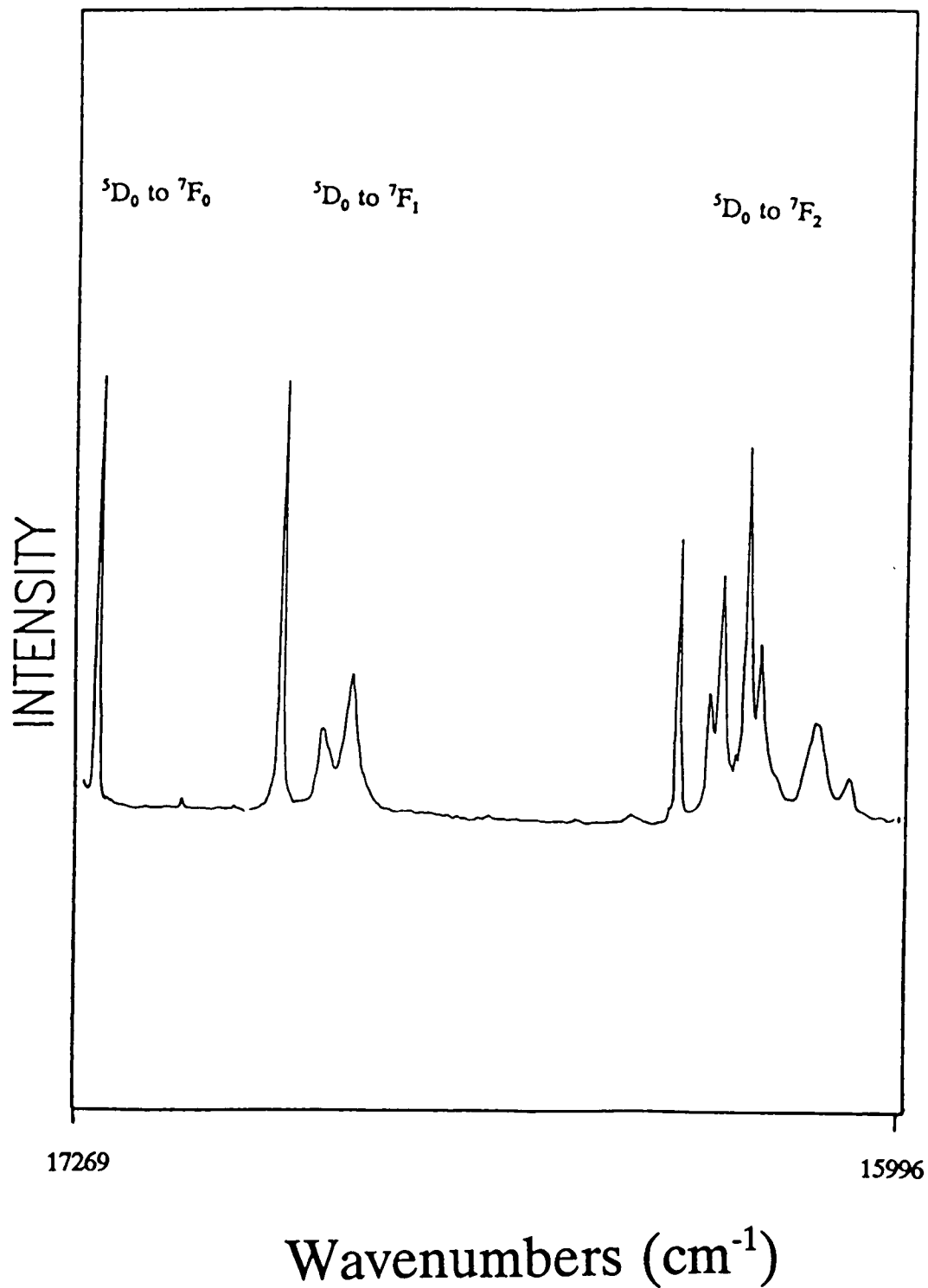


Figure 35. Emission Spectrum of  $\text{Eu}(\text{dipyridine})_x(\text{benzoate})_3$  ( $x = 1, 2$ , or  $3$ )

promote precipitation. The collected solid was then washed twice with aliquots of tetrahydrofuran.

### 1. The Chloride Salt

The emission spectrum resulting from the chloride salt synthesized as described above is shown in Figure 36. There appear to be an allowed  $^5D_0$  to  $^7F_0$  transition, three allowed  $^5D_0$  to  $^7F_1$  transitions, and two strongly allowed  $^5D_0$  to  $^7F_2$  transitions which are assignable as a singlet and a doublet. This splitting is indicative of  $C_4$  or  $C_{4v}$  site symmetry. Two minor peaks are also observable in the  $^5D_0$  to  $^7F_2$  region which are believed to indicate a distortion of the higher symmetry towards a  $C_2$  site symmetry. This assignment indicates that the europium coordination sphere probably forms a type of a square antiprismatic geometry.

The chloride salt was also synthesized in a tetrahydrofuran solution. The spectrum resulting from this compound is shown in Figure 36. The splitting pattern of the transitions in this compound (no  $^5D_0$  to  $^7F_0$ , three allowed in  $^5D_0$  to  $^7F_1$ , and a singlet and a doublet in  $^5D_0$  to  $^7F_2$ ) are indicative of a  $D_{2d}$  symmetry. This site symmetry implies that the  $Eu^{3+}$  coordination sphere displays a triangulated dodecahedral geometry.

### 2. The Bromide Salt

The bromide salt exhibited the spectrum shown in Figure 37. The splitting pattern of the transitions is indicative of a  $D_{2d}$  site symmetry (no  $^5D_0$  to  $^7F_0$ , three allowed in  $^5D_0$  to  $^7F_1$ , and a singlet and a doublet in  $^5D_0$  to  $^7F_2$ ). This assignment can be justified only through the assumption of an unusually large shift in the spectral position of one of the three  $^5D_0$  to  $^7F_1$  transitions. If such is the case, this transition was shifted almost 200 wavenumbers toward higher energy from the position where it is normally found in most

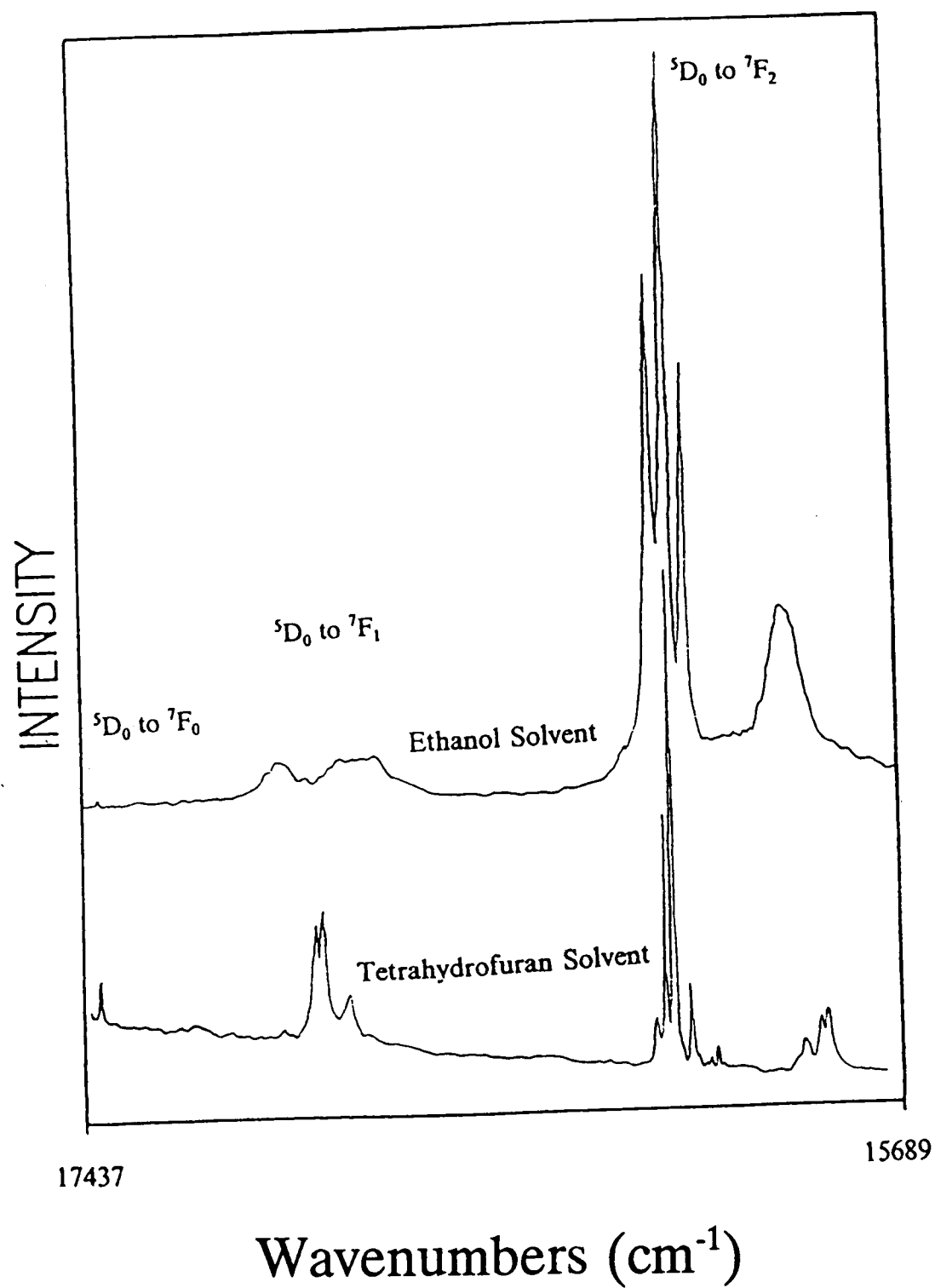


Figure 36. Emission Spectra of  $\text{Eu}(\text{TPPO})_x\text{Cl}_3$  ( $x = 1, 2, 3, \text{ or } 4$ ) Synthesized in Both Ethanol and Tetrahydrofuran

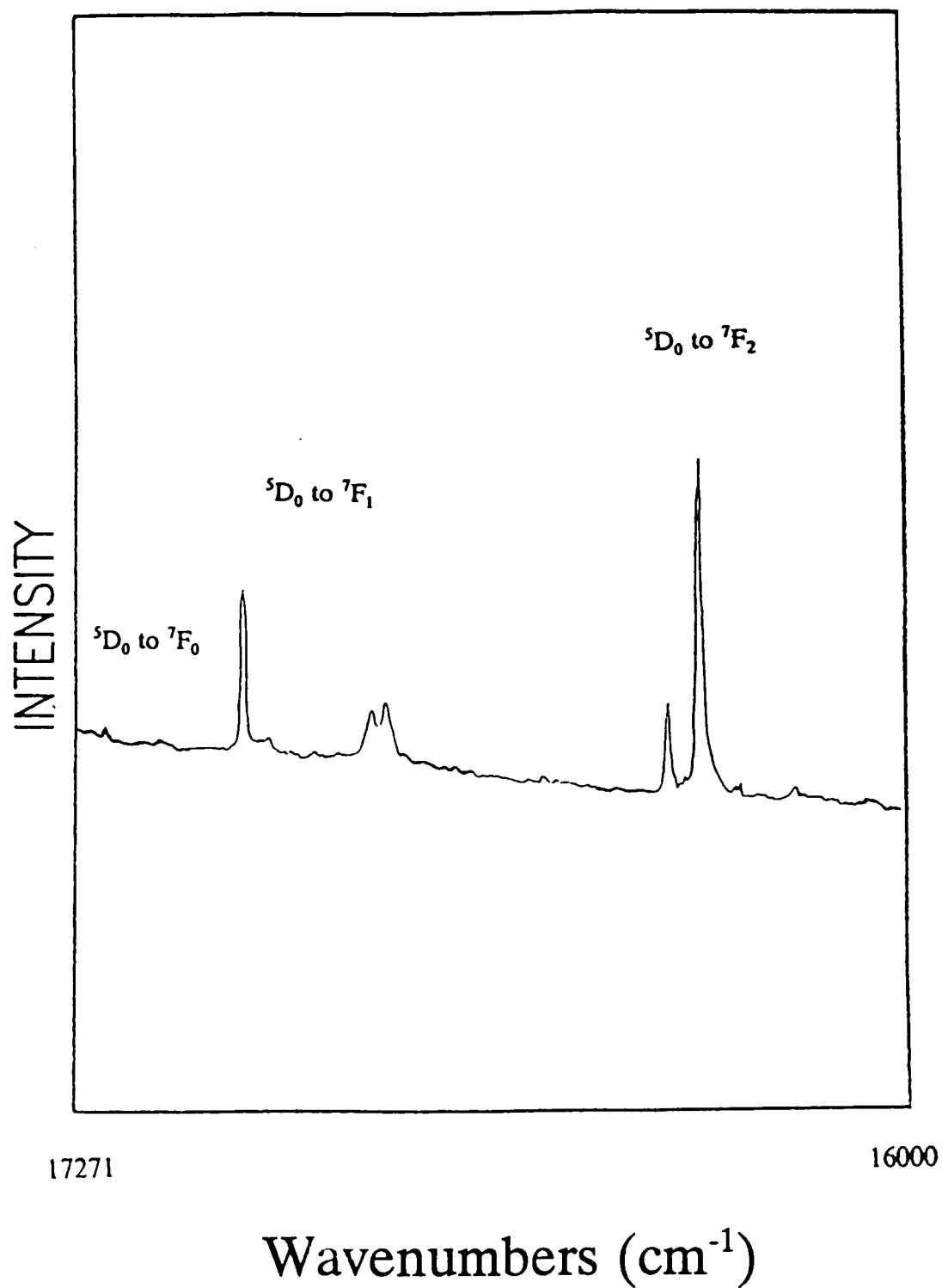


Figure 37. Emission Spectrum of  $\text{Eu}(\text{TPPO})_x\text{Br}_3$  ( $x = 1, 2, 3, \text{ or } 4$ )

$\text{Eu}^{3+}$  emission spectra. Similar shifts have previously been reported for other  $\text{Eu}^{3+}$  containing compounds such as europium oxychloride.<sup>13</sup>

### 3. The Perchlorate Salt

The perchlorate salt, while synthesized as the chloride and bromide salts had been, showed multiple sites as indicated by at least six allowed transitions in the  $^5\text{D}_0$  to  $^7\text{F}_2$  manifold (Figure 38). The nature of the transition intensities appears to indicate that whatever combination is giving rise to the emission characteristics, the components appear to be in almost equal concentrations. This makes the assignment of a predominant site symmetry impossible. However, this compound showed a shift of one of the  $^5\text{D}_0$  to  $^7\text{F}_1$  transitions similar to that seen with the bromide salt. Because of this it is believed that at least one of the sites involved is a  $\text{D}_{2d}$  symmetry site, similar to that assigned to the bromide salt.

### 4. The Acetate Salt

The emission spectrum of the acetate salt is shown in Figure 39. As with the perchlorate salt there appears to be multiple sites for the  $\text{Eu}^{3+}$  ion. Unlike the perchlorate salt there is a predominant species. This species shows a splitting pattern similar to that found for the chloride crystallized from ethanol (an allowed  $^5\text{D}_0$  to  $^7\text{F}_0$ , three allowed in  $^5\text{D}_0$  to  $^7\text{F}_1$ , and a singlet and doublet allowed in  $^5\text{D}_0$  to  $^7\text{F}_2$ ), indicating a  $\text{C}_4$  or  $\text{C}_{4v}$  symmetry.

### 5. Conclusions

The solid state TPPO complex salts appear to form two stable forms when synthesized as described above. Either a  $\text{D}_{2d}$  form in the first case or a  $\text{C}_4$  or  $\text{C}_{4v}$  form in the second case is seen depending upon the identities of both the solvent and the counterion.

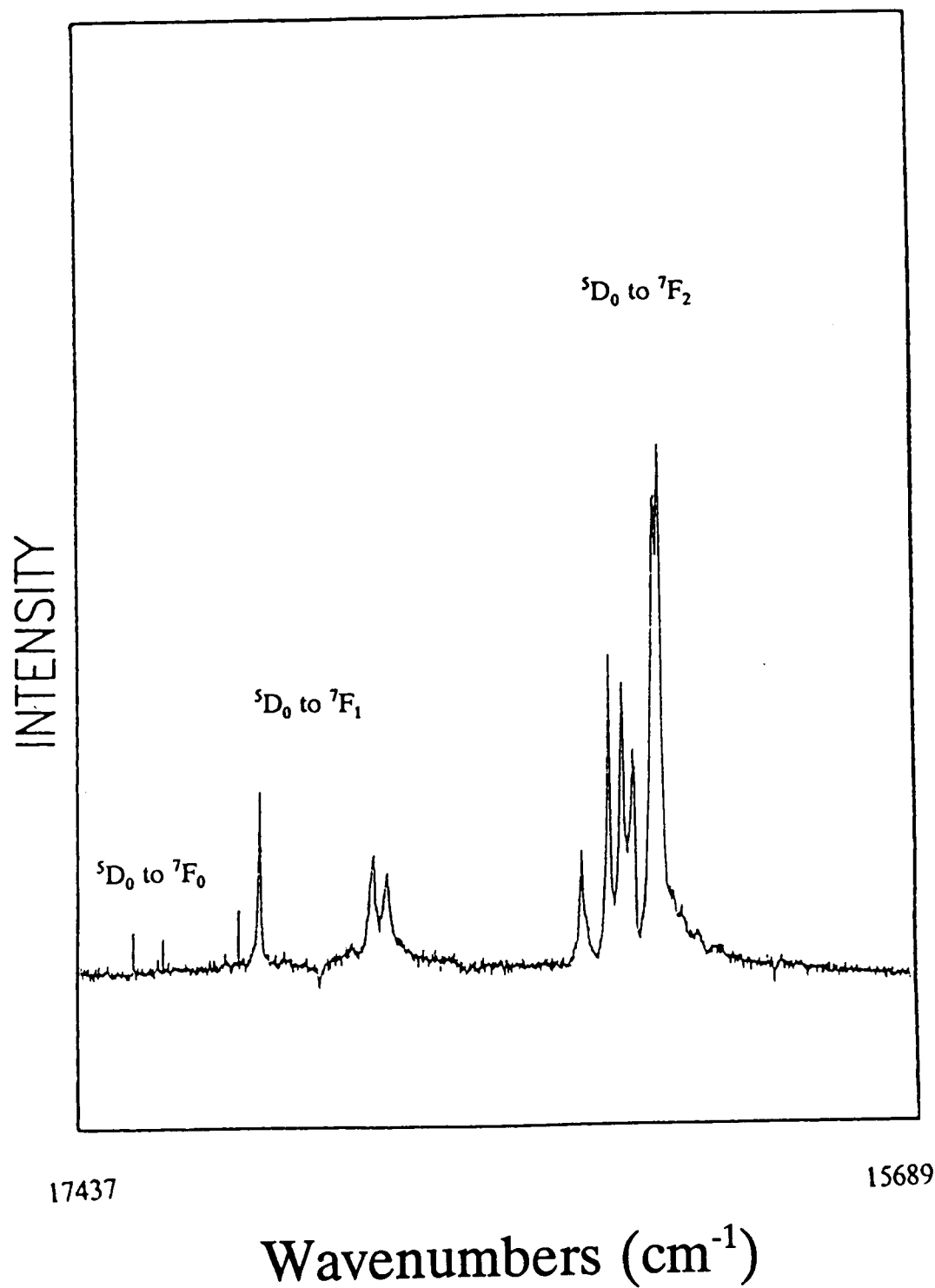


Figure 38. Emission Spectrum of  $\text{Eu}(\text{TPPO})_x(\text{ClO}_4)_3$  ( $x = 1, 2, 3$ , or  $4$ )

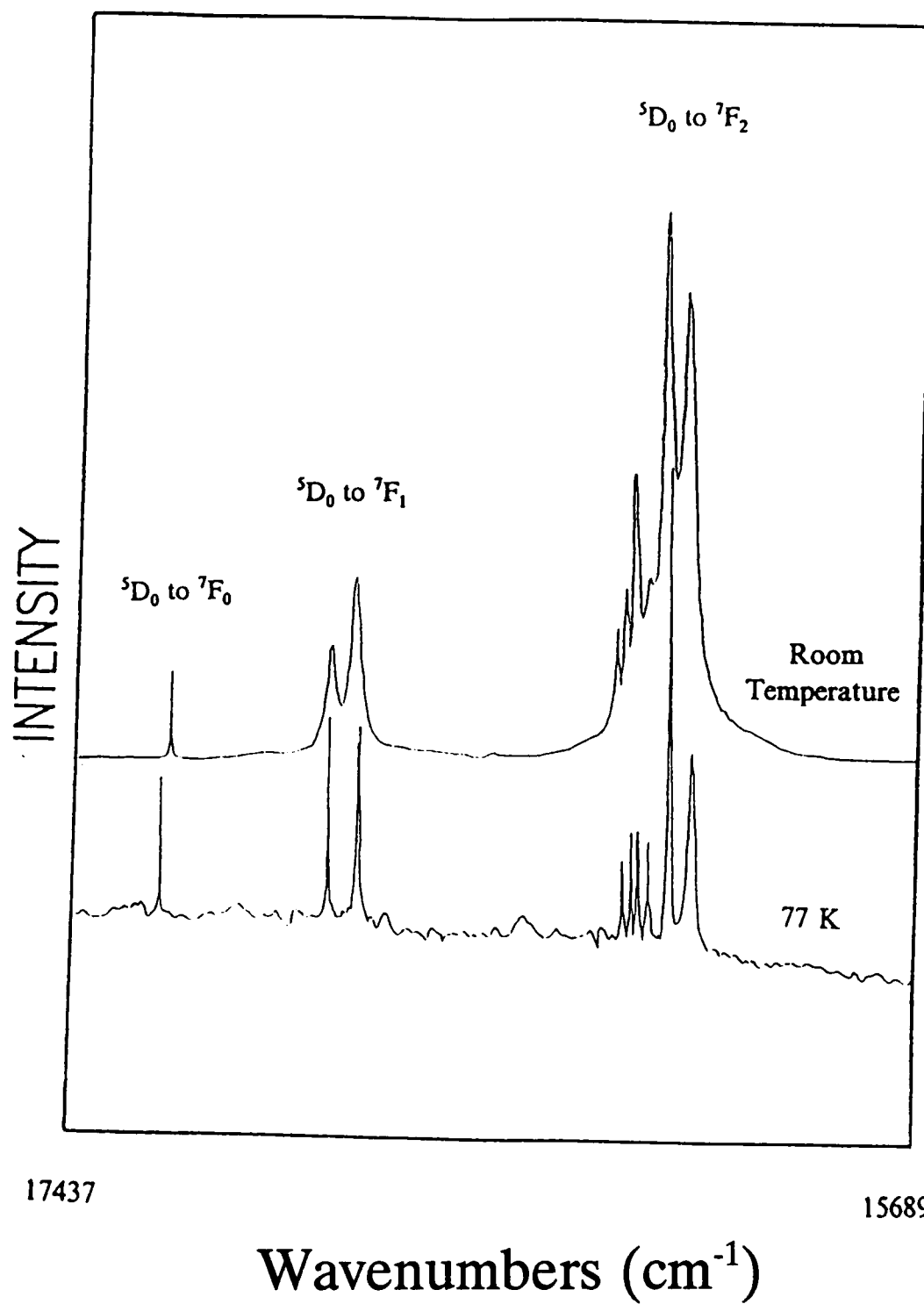


Figure 39. Emission Spectra at Room Temperature and 77 K of  $\text{Eu}(\text{TPPO})_x(\text{acetate})_3$  ( $x = 1, 2, 3, \text{ or } 4$ )

The two possible cases both indicate that the ligand-to-metal ratio is either 2:1 or 4:1, in that an odd number of ligands would not yield a coordination sphere with these symmetries. Syntheses of spectroscopically pure compounds was again hampered by the formation of multiple sites. This was probably due to equilibria formed between compounds showing different metal-ligand ratios (monokis, bis, or tris).

### C. Solution Salts of Triphenylphosphine-Oxide

Solutions of TPPO have been in use for some time for the extraction of lanthanide metals from solution. In this study five drops of an aqueous  $\text{Eu}^{3+}$  salt was added to 3 mL of a TPPO saturated methanol solution. The solutions were then frozen at 77 K and the emission spectra recorded. The spectra of the compounds resulting from the use of the different  $\text{Eu}^{3+}$  salts are shown in Figure 40. The symmetries of the compounds are surprisingly assignable and are tentatively designated as a  $D_{2d}$  site. This is inferred from the forbidden nature of the  $^5D_0$  to  $^7F_0$  transition and a singlet and a doublet seen in the  $^5D_0$  to  $^7F_2$  manifold.

The most observable shift which could be attributable to the change in counterion is seen in the distances between the singlet and the doublet pair in the  $^5D_0$  to  $^7F_2$  manifold. The acetate complex ion shows the largest splitting followed by the nitrate. The sulphate exhibits the smallest splitting of the three.

To confirm the observed differences in the splitting patterns, the emission spectrum of a mixed salt (nitrate and acetate) was also obtained. The resulting spectrum is shown in Figure 41. The observed transitions are readily assignable to those seen in the solutions of the pure compounds. This is believed to indicate that the complex ion which is formed possibly contains only one of the anionic counterions,  $[\text{Eu}(\text{TPPO})_x]^{3+} \text{A}^-$ , in that no spectrum for a mixed salt was observed.

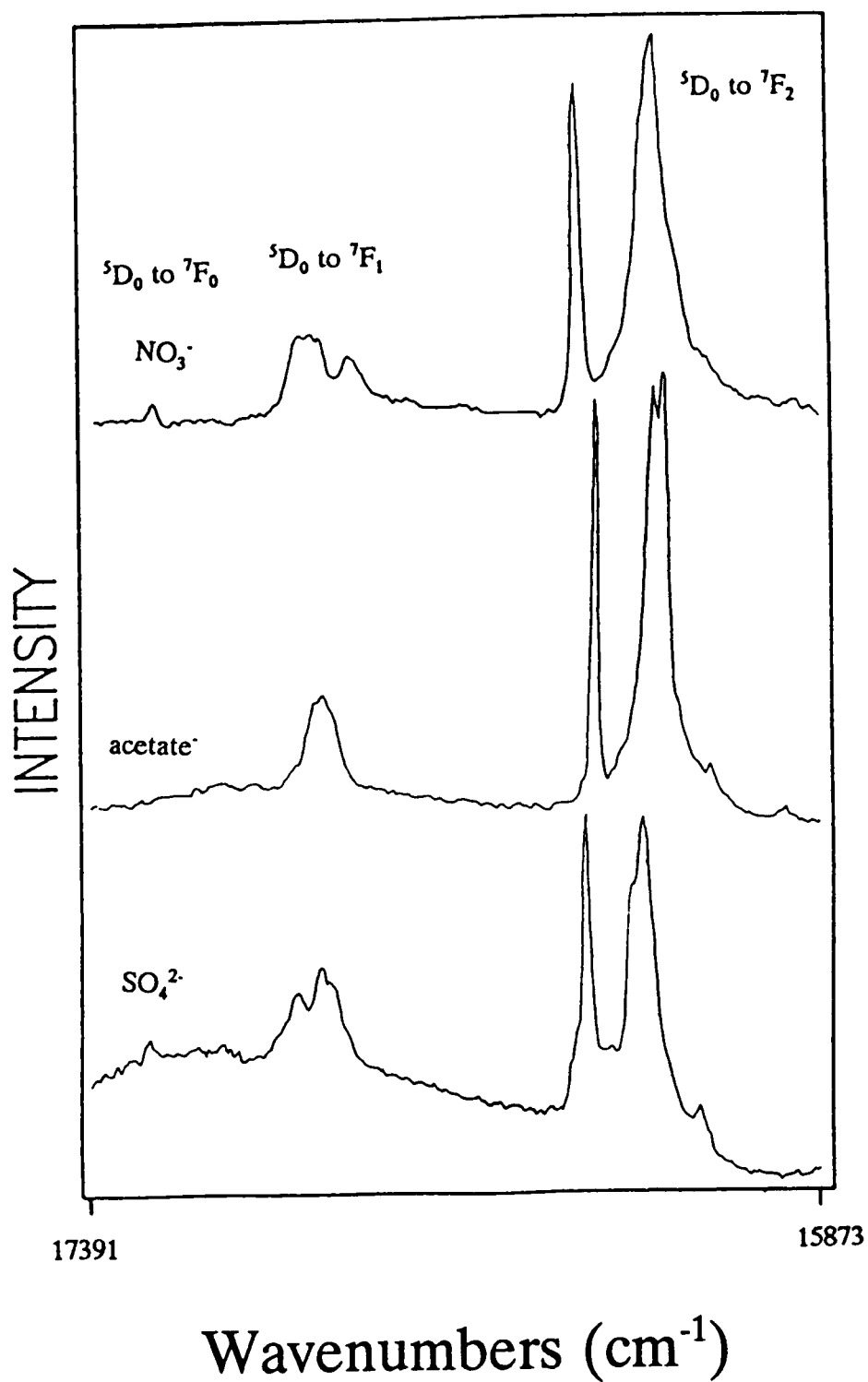


Figure 40. Emission Spectra of Methanolic Solutions of  $\text{Eu}(\text{TPPO})_x(\text{A})_3$  ( $x = 1, 2, 3, \text{ or } 4$ ;  $\text{A} = \text{NO}_3^-$ , acetate $^-$ , and  $\text{SO}_4^{2-}$ )

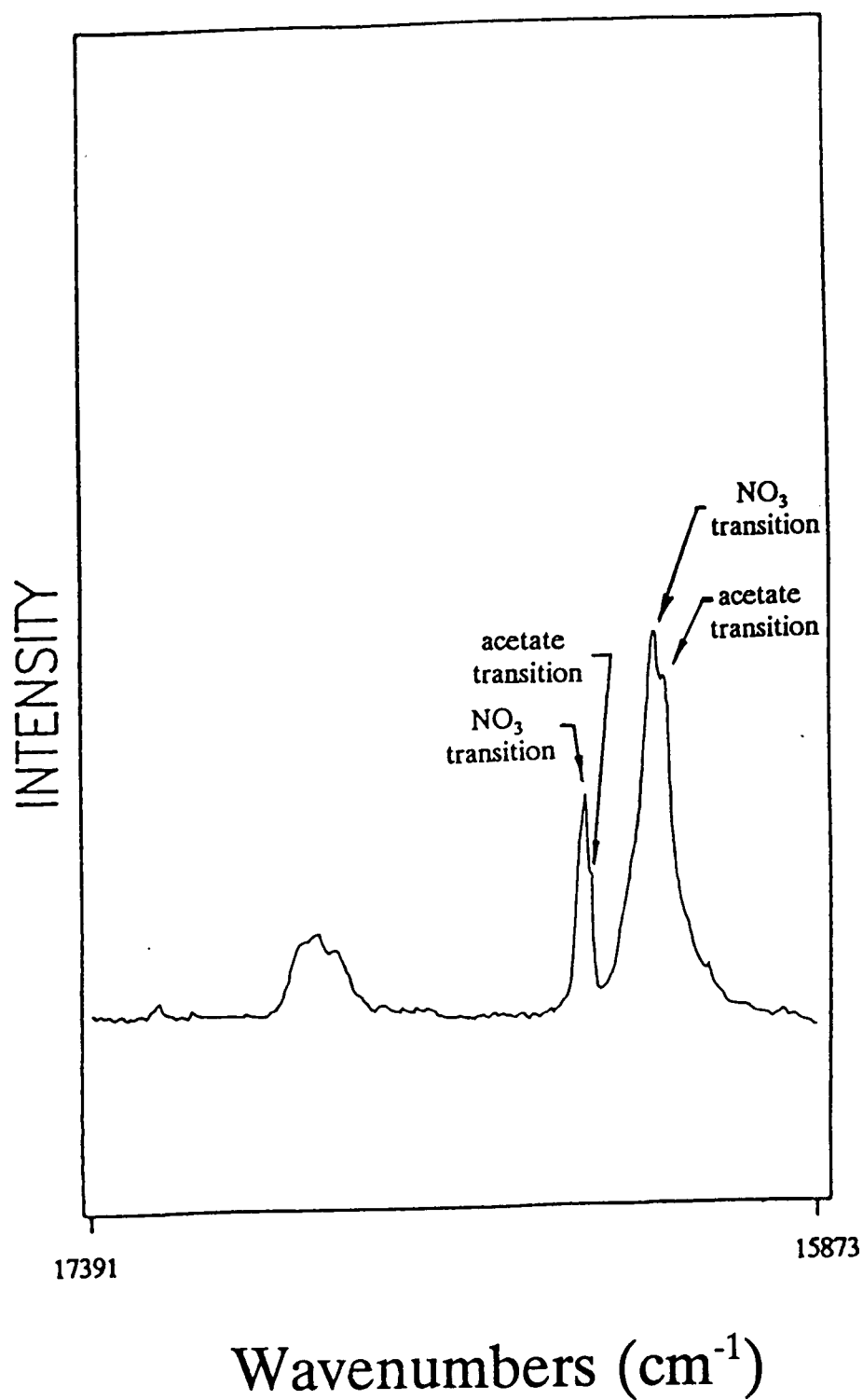


Figure 41. Emission Spectrum of a Methanolic Solution of  $\text{Eu}(\text{TPPO})_x(\text{A})_3$   
( $x = 1, 2, 3$ , or  $4$ ;  $\text{A} = 50\% \text{NO}_3^-$  and  $50\% \text{acetate}^-$ )

## CHAPTER VII

### INORGANIC SALTS

#### A. The Phosphate Salt

The results of a study of the  $\text{Eu}^{3+}$  emission spectrum recorded from  $\text{EuPO}_4$  are presented below. This research has studied the shifts in the  $\text{Eu}^{3+}$  emission spectrum as a function of the synthetic procedure. The study also included an experimental structural determination of other lanthanide phosphate compounds by a one percent doping of europium(III) phosphate into the solid compound. The employed compounds were synthesized by the addition of equimolar quantities of phosphoric acid to freshly precipitated  $\text{Eu}(\text{OH})_3$ . The solution pH was then raised to about 10 with 1 M NaOH yielding a white, crystalline precipitate.

##### 1. Europium Phosphate Spectroscopy

The europium phosphate resulting from the above synthesis was allowed to anneal in water for 12 hours at  $110^\circ\text{C}$  followed by the collection of three samples of the precipitate. The first sample was sealed into a capillary. The second sample was heated in a melting point apparatus at  $400^\circ\text{C}$  for two hours. The third sample was heated at about  $600^\circ\text{C}$  for one hour. The spectra obtained from these three samples are shown in Figure 42. The first sample is the only one for which Table VIII can be employed for structural determination. In the heating of the other compounds, the production of an  $\text{Eu}^{3+}$  ion site with coordination number less than eight is possible. Table VIII, while containing most of the possible symmetries, may not contain all the possible site symmetries for six or seven coordinate species.

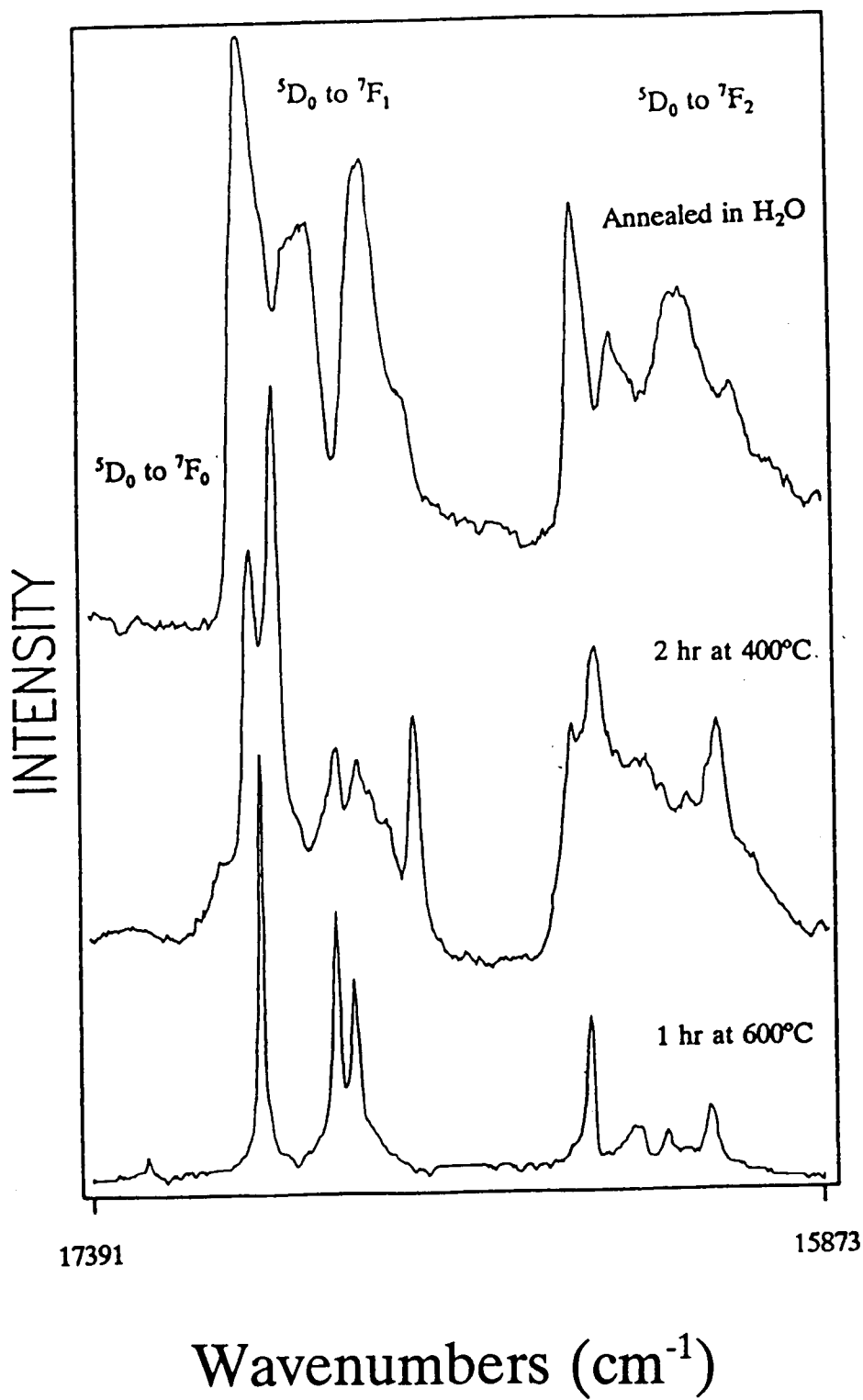


Figure 42. Emission Spectra of Differently Prepared Samples of  $\text{EuPO}_4$

The spectrum of the first sample (Figure 42) showed no observable  $^5D_0$  to  $^7F_0$  transition and extremely broad transitions in the  $^5D_0$  to  $^7F_1$  and  $^5D_0$  to  $^7F_2$  manifolds. This implies multiple sites of symmetries greater than  $C_4$  or  $C_{2v}$ . The large widths of the transitions preclude further assignment.

The second sample's spectrum (Figure 42) also was judged to show no  $^5D_0$  to  $^7F_0$  transition and transitions from multiple sites in the  $^5D_0$  to  $^7F_1$  and  $^5D_0$  to  $^7F_2$  regions. These manifolds showed moderately narrow, predominant transitions which included three dominating the  $^5D_0$  to  $^7F_1$  region and two dominating the  $^5D_0$  to  $^7F_2$  region.

The third sample exhibited an emission spectrum which appeared to show a single site for the  $Eu^{3+}$  ion (Figure 42). These spectral lines were interpreted as showing no  $^5D_0$  to  $^7F_0$  transition, three allowed  $^5D_0$  to  $^7F_1$  transitions, and four allowed  $^5D_0$  to  $^7F_2$  transitions. This pattern is indicative of a  $D_{2d}$  site symmetry according to Table VIII. However, we must also consider sites other than those allowed by eight, nine, or ten coordinate species. These other species might include an  $S_4$  site symmetry which could also show a similar splitting pattern.

## 2. Europium-Doped Lanthanide Salts

Given the results of the above experiment, the  $Eu^{3+}$ -doped lanthanide phosphates were heated for an hour at  $600^\circ C$  to promote the formation of single site species. Two lanthanides,  $La^{3+}$  and  $Tb^{3+}$ , were employed for comparison with the europium phosphate compound. The spectra of these two salts are shown in Figure 43. The emission spectrum of the europium-doped  $LaPO_4$  exhibited a spectral splitting similar to that shown by the predominant species seen in the spectrum of the europium phosphate sample which had been heated at  $400^\circ C$  (Figure 42). However, the spectrum appears to be dominated by the emission from an  $Eu^{3+}$  ion site for which a reliable symmetry assignment can be made.

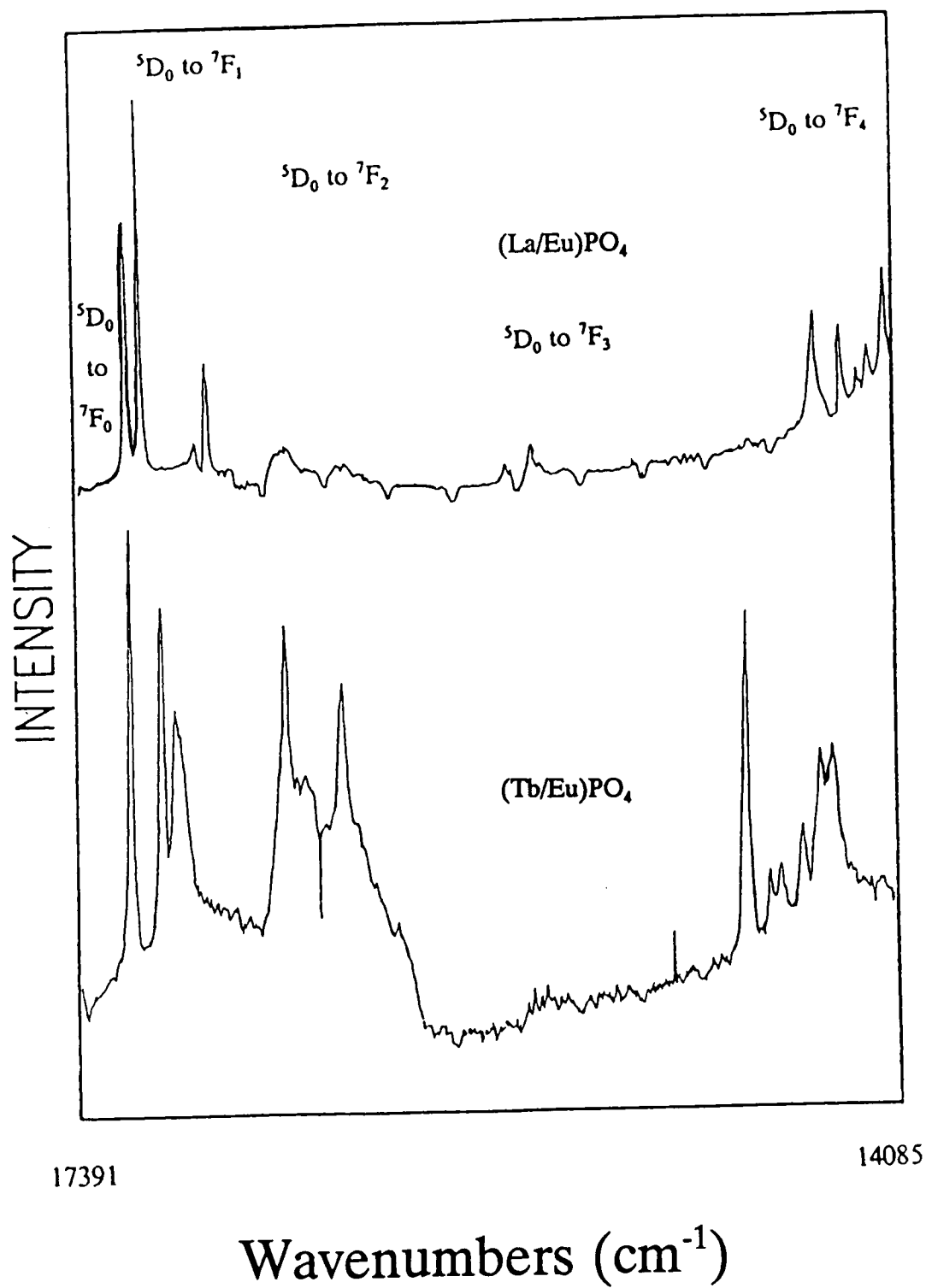


Figure 43. Emission Spectra of Selected Europium-Doped Lanthanide Phosphates

The spectrum was judged to contain no  $^5D_0$  to  $^7F_0$  transition, three  $^5D_0$  to  $^7F_1$  transitions, no allowed  $^5D_0$  to  $^7F_2$  transitions, and five transitions in the  $^5D_0$  to  $^7F_4$  manifold. This pattern is indicative of a  $D_{4d}$  site symmetry that is distorting into a  $D_4$  symmetry.

The europium-doped  $TbPO_4$  exhibited a spectrum corresponding to that seen for the europium phosphate heated at  $600^\circ C$ . The spectrum was interpreted as showing no  $^5D_0$  to  $^7F_0$  transition, three  $^5D_0$  to  $^7F_1$  transitions, four allowed  $^5D_0$  to  $^7F_2$  transitions, and six transitions in the  $^5D_0$  to  $^7F_4$  manifold. The added manifold ( $^5D_0$  to  $^7F_4$ ) distinguishes between the two symmetries,  $D_{2d}$  and  $S_4$ , discussed for the pure europium compound. Six transitions in the  $^5D_0$  to  $^7F_4$  manifold is indicative of  $D_{2d}$  site symmetry.

### 3. Conclusions

There appear to be two predominate forms of the lanthanide phosphate compound seen for the three lanthanides (La, Eu, and Tb). These include a form with a  $D_{4d}$  site symmetry and a form with a  $D_{2d}$  site symmetry. The europium compound primarily forms the second type, but can form, with the appropriate change in synthetic procedure, a mixture with the first type as the predominant species.

X-ray data for the smaller lanthanide phosphates (Tb-Lu) indicate a  $D_{2d}$  site for the lanthanide.<sup>27</sup> Similar studies of the larger lanthanide phosphates (La-Gd) describe a  $C_1$  site for the lanthanide ion.<sup>27,28</sup>

### B. The Sulphate Salt

A europium-doping experiment similar to that performed on the phosphate salts was accomplished for several rare-earth sulphates ( $Y^{3+}$ ,  $La^{3+}$ ,  $Tb^{3+}$ ,  $Er^{3+}$ , and  $Lu^{3+}$ ). The salts were synthesized by the neutralization of freshly precipitated rare-earth hydroxide (doped with  $\sim 1\%$   $Eu^{3+}$ ) with a slight excess of sulfuric acid. The solid precipitate which formed was allowed to anneal at least three hours in the native solution. This resulted in moderately large crystals of the rare-earth sulphate. For the europium salt, a commercial europium sulphate (ALFA/Johnson Matthey) was annealed in a 1 M sulfuric acid solution.

The europium emission spectra which were exhibited by the sulphate compounds are shown in Figure 44. The spectra for the  $\text{La}^{3+}$  and  $\text{Er}^{3+}$  salts show a remarkable resemblance to that seen for the dipicolinate salts discussed in Chapter IV (deemed to contain no  $^5\text{D}_0$  to  $^7\text{F}_0$  transition, three  $^5\text{D}_0$  to  $^7\text{F}_1$  transitions, and two  $^5\text{D}_0$  to  $^7\text{F}_2$  transitions). Because of this, a site symmetry of  $\text{D}_{3h}$  will be tentatively assigned to the  $\text{Eu}^{3+}$  ion in these sulphates. The  $\text{Y}^{3+}$  and  $\text{Lu}^{3+}$  salts were judged to exhibit no  $^5\text{D}_0$  to  $^7\text{F}_0$  transition, three  $^5\text{D}_0$  to  $^7\text{F}_1$  transitions, and three  $^5\text{D}_0$  to  $^7\text{F}_2$  transitions (a doublet and a singlet). This splitting pattern is indicative of a  $\text{D}_{2d}$  site symmetry. The  $\text{Tb}^{3+}$  salt appears to show the presence of both forms in almost equal concentrations. The  $\text{Eu}^{3+}$  compound, though synthesized in a somewhat different manner, yields a spectrum of the same type as that exhibited by the smaller rare earth sulphates ( $\text{Y}^{3+}$  and  $\text{Lu}^{3+}$ ). The  $\text{Tb}^{3+}$  salt was resynthesized using the same synthetic procedure. The resynthesized compound exhibited a spectrum like those of the  $\text{Y}^{3+}$  and  $\text{Lu}^{3+}$  salts indicating a probable site symmetry of  $\text{D}_{3h}$ .

From the results seen above, it would appear that lanthanide and other rare earth sulphates precipitate in two symmetries, with the metal ion in a  $\text{D}_{3h}$  site ( $\text{La}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Er}^{3+}$ ) and/or a  $\text{D}_{2d}$  site ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Y}^{3+}$ , and  $\text{Lu}^{3+}$ ). The successful resynthesis of the  $\text{Tb}^{3+}$  salt in a pure form is believed to indicate a very low transition energy between the two crystallographic forms.

The assigned  $\text{Eu}^{3+}$  site symmetries appear to be consistent with x-ray studies for the compounds of the larger rare earths. X-ray studies of  $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  showed a hexagonal crystal structure for the compound and a tricapped trigonal prismatic coordination polyhedron with the three equatorial positions being filled by sulphate oxygens.<sup>29</sup> Studies of  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  showed a square antiprismatic polyhedron much less symmetrical than was observed by the present emission study.<sup>29</sup> It is believed, because of the observation of  $\text{D}_{2d}$  symmetry, that the compounds which we obtained crystallized in a triangulated dodecahedral polyhedron rather than a square antiprismatic one.

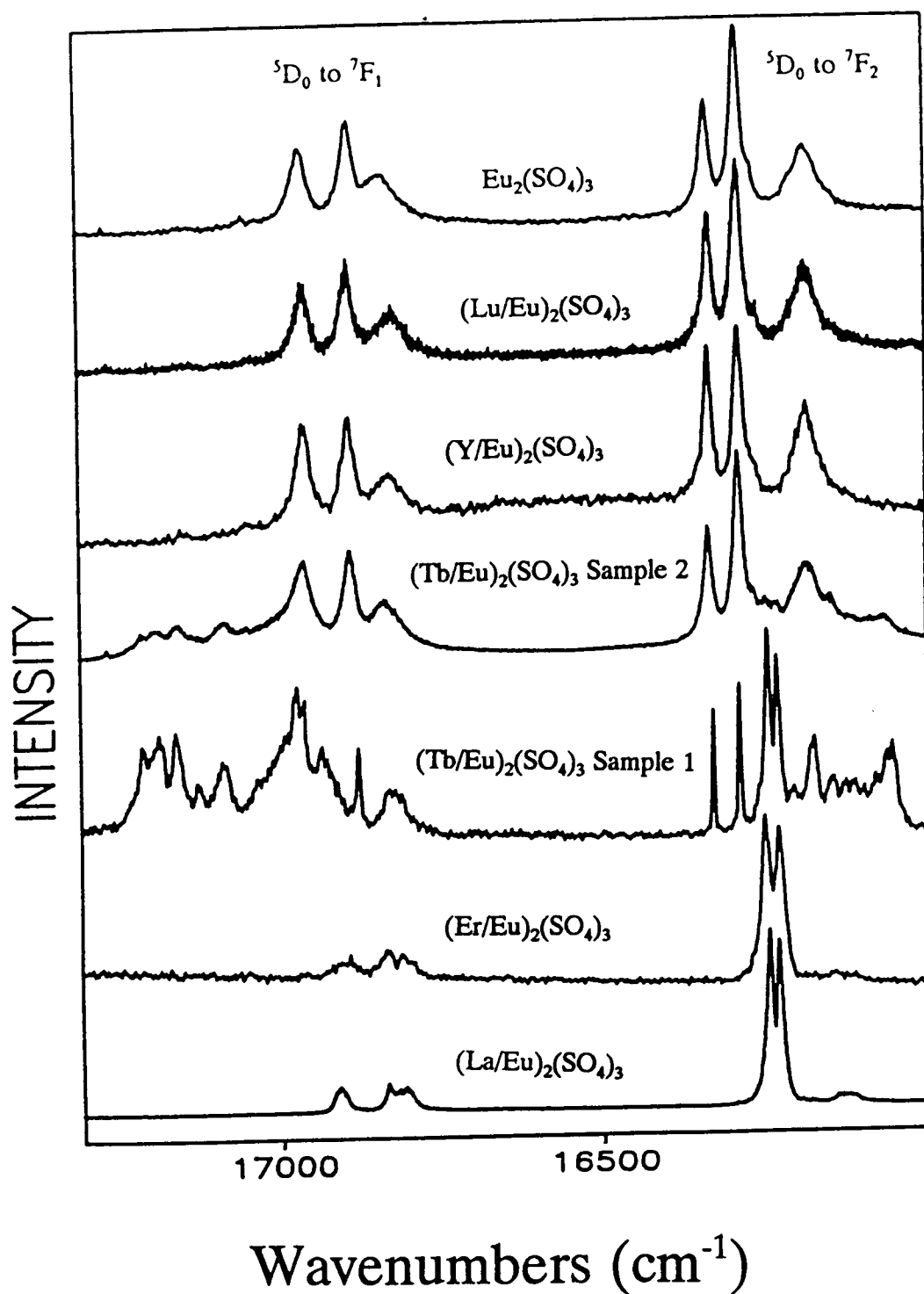


Figure 44. Emission Spectra of  $\text{Eu}_2(\text{SO}_4)_3$  and Selected Europium-Doped Lanthanide Sulphates

## CHAPTER VIII

### CONCLUSION

#### A. Summary

The purpose of this work, as stated previously, was the advancement and refinement of the use of lanthanide emission spectroscopy for the study of structural changes in molecules and molecular ions. Greater incident excitation power and better spectral resolution have opened the door to the detection of a larger number of manifolds and more consistent assignments of transition energies. The advantages which arise from more complete assignments and multiple manifolds are best seen in the spectra of the dipicolinates. Previous studies are believed to have mistakenly identified the site symmetry of the lanthanide ion in the tris(dipicolinate) compounds as  $D_3$ .<sup>8</sup> Through the observation of an extra manifold in this work, it has been determined that it should rather be assigned a site symmetry of  $D_{3h}$ .

A presentation of a theoretical treatment of lanthanide emission can be found in Chapter II. This treatment has been employed to create a compilation of allowed transitions for eight, nine, and ten coordinate europium-containing compounds (Table VIII). For several of the compounds studied, this compilation made possible a tentative assignment of the  $\text{Eu}^{3+}$  ion site symmetry. All the compounds for which an  $\text{Eu}^{3+}$  ion site symmetry has been assigned in this work are listed in Table XI along with the assigned site symmetry.

#### B. Prospects

The investigations which have been reported here have shown a method of detection which is an extremely sensitive monitor of changes in structure and

TABLE XI

Eu<sup>3+</sup> ION SITE SYMMETRIES ASSIGNED IN THIS WORK

| Studied Compound                                                                                                                                                   | Proposed Eu <sup>3+</sup><br>Ion Site<br>Symmetry |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|
| M <sub>3</sub> Eu(2,6-Pyridinedicarboxylate) <sub>3</sub> M = Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Pyr <sup>+</sup> | D <sub>3h</sub>                                   |
| HEu(2,6-Pyridinedicarboxylate) <sub>2</sub>                                                                                                                        | C <sub>4v</sub>                                   |
| Eu(2,6-Pyridinedicarboxylate) <sub>3</sub> <sup>3-</sup>                                                                                                           | D <sub>3h</sub>                                   |
| M <sub>3</sub> [Eu(2,6-Pyridinedicarboxylate) <sub>3</sub> ] <sub>2</sub> M = Mg <sup>2+</sup> , Ca <sup>2+</sup> , Zn <sup>2+</sup>                               | multiple D <sub>3h</sub>                          |
| MEu(2-Pyridinecarboxylate-N-Oxide) <sub>4</sub> M = Li <sup>+</sup> , Na <sup>+</sup>                                                                              | D <sub>2</sub> →D <sub>4</sub>                    |
| MEu(2-Pyridinecarboxylate-N-Oxide) <sub>4</sub> M = K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>                              | D <sub>2</sub> →D <sub>2d</sub>                   |
| Mg[Eu(2-Pyridinecarboxylate-N-Oxide) <sub>4</sub> ] <sub>2</sub>                                                                                                   | D <sub>2</sub> →D <sub>4</sub>                    |
| M[Eu(2-Pyridinecarboxylate-N-Oxide) <sub>4</sub> ] <sub>2</sub> M = Ca <sup>2+</sup> , Ba <sup>2+</sup>                                                            | D <sub>2</sub> →D <sub>2d</sub>                   |
| Al[Eu(2-Pyridinecarboxylate-N-Oxide) <sub>4</sub> ] <sub>3</sub>                                                                                                   | D <sub>2</sub> →D <sub>2d</sub>                   |
| Eu <sub>2</sub> (Malonate) <sub>3</sub>                                                                                                                            | C <sub>4</sub> or C <sub>4v</sub>                 |
| NaEu(Malonate) <sub>2</sub>                                                                                                                                        | D <sub>2d</sub>                                   |
| Eu(dipyridine) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>                                                                                                        | D <sub>4</sub>                                    |
| Eu(dipyridine) <sub>2</sub> (Cl) <sub>3</sub>                                                                                                                      | C <sub>4</sub> or C <sub>4v</sub>                 |
| Eu(dipyridine) <sub>n</sub> (acetate) <sub>3</sub> n = 1 or 2                                                                                                      | C <sub>2v</sub>                                   |
| Eu(Triphenylphosphine-Oxide) <sub>n</sub> Cl <sub>3</sub> methanol n = 2 or 4                                                                                      | C <sub>4</sub> or C <sub>4v</sub>                 |
| Eu(Triphenylphosphine-Oxide) <sub>n</sub> Cl <sub>3</sub> tetrahydrofuran n = 2 or 4                                                                               | D <sub>2d</sub>                                   |
| Eu(Triphenylphosphine-Oxide) <sub>n</sub> Br <sub>3</sub> n = 2 or 4                                                                                               | D <sub>2d</sub>                                   |
| Eu(Triphenylphosphine-Oxide) <sub>n</sub> (ClO <sub>4</sub> ) <sub>3</sub> n = 2 or 4                                                                              | D <sub>2d</sub>                                   |
| Eu(Triphenylphosphine-Oxide) <sub>n</sub> (Acetate) <sub>3</sub> n = 2 or 4                                                                                        | C <sub>4</sub> or C <sub>4v</sub>                 |
| Eu(Triphenylphosphine-Oxide) <sub>n</sub> (A) <sup>2+</sup> A = NO <sub>3</sub> <sup>-</sup> , Acetate <sup>-</sup>                                                | D <sub>2d</sub>                                   |
| LaPO <sub>4</sub>                                                                                                                                                  | D <sub>4</sub> →D <sub>4d</sub>                   |
| LnPO <sub>4</sub> Ln = Eu <sup>3+</sup> , Tb <sup>3+</sup>                                                                                                         | D <sub>2</sub>                                    |
| Ln <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Ln = La <sup>3+</sup> , Er <sup>3+</sup> , Tb <sup>3+</sup>                                                        | D <sub>3h</sub>                                   |
| RE <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> RE = Eu <sup>3+</sup> , Tb <sup>3+</sup> , Y <sup>3+</sup> , Lu <sup>3+</sup>                                      | D <sub>2d</sub>                                   |

composition. Slight perturbations in the first coordination sphere of an  $\text{Eu}^{3+}$  ion were detectable in its resulting electronic emission spectrum. The studied perturbations might result from either changes in the first coordination sphere, such as a change in the coordinating anionic counterion or solvent molecule, or a substitution of noncomplexing counterions or solvent molecules, where the size and ionicity of the entity caused a perturbation of the crystal structure and/or a slight distortion of the first coordination sphere.

Structural and compositional determination of compounds which contain lanthanides or are doped with lanthanides by emission spectroscopy is now beginning to be utilized with more frequency. However, only a portion of the full capability is being used. Preceding these applications, more research is needed for a better understanding of the emission characteristics of the lanthanide ions. These characteristics should include vibronic allowedness, splitting of degenerate transitions by distortion, distortions of geometric polyhedra, and other similar traits.

The effects of ion exchange of the counterion seen in this work and the individuality of the counterion's complex salt show that an analytical method for inorganic ions may be feasible. However, the method still requires an abundance of work for its optimization. It also allows for the synthesis of other salts of the complexes. Both of these practical applications should be seen in the near future.

The extreme sensitivity of the emission spectrum of lanthanide compounds to the metal ion's environment should also be applicable to other areas of chemistry and physics. The characterization of actinide species is possible through doping experiments with the sensitive and closely related lanthanide ions. Lanthanide ions have already been employed as lasing media; this sensitivity could allow for a solid state laser with emission lines being

dependent upon pressure, temperature, and/or composition of the compound or its solution. The spectral sensitivity might also be employed in liquid chromatographic columns as a post column derivitization, in that a coating of an insoluble compound on the wall of the column could detect changes in solution composition. Temperature and pressure measurements are also possible through the detection of lanthanide fluorescence. There are many avenues open in this field waiting to fascinate and puzzle willing scientists!

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## APPENDIX

## EXAMPLE THEORETICAL CALCULATIONS

### A. Calculations With Integer J Values

This series of calculations will deal with an  $\text{Eu}^{3+}$  ion which has an integer J value. The ion will be dealt with in the  $D_{3d}$  symmetry group which has the character table shown in Table A1.

Table A1

$D_{3d}$  Character Table

| $D_{3d}$        | E | $2C_3$ | $3C_2$ | i  | $2S_6$ | $3\sigma_d$ | Electric and Magnetic dipole operators |
|-----------------|---|--------|--------|----|--------|-------------|----------------------------------------|
| A <sub>1g</sub> | 1 | 1      | 1      | 1  | 1      | 1           |                                        |
| A <sub>2g</sub> | 1 | 1      | -1     | 1  | 1      | -1          | R <sub>z</sub>                         |
| E <sub>g</sub>  | 2 | -1     | 0      | 2  | -1     | 0           | R <sub>x</sub> , R <sub>y</sub>        |
| A <sub>1u</sub> | 1 | 1      | 1      | -1 | -1     | -1          |                                        |
| A <sub>2u</sub> | 1 | 1      | -1     | -1 | -1     | 1           | z                                      |
| E <sub>u</sub>  | 2 | -1     | 0      | -2 | 1      | 0           | x, y                                   |

#### 1. Allowed Representations

For  $J = 0$ , the reducible representation equals:

$$E = 2 \cdot 0 + 1 = 1$$

$$C_3 = [\sin(120^\circ(0+1/2))]/\sin(120^\circ/2) = 1$$

$$C_2 = [\sin(180^\circ(0+1/2))]/\sin(180^\circ/2) = 1$$

$$i = 2 \cdot 0 + 1 = 1 \text{ (integer J)}$$

$$S_6 = [\sin((60^\circ+180^\circ)(0+1/2))]/\sin((60^\circ+180^\circ)/2) = 1$$

$$\sigma_d = \sin(180^\circ(0+1/2)) = 1$$

Any state with  $J = 0$  will contain an A<sub>1g</sub> level.

For  $J = 1$ , the reducible representation equals:

$$E = 2 \cdot 1 + 1 = 3$$

$$C_3 = [\sin(120^\circ(1+1/2))]/\sin(120^\circ/2) = 0$$

$$C_2 = [\sin(180^\circ(1+1/2))]/\sin(180^\circ/2) = -1$$

$$i = 2 \cdot 1 + 1 = 3 \text{ (integer } J)$$

$$S_6 = [\sin((60^\circ+180^\circ)(1+1/2))]/\sin((60^\circ+180^\circ)/2) = 0$$

$$\sigma_d = \sin(180^\circ(1+1/2)) = -1$$

The reduction equation yields:

$$\# \text{ of } A_{1g} = (1 \cdot 3 \cdot 1) + (1 \cdot 0 \cdot 2) + (1 \cdot -1 \cdot 3) + (1 \cdot 3 \cdot 1) + (1 \cdot 0 \cdot 2) + (1 \cdot -1 \cdot 3)/12 = 0$$

$$\# \text{ of } A_{2g} = (1 \cdot 3 \cdot 1) + (1 \cdot 0 \cdot 2) + (-1 \cdot -1 \cdot 3) + (1 \cdot 3 \cdot 1) + (1 \cdot 0 \cdot 2) + (-1 \cdot -1 \cdot 3)/12 = 1$$

$$\# \text{ of } E_g = (2 \cdot 3 \cdot 1) + (-1 \cdot 0 \cdot 2) + (0 \cdot -1 \cdot 3) + (2 \cdot 3 \cdot 1) + (-1 \cdot 0 \cdot 2) + (0 \cdot -1 \cdot 3)/12 = 1$$

Upon looking back at the reducible representation, it is found that it equals the sum of these two, therefore any state with  $J = 1$  will contain an  $A_{2g}$  and an  $E_g$  level.

For  $J = 2$ , the reducible representation equals:

$$E = 2 \cdot 2 + 1 = 5$$

$$C_3 = [\sin(120^\circ(2+1/2))]/\sin(120^\circ/2) = -1$$

$$C_2 = [\sin(180^\circ(2+1/2))]/\sin(180^\circ/2) = 1$$

$$i = 2 \cdot 2 + 1 = 5 \text{ (integer } J)$$

$$S_6 = [\sin((60^\circ+180^\circ)(2+1/2))]/\sin((60^\circ+180^\circ)/2) = -1$$

$$\sigma_d = \sin(180^\circ(2+1/2)) = 1$$

The reduction equation yields:

$$\# \text{ of } A_{1g} = (1 \cdot 5 \cdot 1) + (1 \cdot -1 \cdot 2) + (1 \cdot 1 \cdot 3) + (1 \cdot 5 \cdot 1) + (1 \cdot -1 \cdot 2) + (1 \cdot 1 \cdot 3)/12 = 1$$

$$\# \text{ of } A_{2g} = (1 \cdot 5 \cdot 1) + (1 \cdot -1 \cdot 2) + (-1 \cdot 1 \cdot 3) + (1 \cdot 5 \cdot 1) + (1 \cdot -1 \cdot 2) + (-1 \cdot 1 \cdot 3)/12 = 0$$

$$\# \text{ of } E_g = (2 \cdot 5 \cdot 1) + (-1 \cdot -1 \cdot 2) + (0 \cdot 1 \cdot 3) + (2 \cdot 5 \cdot 1) + (-1 \cdot -1 \cdot 2) + (0 \cdot 1 \cdot 3)/12 = 2$$

Upon looking back at the reducible representation, it is found that it equals the sum of these three, therefore any state with  $J = 2$  will contain an  $A_{1g}$  and two  $E_g$  levels.

For  $J = 3$ , the reducible representation equals:

$$E = 2 \cdot 3 + 1 = 7$$

$$C_3 = [\sin(120^\circ(3+1/2))]/\sin(120^\circ/2) = 1$$

$$C_2 = [\sin(180^\circ(3+1/2))]/\sin(180^\circ/2) = -1$$

$$i = 2 \cdot 3 + 1 = 7 \text{ (integer } J)$$

$$S_6 = [\sin((60^\circ+180^\circ)(3+1/2))]/\sin((60^\circ+180^\circ)/2) = 1$$

$$\sigma_d = \sin(180^\circ(3+1/2)) = -1$$

The reduction equation yields:

$$\begin{aligned}\# \text{ of } A_{1g} &= (1 \cdot 7 \cdot 1) + (1 \cdot 1 \cdot 2) + (1 \cdot -1 \cdot 3) + (1 \cdot 7 \cdot 1) + (1 \cdot 1 \cdot 2) + (1 \cdot -1 \cdot 3) / 12 = 1 \\ \# \text{ of } A_{2g} &= (1 \cdot 7 \cdot 1) + (1 \cdot 1 \cdot 2) + (-1 \cdot -1 \cdot 3) + (1 \cdot 7 \cdot 1) + (1 \cdot 1 \cdot 2) + (-1 \cdot -1 \cdot 3) / 12 = 2 \\ \# \text{ of } E_g &= (2 \cdot 7 \cdot 1) + (-1 \cdot 1 \cdot 2) + (0 \cdot -1 \cdot 3) + (2 \cdot 7 \cdot 1) + (-1 \cdot 1 \cdot 2) + (0 \cdot -1 \cdot 3) / 12 = 2\end{aligned}$$

Upon looking back at the reducible representation, it is found that it equals the sum of these five, therefore any state with  $J = 3$  will contain an  $A_{1g}$ , two  $A_{2g}$ , and two  $E_g$  levels.

## 2. Transition Allowedness

In terms of transitions (using the  $\text{Eu}^{3+}$  ion), if the first excited state and the ground state are used as the initial and final states of the transition, the transition would be from the  ${}^5D_0 A_{1g}$  to the  ${}^7F_0 A_{1g}$  level. The product of the two representations and the dipole operators are:

Electric:

$$\begin{aligned}x &= A_{1g} \cdot A_{1g} \cdot E_u = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 0), (1 \cdot 1 \cdot -2), (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 0) = 2, -1, 0, -2, 1, 0 \\ y &= A_{1g} \cdot A_{1g} \cdot E_u = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 0), (1 \cdot 1 \cdot -2), (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 0) = 2, -1, 0, -2, 1, 0 \\ z &= A_{1g} \cdot A_{1g} \cdot A_{2u} = (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 1) = 1, 1, -1, -1, -1, 1\end{aligned}$$

As stated in Chapter II, the parity selection rule implies that in a symmetry containing an  $i$ , no electronic transitions are allowed.

Magnetic:

$$\begin{aligned}R_x &= A_{1g} \cdot A_{1g} \cdot E_g = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 0), (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 0) = 2, -1, 0, 2, -1, 0 \\ R_y &= A_{1g} \cdot A_{1g} \cdot E_g = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 0), (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 0) = 2, -1, 0, 2, -1, 0 \\ R_z &= A_{1g} \cdot A_{1g} \cdot A_{2g} = (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot -1) = 1, 1, -1, 1, 1, -1\end{aligned}$$

Since none of the above triple products contains the  $A_{1g}$  representation, the  $A_{1g}$  to  $A_{1g}$  transition will not be allowed electronically or magnetically. This transition is also forbidden magnetically by the  $J$  selection rule that forbids transitions between levels which both have  $J$  values of 0.

For  ${}^5D_0$  going to  ${}^7F_1$ , triple products for the transition from  $A_{1g}$  to  $A_{2g}$  levels are:

Electric:

$$\begin{aligned}x &= A_{1g} \cdot A_{2g} \cdot E_u = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot -1 \cdot 0), (1 \cdot 1 \cdot -2), (1 \cdot 1 \cdot 1), (1 \cdot -1 \cdot 0) = 2, -1, 0, -2, 1, 0 \\ y &= A_{1g} \cdot A_{2g} \cdot E_u = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot -1 \cdot 0), (1 \cdot 1 \cdot -2), (1 \cdot 1 \cdot 1), (1 \cdot -1 \cdot 0) = 2, -1, 0, -2, 1, 0 \\ z &= A_{1g} \cdot A_{2g} \cdot A_{2u} = (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 1), (1 \cdot -1 \cdot -1), (1 \cdot 1 \cdot -1), (1 \cdot 1 \cdot -1), (1 \cdot -1 \cdot 1) = 1, 1, 1, -1, -1, -1\end{aligned}$$

Since none contains the  $A_{1g}$  representation, no electronic transition is allowed.

Magnetic:

$$R_x = A_{1g} \cdot A_{2g} \cdot E_g = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot -1 \cdot 0), (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot -1 \cdot 0) = 2, -1, 0, 2, -1, 0$$

$$R_y = A_{1g} \cdot A_{2g} \cdot E_g = (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot -1 \cdot 0), (1 \cdot 1 \cdot 2), (1 \cdot 1 \cdot -1), (1 \cdot -1 \cdot 0) = 2, -1, 0, 2, -1, 0$$

$$R_z = A_{1g} \cdot A_{2g} \cdot A_{2g} = (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 1), (1 \cdot -1 \cdot -1), (1 \cdot 1 \cdot 1), (1 \cdot 1 \cdot 1), (1 \cdot -1 \cdot -1) = 1, 1, 1, 1, 1, 1$$

The  $A_{1g}$  to  $A_{2g}$  transition will be allowed symmetrically through the  $R_z$  axis.  $\Delta J = 1$ , thereby allowing the transition through the J selection rule.

The other transitions which are a part of  ${}^5D_0$  going to  ${}^7F_1$ , that of  $A_{1g}$  to  $E_g$ , yields for its triple products:

Electric:

$$x = A_{1g} \cdot E_g \cdot E_u = (1 \cdot 2 \cdot 2), (1 \cdot -1 \cdot -1), (1 \cdot 0 \cdot 0), (1 \cdot 2 \cdot -2), (1 \cdot -1 \cdot 1), (1 \cdot 0 \cdot 0) = 4, 1, 0, -4, -1, 0$$

$$y = A_{1g} \cdot E_g \cdot E_u = (1 \cdot 2 \cdot 2), (1 \cdot -1 \cdot -1), (1 \cdot 0 \cdot 0), (1 \cdot 2 \cdot -2), (1 \cdot -1 \cdot 1), (1 \cdot 0 \cdot 0) = 4, 1, 0, -4, -1, 0$$

$$z = A_{1g} \cdot E_g \cdot A_{2u} = (1 \cdot 2 \cdot 1), (1 \cdot -1 \cdot 1), (1 \cdot 0 \cdot -1), (1 \cdot 2 \cdot -1), (1 \cdot -1 \cdot -1), (1 \cdot 0 \cdot 1) = 2, -1, 0, -2, 1, 0$$

The x and y reducible representations both reduce to an  $A_{1u}$ , an  $A_{2u}$ , and an  $E_u$ . Since none of the representations contains the  $A_{1g}$  representation, the transition is electronically forbidden.

Magnetic:

$$R_x = A_{1g} \cdot E_g \cdot E_g = (1 \cdot 2 \cdot 2), (1 \cdot -1 \cdot -1), (1 \cdot 0 \cdot 0), (1 \cdot 2 \cdot 2), (1 \cdot -1 \cdot -1), (1 \cdot 0 \cdot 0) = 4, 1, 0, 4, 1, 0$$

$$R_y = A_{1g} \cdot E_g \cdot E_g = (1 \cdot 2 \cdot 2), (1 \cdot -1 \cdot -1), (1 \cdot 0 \cdot 0), (1 \cdot 2 \cdot 2), (1 \cdot -1 \cdot -1), (1 \cdot 0 \cdot 0) = 4, 1, 0, 4, 1, 0$$

$$R_z = A_{1g} \cdot E_g \cdot A_{2g} = (1 \cdot 2 \cdot 1), (1 \cdot -1 \cdot 1), (1 \cdot 0 \cdot -1), (1 \cdot 2 \cdot 1), (1 \cdot -1 \cdot 1), (1 \cdot 0 \cdot -1) = 2, -1, 0, 2, -1, 0$$

The  $R_x$  and  $R_y$  both reduce to an  $A_{1g}$ , an  $A_{2g}$ , and an  $E_g$ . Since both the  $R_x$  and  $R_y$  representations contain the  $A_{1g}$ , the  $A_{1g}$  to  $E_g$  transition will be allowed symmetrically through the  $R_x$  and  $R_y$  axes.  $\Delta J = 1$ , thereby allowing the transition through the J selection rule.

For  ${}^5D_0$  going to  ${}^7F_2$ , the  $A_{1g}$  to  $A_{1g}$  transition is again forbidden electronically as well as magnetically, and both of the  $A_{1g}$  to  $E_g$  transitions will be allowed symmetrically through the  $R_x$  and  $R_y$  axes but are forbidden since  $\Delta J = 2$  forbids magnetic transitions.

For  ${}^5D_0$  going to  ${}^7F_3$ , the  $A_{1g}$  to  $A_{1g}$  transition is forbidden, the two  $A_{1g}$  to  $A_{2g}$  transitions will be allowed symmetrically through the  $R_z$  axis but forbidden since  $\Delta J = 3$ , and the two  $A_{1g}$  to  $E_g$  transitions will be allowed symmetrically but forbidden since  $\Delta J = 3$  forbids magnetic transitions.

For  ${}^5D_1$  going to  ${}^7F_0$ , analysis should give a similar result as the  ${}^5D_0$  going to  ${}^7F_1$  in that the  $A_{2g}$  to  $A_{1g}$  transition will be allowed magnetically through the  $R_z$  axis and the  $E_g$  to  $A_{1g}$  transition will be allowed magnetically through the  $R_x$  and  $R_y$  axes.  $\Delta J = -1$ , thus allowing the both transitions through the J selection rule.

For  $^5D_1$  going to  $^7F_1$ , triple products for the transition from A2g to A2g levels are:

Electric:

$$\begin{aligned}x &= A2g^*A2g^*Eu = (1^*1^*2), (1^*1^*-1), (-1^*-1^*0), (1^*1^*-2), (1^*1^*1), (-1^*-1^*0) = 2, -1, 0, -2, 1, 0 \\y &= A2g^*A2g^*Eu = (1^*1^*2), (1^*1^*-1), (-1^*-1^*0), (1^*1^*-2), (1^*1^*1), (-1^*-1^*0) = 2, -1, 0, -2, 1, 0 \\z &= A2g^*A2g^*A2u = (1^*1^*1), (1^*1^*1), (-1^*-1^*-1), (1^*1^*-1), (1^*1^*-1), (-1^*-1^*1) = 1, 1, -1, -1, -1, 1\end{aligned}$$

Since none contains the A1g representation, no electronic transition is allowed.

Magnetic:

$$\begin{aligned}R_x &= A2g^*A2g^*Eg = (1^*1^*2), (1^*1^*-1), (-1^*-1^*0), (1^*1^*2), (1^*1^*-1), (-1^*-1^*0) = 2, -1, 0, 2, -1, 0 \\R_y &= A2g^*A2g^*Eg = (1^*1^*2), (1^*1^*-1), (-1^*-1^*0), (1^*1^*2), (1^*1^*-1), (-1^*-1^*0) = 2, -1, 0, 2, -1, 0 \\R_z &= A2g^*A2g^*A2g = (1^*1^*1), (1^*1^*1), (-1^*-1^*-1), (1^*1^*1), (1^*1^*1), (-1^*-1^*-1) = 1, 1, -1, 1, 1, -1\end{aligned}$$

The A2g to A2g transition will be forbidden magnetically.

Two other transitions which are a part of  $^5D_1$  going to  $^7F_1$ , those of A2g to Eg and Eg to A2g, both yield for their triple products:

Electric:

$$\begin{aligned}x &= A2g^*Eg^*Eu = (1^*2^*2), (1^*-1^*-1), (-1^*0^*0), (1^*2^*-2), (1^*-1^*1), (-1^*0^*0) = 4, 1, 0, -4, -1, 0 \\y &= A2g^*Eg^*Eu = (1^*2^*2), (1^*-1^*-1), (-1^*0^*0), (1^*2^*-2), (1^*-1^*1), (-1^*0^*0) = 4, 1, 0, -4, -1, 0 \\z &= A2g^*Eg^*A2u = (1^*2^*1), (1^*-1^*1), (-1^*0^*-1), (1^*2^*-1), (1^*-1^*-1), (-1^*0^*1) = 2, -1, 0, -2, 1, 0\end{aligned}$$

The x and y reducible representations both reduce to an A1u, an A2u, and an Eu. Since none of the representations contains A1g, the transition is electronically forbidden.

Magnetic:

$$\begin{aligned}R_x &= A2g^*Eg^*Eg = (1^*2^*2), (1^*-1^*-1), (-1^*0^*0), (1^*2^*2), (1^*-1^*-1), (-1^*0^*0) = 4, 1, 0, 4, 1, 0 \\R_y &= A2g^*Eg^*Eg = (1^*2^*2), (1^*-1^*-1), (-1^*0^*0), (1^*2^*2), (1^*-1^*-1), (-1^*0^*0) = 4, 1, 0, 4, 1, 0 \\R_z &= A2g^*Eg^*A2g = (1^*2^*1), (1^*-1^*1), (-1^*0^*-1), (1^*2^*1), (1^*-1^*1), (-1^*0^*-1) = 2, -1, 0, 2, -1, 0\end{aligned}$$

The Rx and Ry both reduce to an A1g, an A2g, and an Eg. Since both the Rx and Ry representations contain the A1g, the A1g to Eg transition will be allowed symmetrically through the Rx and Ry axes.  $\Delta J = 0$ , thereby allowing the transition through the J selection rule.

The Eg to Eg transition gives the following as triple products:

Electric:

$$\begin{aligned}x &= Eg^*Eg^*Eu = (2^*2^*2), (-1^*-1^*-1), (0^*0^*0), (2^*2^*-2), (-1^*-1^*1), (0^*0^*0) = 8, -1, 0, -8, 1, 0 \\y &= Eg^*Eg^*Eu = (2^*2^*2), (-1^*-1^*-1), (0^*0^*0), (2^*2^*-2), (-1^*-1^*1), (0^*0^*0) = 8, -1, 0, -8, 1, 0 \\z &= Eg^*Eg^*A2u = (2^*2^*1), (-1^*-1^*1), (0^*0^*-1), (2^*2^*-1), (-1^*-1^*-1), (0^*0^*1) = 4, 1, 0, -4, -1, 0\end{aligned}$$

The x and y reducible representations both reduce to an A1u, an A2u, and three Eu. The z reducible representation reduces to an A1u, an A2u, and an Eu. Since none of the representations contains the A1g representation, the transition is electronically forbidden.

Magnetic:

$$R_x = E_g \cdot E_g \cdot E_g = (2 \cdot 2 \cdot 2), (-1 \cdot -1 \cdot -1), (0 \cdot 0 \cdot 0), (2 \cdot 2 \cdot 2), (-1 \cdot -1 \cdot -1), (0 \cdot 0 \cdot 0) = 8, -1, 0, 8, -1, 0$$

$$R_y = E_g \cdot E_g \cdot E_g = (2 \cdot 2 \cdot 2), (-1 \cdot -1 \cdot -1), (0 \cdot 0 \cdot 0), (2 \cdot 2 \cdot 2), (-1 \cdot -1 \cdot -1), (0 \cdot 0 \cdot 0) = 8, -1, 0, 8, -1, 0$$

$$R_z = E_g \cdot E_g \cdot A_{2g} = (2 \cdot 2 \cdot 1), (-1 \cdot -1 \cdot 1), (0 \cdot 0 \cdot -1), (2 \cdot 2 \cdot 1), (-1 \cdot -1 \cdot 1), (0 \cdot 0 \cdot -1) = 4, 1, 0, 4, 1, 0$$

The  $R_x$  and  $R_y$  both reduce to an  $A_{1g}$ , an  $A_{2g}$ , and three  $E_g$ . The  $R_z$  reduces to an  $A_{1g}$ ,  $A_{2g}$ , and an  $E_g$ . Since all the  $R_x$ ,  $R_y$ , and  $R_z$  representations contain the  $A_{1g}$  representation, the  $E_g$  to  $E_g$  transition will be allowed symmetrically through the  $R_x$ ,  $R_y$ , and  $R_z$  axes.  $\Delta J = 0$ , thereby allowing the transition through the  $J$  selection rule.

For the  ${}^5D_1$  going to  ${}^7F_2$ , the  $A_{2g}$  to  $A_{1g}$  transition will be allowed through the  $R_z$  axis only, the  $A_{2g}$  to  $E_g$  transitions will be allowed through the  $R_x$  and  $R_y$  axes. The  $E_g$  to  $A_{1g}$  transition will be allowed magnetically. The  $E_g$  to  $E_g$  transitions will be allowed magnetically.

As stated in Chapter II, it will be assumed that a europium-containing molecule would have all representations as vibrational operators. Therefore all transitions are vibronically allowed.

In summary, this set of manifolds of the fluorescence spectra will contain a vibronically allowed transition for the  ${}^5D_0$  to  ${}^7F_0$  manifold. The  ${}^5D_0$  to  ${}^7F_1$  manifold will contain two magnetically allowed transitions, both also allowed vibronically. The  ${}^5D_0$  to  ${}^7F_2$  manifold will contain three vibronically allowed transitions. The  ${}^5D_0$  to  ${}^7F_3$  manifold will contain five vibronically allowed transitions. The  ${}^5D_1$  to  ${}^7F_0$  manifold will contain two magnetically allowed transitions, both of which are also vibronically allowed. The  ${}^5D_1$  to  ${}^7F_1$  manifold will contain three magnetically and vibronically allowed transitions and one transition allowed only vibronically. The  ${}^5D_1$  to  ${}^7F_2$  manifold will contain six magnetically and vibronically allowed transitions. The transitions allowed magnetically will usually be ten to one hundred times as strong as the exclusively vibronically allowed transitions, but this is a viable standard only within a single manifold.

## B. Calculations With Half-Integer J Values

The next series of calculations will deal with a  $\text{Nd}^{3+}$  ion which has half integer J values. The ion will be dealt with in the  $D_{2d}$  symmetry double group which has the character table shown in Table A2. The transitions that will be dealt with are those from the  $^4S_{3/2}$  J state to the four J states of the  $^4I$  ground state.

Table A2

 $D_{2d}$  Double Group Character Table

| $D_{2d}'$ | E | R  | $S_4,$<br>$S_4^3R$ | $S_4^3,$<br>$S_4R$ | $C_2,$<br>$C_2R$ | $2C_2',$<br>$2C_2'R$ | $2\sigma_d,$<br>$2\sigma_dR$ | dipole operators |
|-----------|---|----|--------------------|--------------------|------------------|----------------------|------------------------------|------------------|
| A1'       | 1 | 1  | 1                  | 1                  | 1                | 1                    | 1                            |                  |
| A2'       | 1 | 1  | 1                  | 1                  | 1                | -1                   | -1                           | Rz               |
| B1'       | 1 | 1  | -1                 | -1                 | 1                | 1                    | -1                           |                  |
| B2'       | 1 | 1  | -1                 | -1                 | 1                | -1                   | 1                            | z                |
| E1'       | 2 | 2  | 0                  | 0                  | -2               | 0                    | 0                            | x,y,Rx,Ry        |
| E2'       | 2 | -2 | 1.4                | -1.4               | 0                | 0                    | 0                            |                  |
| E3'       | 2 | -2 | -1.4               | 1.4                | 0                | 0                    | 0                            |                  |

## 1. Allowed Representations

For  $J = 3/2$ , the reducible representation equals:

$$E = 2 \cdot 3/2 + 1 = 4$$

$$R = -(2 \cdot 3/2 + 1) = -4$$

$$S_4 = [\sin((90^\circ + 180^\circ)(3/2 + 1/2))]/\sin((90^\circ + 180^\circ)/2) = 0$$

$$S_4^3R = -[\sin((270^\circ + 180^\circ)(3/2 + 1/2))]/\sin((270^\circ + 180^\circ)/2) = 0$$

$$S_4^3 = [\sin((270^\circ + 180^\circ)(3/2 + 1/2))]/\sin((270^\circ + 180^\circ)/2) = 0$$

$$S_4R = -[\sin((90^\circ + 180^\circ)(3/2 + 1/2))]/\sin((90^\circ + 180^\circ)/2) = 0$$

$$C_2 = [\sin(180^\circ(3/2 + 1/2))]/\sin(180^\circ/2) = 0$$

$$C_2R = -[\sin(180^\circ(3/2 + 1/2))]/\sin(180^\circ/2) = 0$$

$$C_2' = [\sin(180^\circ(3/2 + 1/2))]/\sin(180^\circ/2) = 0$$

$$C_2'R = -[\sin(180^\circ(3/2 + 1/2))]/\sin(180^\circ/2) = 0$$

$$\sigma_d = \sin(180^\circ(3/2 + 1/2)) = 0$$

$$\sigma_dR = -\sin(180^\circ(3/2 + 1/2)) = 0$$

Any state with  $J = 3/2$  will contain an E2' and an E3' level.

For  $J = 9/2$ , the reducible representation equals:

$$\begin{aligned}
 E &= 2 \cdot 9/2 + 1 = 10 \\
 R &= -(2 \cdot 9/2 + 1) = -10 \\
 S_4 &= [\sin((90^\circ + 180^\circ)(9/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = -1.4 \\
 S_4^3 R &= -[\sin((-90^\circ + 180^\circ)(9/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = -1.4 \\
 S_4^3 &= [\sin((-90^\circ + 180^\circ)(9/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = 1.4 \\
 S_4 R &= -[\sin((90^\circ + 180^\circ)(9/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = 1.4 \\
 C_2 &= [\sin(180^\circ(9/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2 R &= -[\sin(180^\circ(9/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' &= [\sin(180^\circ(9/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' R &= -[\sin(180^\circ(9/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 \sigma_d &= \sin(180^\circ(9/2 + 1/2)) = 0 \\
 \sigma_d R &= -\sin(180^\circ(9/2 + 1/2)) = 0
 \end{aligned}$$

Any state with  $J = 9/2$  will contain two  $E_2'$  and three  $E_3'$  levels.

For  $J = 11/2$ , the reducible representation equals:

$$\begin{aligned}
 E &= 2 \cdot 11/2 + 1 = 12 \\
 R &= -(2 \cdot 11/2 + 1) = -12 \\
 S_4 &= [\sin((90^\circ + 180^\circ)(11/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = 0 \\
 S_4^3 R &= -[\sin((-90^\circ + 180^\circ)(11/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = 0 \\
 S_4^3 &= [\sin((-90^\circ + 180^\circ)(11/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = 0 \\
 S_4 R &= -[\sin((90^\circ + 180^\circ)(11/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = 0 \\
 C_2 &= [\sin(180^\circ(11/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2 R &= -[\sin(180^\circ(11/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' &= [\sin(180^\circ(11/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' R &= -[\sin(180^\circ(11/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 \sigma_d &= \sin(180^\circ(11/2 + 1/2)) = 0 \\
 \sigma_d R &= -\sin(180^\circ(11/2 + 1/2)) = 0
 \end{aligned}$$

Any state with  $J = 11/2$  will contain three  $E_2'$  and three  $E_3'$  levels.

For  $J = 13/2$ , the reducible representation equals:

$$\begin{aligned}
 E &= 2 \cdot 13/2 + 1 = 14 \\
 R &= -(2 \cdot 13/2 + 1) = -14 \\
 S_4 &= [\sin((90^\circ + 180^\circ)(13/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = 1.4 \\
 S_4^3 R &= -[\sin((-90^\circ + 180^\circ)(13/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = 1.4 \\
 S_4^3 &= [\sin((-90^\circ + 180^\circ)(13/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = -1.4 \\
 S_4 R &= -[\sin((90^\circ + 180^\circ)(13/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = -1.4 \\
 C_2 &= [\sin(180^\circ(13/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2 R &= -[\sin(180^\circ(13/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' &= [\sin(180^\circ(13/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' R &= -[\sin(180^\circ(13/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 \sigma_d &= \sin(180^\circ(13/2 + 1/2)) = 0 \\
 \sigma_d R &= -\sin(180^\circ(13/2 + 1/2)) = 0
 \end{aligned}$$

Any state with  $J = 13/2$  will contain four  $E_2'$  and three  $E_3'$  levels.

For  $J = 15/2$ , the reducible representation equals:

$$\begin{aligned}
 E &= 2 \cdot 15/2 + 1 = 16 \\
 R &= -(2 \cdot 15/2 + 1) = -16 \\
 S_4 &= [\sin((90^\circ + 180^\circ)(15/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = 0 \\
 S_4^3 R &= -[\sin((-90^\circ + 180^\circ)(15/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = 0 \\
 S_4^3 &= [\sin((-90^\circ + 180^\circ)(15/2 + 1/2))] / \sin((-90^\circ + 180^\circ)/2) = 0 \\
 S_4 R &= -[\sin((90^\circ + 180^\circ)(15/2 + 1/2))] / \sin((90^\circ + 180^\circ)/2) = 0 \\
 C_2 &= [\sin(180^\circ(15/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2 R &= -[\sin(180^\circ(15/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' &= [\sin(180^\circ(15/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 C_2' R &= -[\sin(180^\circ(15/2 + 1/2))] / \sin(180^\circ/2) = 0 \\
 \sigma_d &= \sin(180^\circ(15/2 + 1/2)) = 0 \\
 \sigma_d R &= -\sin(180^\circ(15/2 + 1/2)) = 0
 \end{aligned}$$

Any state with  $J = 15/2$  will contain four  $E_2'$  and four  $E_3'$  levels.

For the transitions from the  $^4S_{3/2}$   $J$  state to the  $^4I_{9/2}$  ground state, there are possible transitions from an  $E_2'$  to  $E_2'$ ,  $E_2'$  to  $E_3'$ ,  $E_3'$  to  $E_3'$ , and  $E_3'$  to  $E_2'$ . Again, these will be allowed if the triple product of the representations of the two and the representation of a dipole operator contains the  $A_1'$  representation.

## 2. Transition Allowedness

For the  $E_2'$  to  $E_2'$  transition the products are

Electric:

$$\begin{aligned}
 x &= E_2'' E_2' E_1' = (2 \cdot 2 \cdot 2), (-2 \cdot -2 \cdot 2), (2 \cdot 0), (2 \cdot 0), (0 \cdot 0 \cdot -2), (0 \cdot 0 \cdot 0), (0 \cdot 0 \cdot 0) = 8, 8, 0, 0, 0, 0, 0 \\
 y &= E_2'' E_2' E_1' = (2 \cdot 2 \cdot 2), (-2 \cdot -2 \cdot 2), (2 \cdot 0), (2 \cdot 0), (0 \cdot 0 \cdot -2), (0 \cdot 0 \cdot 0), (0 \cdot 0 \cdot 0) = 8, 8, 0, 0, 0, 0, 0 \\
 z &= E_2'' E_2' B_2' = (2 \cdot 2 \cdot 1), (-2 \cdot -2 \cdot 1), (2 \cdot -1), (2 \cdot -1), (0 \cdot 0 \cdot 1), (0 \cdot 0 \cdot -1), (0 \cdot 0 \cdot -1) = 4, 4, -2, -2, 0, 0, 0
 \end{aligned}$$

Since 8, 8, 0, 0, 0, 0, 0 contains the  $A_1'$  representation and 4, 4, -2, -2, 0, 0, 0 does not, the transition will be allowed electronically through the  $x$  and  $y$  axes.

Magnetic:

$$\begin{aligned}
 R_x &= E_2'' E_2' E_1' = (2 \cdot 2 \cdot 2), (-2 \cdot -2 \cdot 2), (2 \cdot 0), (2 \cdot 0), (0 \cdot 0 \cdot -2), (0 \cdot 0 \cdot 0), (0 \cdot 0 \cdot 0) = 8, 8, 0, 0, 0, 0, 0 \\
 R_y &= E_2'' E_2' E_1' = (2 \cdot 2 \cdot 2), (-2 \cdot -2 \cdot 2), (2 \cdot 0), (2 \cdot 0), (0 \cdot 0 \cdot -2), (0 \cdot 0 \cdot 0), (0 \cdot 0 \cdot 0) = 8, 8, 0, 0, 0, 0, 0 \\
 R_z &= E_2'' E_2' A_2' = (2 \cdot 2 \cdot 1), (-2 \cdot -2 \cdot 1), (2 \cdot 1), (2 \cdot 1), (0 \cdot 0 \cdot 1), (0 \cdot 0 \cdot -1), (0 \cdot 0 \cdot -1) = 4, 4, 2, 2, 0, 0, 0
 \end{aligned}$$

Since all of the above triple products contain the  $A_1'$  representation, this transition would be allowed through all axes by the magnetic symmetry selection rules. However, it is disallowed since  $\Delta J$  is not 0, 1, or -1.

For the  $E_2'$  to  $E_3'$  and  $E_3'$  to  $E_2'$  transitions the products are

Electric:

$$\begin{aligned}x &= E2''E3'E1' = (2^*2^*2), (-2^*-2^*2), (-2^*0), (-2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\y &= E2''E3'E1' = (2^*2^*2), (-2^*-2^*2), (-2^*0), (-2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\z &= E2''E3'B2' = (2^*2^*1), (-2^*-2^*1), (-2^*-1), (-2^*-1), (0^*0^*1), (0^*0^*-1), (0^*0^*-1) = 4,4,2,2,0,0,0\end{aligned}$$

Since both contain the  $A1'$  representation, the transition will be allowed electronically through the x, y, and z axes.

Magnetic:

$$\begin{aligned}R_x &= E2''E3'E1' = (2^*2^*2), (-2^*-2^*2), (-2^*0), (-2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\R_y &= E2''E3'E1' = (2^*2^*2), (-2^*-2^*2), (-2^*0), (-2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\R_z &= E2''E3'A2' = (2^*2^*1), (-2^*-2^*1), (-2^*-1), (-2^*-1), (0^*0^*1), (0^*0^*-1), (0^*0^*-1) = 4,4,-2,-2,0,0,0\end{aligned}$$

The transition would be allowed through the  $R_x$  and  $R_y$  axes by the magnetic symmetry selection rules. However, it is disallowed since  $\Delta J$  is not 0, 1, or -1.

For the  $E3'$  to  $E3'$  transition the products are

Electric:

$$\begin{aligned}x &= E2''E2'E1' = (2^*2^*2), (-2^*-2^*2), (2^*0), (2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\y &= E2''E2'E1' = (2^*2^*2), (-2^*-2^*2), (2^*0), (2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\z &= E2''E2'B2' = (2^*2^*1), (-2^*-2^*1), (2^*-1), (2^*-1), (0^*0^*1), (0^*0^*-1), (0^*0^*-1) = 4,4,-2,-2,0,0,0\end{aligned}$$

Since 8,8,0,0,0,0 contains the  $A1'$  representation and 4,4,-2,-2,0,0,0 does not, the transition will be allowed electronically through the x and y axes.

Magnetic:

$$\begin{aligned}R_x &= E2''E2'E1' = (2^*2^*2), (-2^*-2^*2), (2^*0), (2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\R_y &= E2''E2'E1' = (2^*2^*2), (-2^*-2^*2), (2^*0), (2^*0), (0^*0^*-2), (0^*0^*0), (0^*0^*0) = 8,8,0,0,0,0,0 \\R_z &= E2''E2'A2' = (2^*2^*1), (-2^*-2^*1), (2^*-1), (2^*-1), (0^*0^*1), (0^*0^*-1), (0^*0^*-1) = 4,4,2,2,0,0,0\end{aligned}$$

Since all of the above triple products contain the  $A1'$  representation, this transition would be allowed through all axes by the magnetic symmetry selection rules. However, it is disallowed since  $\Delta J$  is not 0, 1, or -1.

From the above calculations it is inferred that the transitions from the  ${}^4S_{3/2}$  J state to the  ${}^4I_{9/2}$  ground state which are allowed electronically include those between an  $E2'$  level and two  $E2'$  levels, an  $E2'$  level and three  $E3'$  levels, an  $E3'$  level and two  $E2'$  levels, and an  $E3'$  level and three  $E3'$  levels. No transitions will be allowed magnetically.

For the transitions making up the  ${}^4S_{3/2}$  J state to the  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$ , and  ${}^4I_{15/2}$  J states, the same transitions are possible as those dealt with in the previous example. In summary, all the transitions will be allowed electronically and none magnetically ( $\Delta J$  is not 0, 1, or -1) for the four transition manifolds ( ${}^4S_{3/2}$  to  ${}^4I_{9/2}$ ,  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$ , and  ${}^4I_{15/2}$ ) discussed.

## VITA

Nathan Aaron Stump was born in LaGrange, Indiana on January 6, 1965.

Following his graduation from Prairie Heights High School in 1983, he entered Huntington College, at Huntington, Indiana. In the spring of 1987, Nathan was awarded a Bachelor of Science degree in Chemistry and an Associate of Arts degree in Computer Science. Following his graduation from Huntington, Nathan entered the Ph.D. program in chemistry at the University of Tennessee at Knoxville, Tennessee. During the first three years at Knoxville, Nathan served as a teaching assistant for the chemistry department. He was supported the final year and a half as a research assistant at the Transuranium Research Laboratory located at the Oak Ridge National Laboratory.