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# The absorption spectra and excited state relaxation properties of lanthanide and actinide halide vapor complexes. I. $ErCl_3(AlCl_3)_x^{a)}$

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The absorption spectrum of the vapor complex formed at elevated temperatures between  $\text{ErCl}_3$  and  $\text{AlCl}_3$  has been measured in the region 6000–44000 cm<sup>-1</sup>. The absorption band intensities were analyzed using the Judd–Ofelt theory for electric–dipole transitions. A good correlation between theory and experiment was obtained with the intensity parameters  $\Omega_2 = 25.8$ ,  $\Omega_4 = 2.70$ ,  $\Omega_6 = 2.01$ , all  $\times 10^{-20}$  cm<sup>2</sup>. Based on this analysis, the radiative lifetimes of several excited states were computed, and the principal paths for radiative relaxation of these states were determined. The relationship between the existence of intense hypersensitive bands in the spectrum of the vapor complex and the site symmetry of the Er atoms is discussed, as is the possible use of Rydberg and charge transfer states for optically pumping the  $f^n$  states.

### I. INTRODUCTION

The existence of metal halide vapor complexes at elevated temperatures has stimulated considerable interest in recent years. An example of the formation of such complexes, the reaction between solid (s),  $ErCl_3$ , and a molecular species of  $AlCl_3$  in the gas phase (g) to form a volatile complex containing  $ErCl_3$ . can be formally written:  $ErCl_3(s) + x AlCl_3(g)$ =ErCl<sub>3</sub>(AlCl<sub>3</sub>)<sub>r</sub>(g). Much of the emphasis has been on the nature and thermodynamic stability of the complexes formed,<sup>1</sup> and their use for synthesis via chemical transport.<sup>2</sup> At the present time, there is additional motivation for characterizing the spectroscopic and thermodynamic properties of lanthanide halide containing vapor complexes. Such complexes warrant serious consideration as energy storage media for high power optical gain systems.<sup>3</sup> Recently, we demonstrated for the first time that fluorescence between states within the  $4f^n$  configuration can be observed in lanthanide chloride-aluminum chloride vapor complexes, and that the lifetimes associated with certain excited states can approach their purely radiative limits.<sup>4,5</sup> Similar experiments with a terbium organometallic vapor complex were also successful in exciting fluorescence characteristic of the lanthanide ion, but very short fluorescent lifetimes were observed.<sup>6</sup> This was attributed to efficient paths for nonradiative relaxation provided by the light atoms in the organic complexing molecule. The halide complexes studied here exhibit much lower fundamental vibration frequencies and thus do not provide the same paths for nonradiative relaxation as were characteristic of the terbium organometallic species.

The nature of the NdCl<sub>3</sub>-AlCl<sub>3</sub> vapor complex system was investigated some years ago by Øye and Gruen,<sup>7</sup> and it remains the only lanthanide chloride-AlCl<sub>3</sub> complex for which absorption spectroscopic data have been published. Using similar techniques, we report here

the characteristics of the vapor complex formed between  $ErCl_3$  and  $AlCl_3$  with emphasis on the absorption of radiation in the optical region. In both the  $NdCl_3$ - $AlCl_3$  and  $ErCl_3$ - $AlCl_3$  systems, the apparent volatility of the lanthanide chloride (LnCl<sub>3</sub>) at elevated temperatures is greatly increased by the presence of AlCl<sub>3</sub>. This occurs via the formation of a volatile complex or series of complexes  $LnCl_3^{\circ}(AlCl_3)_x$ . The  $ErCl_3(AlCl_3)_x$ system exhibits a number of optical absorption bands characteristic of Er<sup>3+</sup> which while providing some insight into the structure of the vapor complex, also serve as a basis for carrying out an intensity analysis using the Judd-Ofelt theory of forced electric-dipole transition probabilities.<sup>8,9</sup> The parameters of this theory have been determined and then used to compute the radiative lifetimes of the longer-lived fluorescing states. This makes it possible to predict the principal paths for radiative relaxation of these states. Possible modes of optical excitation of the  $ErCl_3(AlCl_3)_x$ system are also discussed.

### II. EXPERIMENTAL

Absorption spectra were recorded in the same prismgrating spectrophotometer modified for use with samples at high temperature, and the same furnace system as was described by Øye and Gruen.<sup>7</sup>

Aluminum chloride was prepared by reacting 99.999% Al discs with HCl gas generated in a  $H_2SO_4$ -NaCl reactor. Anhydrous  $ErCl_3$  was synthesized in gram quantities from 99.9%  $Er_2O_3$  using a procedure in which the sesquioxide was dissolved in 6 M HCl; 6 mol NH<sub>4</sub>Cl/ mol Er were added and the resultant solution evaporated to dryness. The solid NH<sub>4</sub>Cl- $ErCl_3 \cdot 6H_2O$  mixture was then heated slowly under vacuum to 500 °C over a period of 8 hours to dehydrate the salt.<sup>10</sup>

The fused silica spectrophotometer cells had uv-grade windows and path lengths of 10 or 20 cm. These cells were loaded with  $ErCl_3$  in a dry box, attached to a vacuum system, and evacuated to  $<10^{-6}$  Torr. The AlCl<sub>3</sub> was prepared *in situ* as indicated in Fig. 1 and sublimed into the cell. The cell was sealed off under high vacuum.

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<sup>&</sup>lt;sup>a)</sup>Work performed under the auspices of the Division of Basic Energy Sciences of the Department of Energy.



FIG. 1. Apparatus for preparation of AlCl<sub>3</sub> and sublimation into the spectrophotometer cell C. D, filter frits; F, furnace; G, H<sub>2</sub>SO<sub>1</sub>-NaCl reactor; S, position of final seal off of cell from system; and T, liquid N<sub>2</sub> trap.

Molar absorptivities for the observed absorption bands were computed from the results of three separate experiments. Milligram quantities of ErCl<sub>3</sub> and sufficient AlCl<sub>3</sub> to insure complexing of all of the ErCl<sub>3</sub> were loaded into cells of known volume. The furnace temperature was progressively increased beyond the point at which all ErCl<sub>3</sub> was present in the vapor phase as indicated by constant values for the absorptivities of the major absorption bands. The results are shown in Table I. Assuming monatomic complexes, and determining the weight of ErCl<sub>3</sub> present by analytical methods subsequent to completion of each experiment, the molar absorptivity,  $\epsilon$ , at a given wave number is:  $\epsilon(\sigma) = A(\sigma)/cl$ , where  $A(\sigma)$  is the absorptivity at  $\sigma$  (cm<sup>-1</sup>), c is the concentration of Er (mol/l), and l is the optical path length of the cell (cm).

In addition to those experiments designed to establish the molar absorptivity of the most intense bands, a number of runs were made in which excess  $ErCl_3$  was present in the spectrophotometer cell with the AlCl<sub>3</sub>. The spectra could then be studied as a function of temperature and AlCl<sub>3</sub> pressure. Concentrations of the  $ErCl_{3}(AlCl_{3})_{x}$  complex were deduced in these cases using the molar absorptivities of the more intense bands,  $\epsilon_{(19100 \text{ cm}^{-1})} = 21.4 \pm 0.3 \text{ and } \epsilon_{(26300 \text{ cm}^{-1})} = 33.6 \pm 0.9 (1/2)$ mol cm). To provide the basis for intensity correlations, the areas under the absorption bands over the whole spectrum at several different temperatures and pressures of AlCl<sub>3</sub> were integrated using standard computer methods.<sup>11</sup> No significant departures from Beer's law, i.e., a strict proportionality between absorbance and concentration-path length, and no change in the ratios of major absorption band areas were noted at temperatures > 300 °C.

### **III. RESULTS**

### A. Absorption spectrum and structure of the $ErCl_3(AlCl_3)_x$ vapor complex

Absorption spectra of the  $ErCl_3(AlCl_3)_x$  vapor system at different pressures of  $AlCl_3$  were normalized using the molar absorptivities determined in the calibration experiments. A composite spectrum based on runs which optimized the details of the band structure in the various energy ranges is shown in Fig. 2. Energy level assignments were made based on previous analyses of the spectra of  $\mathrm{Er}^{3*}(\mathrm{aquo})^{11}$  and  $\mathrm{Er}^{3*}$ :  $\mathrm{LaF}_{3}$ , <sup>12</sup> since the centers of gravity of bands observed in the vapor complex are only slightly shifted from those observed in the condensed phases.

By recording spectra near 300 °C with a 10 cm cell we were able to clearly discern a group of bands near 39000 cm<sup>-1</sup>, the most intense of which may be identified primarily with the transition  ${}^{4}I_{15/2} - {}^{4}D_{7/2}$ . Above 33000 cm<sup>-1</sup> an increasingly intense background absorption has been subtracted from the spectrum shown in Fig. 2. This background is attributed to a charge transfer process characteristic of ErCl<sub>3</sub> in the vapor complex, and is discussed in a later section. Bands due to transitions to the first and second excited states in the ground term multiplet,  ${}^{4}I_{15/2} - {}^{4}I_{13/2}$ ,  ${}^{4}I_{11/2}$ , were also observed, so that the spectral region covered is practically as extensive as that observed for  $Er^{3+}(aquo)$ .<sup>11</sup> The vapor complex spectrum is dominated by the intense hypersensitive<sup>13, 14</sup> transitions:  ${}^{4}I_{15/2} - {}^{2}H_{11/2}$ (19100 cm<sup>-1</sup>) and  ${}^{4}I_{15/2} - {}^{4}G_{11/2}$  (26300 cm<sup>-1</sup>).

TABLE I. Molar absorptivity data for the principal bands in  $ErCl_3(AlCl_3)_x$ .

Cell data	Band wave number (cm <sup>-1</sup> )	A <sup>b</sup>	€ <sup>b</sup> (1/mol cm)
$P_{\rm Al_{2}Cl_{2}}^{0}(\rm{atm})^{a} = 7.0 \times 10^{-3} T(\rm{K})$	19100	0.0388	21.6
wt. $(ErCl_3) = 1.4 \text{ mg}$		(14)	(0.8)
l = 20  cm			
$V = 57.1 \text{ cm}^3$	26300	0.0572	31.9
$T_{\min} = 725 \text{ K}$		(38)	(2.1)
$P_{Al_2Cl_2}^0(\text{atm}) = 3.47 \times 10^{-3} T(\text{K})$	19100	0.167	22.6
wt. $(ErCl_3) \approx 5.7 \text{ mg}$		(5)	(.7)
l = 20  cm			
$V = 56.5 \text{ cm}^3$	26300	0.238	32.3
<i>T</i> <sub>min</sub> = 968 K		(19)	(2.6)
$P_{Al_{a}Cl_{a}}^{0}(\text{atm}) = 8.24 \times 10^{-3} T(\text{K})$	19100	0.422	21.0
wt. $(ErCl_3) = 15.9 \text{ mg}$		(6)	(0.4)
<i>l</i> = 9.4 cm			
$V = 27.3 \text{ cm}^3$	26300	0.664	34.2
$T_{\min} = 692 \text{ K}$		(20)	(1.0)
Weighted average	19100		$21.4 \pm 0.3$
_ ~	26300		$33.6 \pm 0.9$

 ${}^{a}P^{0}_{Al_{2}Cl_{6}}$  is the pressure of the dimer computed assuming all AlCl<sub>3</sub> is in the gas phase (ideal gas law) and no monomer is present

<sup>b</sup>Mean errors indicated in parentheses.



FIG. 2. Absorption spectrum of  $ErCl_3(AlCl_3)_x$ . Free-ion levels (for  $Er^{3*}$  aquo<sup>11</sup>) are indicated.

In agreement with experimental results reported for the  $NdCl_3(AlCl_3)_x$  system,<sup>7</sup> the relatively weak associative character of the ErCl<sub>3</sub>-AlCl<sub>3</sub> vapor complex was confirmed by the lack of any evidence for a stable solid phase. When mixtures of ErCl<sub>3</sub> and AlCl<sub>3</sub> were heated in sealed tubes to 600-700 °K, then cooled and the contents examined using x-ray powder diffraction methods, only patterns characteristic of pure AlCl<sub>3</sub> and pure ErCl<sub>3</sub> phases were discerned. Some increased stability of an  $ErCl_3$  solid complex might have been expected. In the case of  $NdCl_3$  and  $AlCl_3$ , two different structural types are involved.  $NdCl_3$  has the hexagonal  $UCl_3$ -type structure, space group  $C_{6h}^2 - C_{63}^2/m$ , while AlCl<sub>3</sub> has a monoclinic structure, space group  $C_{3h}^2 - C2/m$ . In contrast,  $ErCl_3$  and the other lanthanide chlorides heavier than TbCl<sub>3</sub> are all isostructural with AlCl<sub>3</sub>.<sup>15</sup> If, however, we compare the volatility of the  $NdCl_3(AlCl_3)_r$ and  $ErCl_3(AlCl_3)$ , vapor complexes, we find greater volatility in the  $ErCl_3(AlCl_3)_x$  system. Thus at ~740 °K and  $P_{Al_2Cl_6}$  = 3.7 atm, the concentration of Nd atoms is ~ 2.2×10<sup>17</sup>/cm<sup>3</sup>, while under essentially the same conditions the value for Er is  $6.2 \times 10^{17}$ /cm<sup>3</sup>. One might, therefore, expect to obtain evidence for some differences in bonding in the two vapor phase systems.

Since intense (hypersensitive) absorption bands dominate the spectra of both NdCl<sub>3</sub>(AlCl<sub>3</sub>)<sub>x</sub> and  $ErCl_3(AlCl_3)_x$ , and are of potential value as pump bands for laser applications, it is pertinent to examine their relationship to the structure of the complexes. A number of authors have attempted to account for the variation in intensity of bands associated with hypersensitive transitions in different conditions of bonding but no single mechanism appears to encompass all of the experimental observations.<sup>13, 14, 16, 17</sup> A common element in most current theories is a restriction on the lanthanide site symmetries in which the increased intensity would be expected.

Most of what is known about the composition and structure of the  $LnCl_3$ -AlCl<sub>3</sub> vapor complexes is based on indirect measurements. The NdCl<sub>3</sub>-AlCl<sub>3</sub> complex appears to exhibit a Nd: Al ratio of ~1:3.5, suggesting the existence of at least two vapor species, i.e., Nd(AlCl<sub>4</sub>)<sub>3</sub> or NdCl(AlCl<sub>4</sub>)(Al<sub>2</sub>Cl<sub>7</sub>), and Nd(AlCl<sub>4</sub>)<sub>2</sub>(Al<sub>2</sub>Cl<sub>7</sub>) or NdCl(Al<sub>2</sub>Cl<sub>7</sub>)<sub>2</sub>.<sup>7</sup> Two likely species would be Nd(AlCl<sub>4</sub>)<sub>3</sub> and Nd(AlCl<sub>4</sub>)<sub>2</sub>(Al<sub>2</sub>Cl<sub>7</sub>) since they both permit six coordination for Nd. Analogous structures would be anticipated in the ErCl<sub>3</sub>-AlCl<sub>3</sub> system.

Both of the indicated vapor species would require considerable distortion from a regular octahedral configuration in either the Nd or Er system. For example, the calculated Er-Cl bond length for six-coordinate Er is 0.89+1.81=2.70 Å.<sup>18</sup> This distance might be reduced ~ 0.05 Å by the fact that the chloride ion is twofold rather than sixfold coordinated. A regular octahedral arrangement would give Cl-Cl separations of ~ 3.75 Å. Work on the Al<sub>2</sub>Cl<sub>6</sub> vapor and liquid systems<sup>19,20</sup> indicates, however, that the bridging Cl-Cl separations are only 2.83 and 3.28 Å, respectively. Thus, the



grouping would probably assume an intermediate configuration between the 3.75 and 2.83 Å Cl-Cl separations, and result in a rather severely distorted octahedral arrangement about the Er ion. The  $[Al_2Cl_7]^$ ion when bound in a chelating fashion



would probably permit a Cl-Cl distance near 3, 75 Å but this would still leave two  $[AlCl_4]^-$  groups bound to

TABLE II. Oscillator strengths for  $ErCl_3(AlCl_3)_x$ .

Spectral range (cm <sup>-1</sup> )	S'L'J'	f expt.	f calc. <sup>a</sup>	
6400-6800	4/13/2	1.6×10 <sup>-6</sup>	1.6×10-6	
9090-10500	${}^{4}I_{11/2}$	1.1	1.0	
14100-15600	<sup>4</sup> F <sub>9/2</sub>	2.5	2.5	
17700-18300	<sup>4</sup> S <sub>3/2</sub>	1.2	0.55	
18300-19500	${}^{2}H_{11/2}$	24.0	25.7	
19800-20700	${}^{4}\!F_{7/2}$	2.1	2.3	
21400-22600	${}^{4}\!F_{5/2} + {}^{4}\!F_{3/2}$	0.8	1.06	
23800-24800	$({}^{2}G, {}^{4}F, {}^{2}H)_{9/2}$	1.1	0.83	
25300-26700	${}^{4}G_{11/2}$	43.2	45.3	
26700-28200	${}^{4}G_{9/2} + {}^{2}K_{15/2} + {}^{2}G_{7/2}$	4.2	0.04 MD <sup>b</sup> 3.6 ED	
37700-39700	${}^{2}D_{5/2} + {}^{4}D_{7/2}$	18.5	6.6 <sup>c</sup>	

<sup>a</sup> $\Omega_2 = 25.8 \pm 0.5 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 2.70 \pm 0.9 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_6 = 2.01 \pm 0.4 \times 10^{-20} \text{ cm}^2$ .

<sup>b</sup>Magnetic dipole contribution computed from values given in Ref. 11.

<sup>c</sup>Not included in parameter fitting.

the  $Er^{3+}$  ion requiring much lower C1-Cl separations in the bridging atoms.

Evidence that the symmetry of the Er site does not approach an octahedral arrangement is conclusively obtained from the fact that normal<sup>11</sup> intensities are associated with most of the observed transitions. As the site symmetry of a lanthanide ion approaches an octahedral configuration, the intensities of the f - f transitions are greatly reduced and approach zero.<sup>8</sup> The expected distortion required to bond several AlCl<sub>3</sub> molecules to one molecule of ErCl<sub>3</sub> suggests that the actual symmetry will be rather low. While a low site symmetry would also be consistent with the observation of intense hypersensitive transitions in the Nd and Er vapor complexes,<sup>14</sup> the existence of these intense bands does not at present identify a particular symmetry.

#### B. Analysis of transition probabilities

The use of the Judd–Ofelt theory of electric dipole transitions in the calculation of transition probabilities within the  $f^n$  configuration has been discussed in detail in the literature.<sup>11, 21</sup> We express the oscillator strength f in terms of the integrated intensity of a given absorption band as

$$f = \frac{1}{nl} \frac{mc^2}{\pi e^2} \int_{\text{band}} A(\sigma) d\sigma , \qquad (1)$$

where A is the absorptivity of the band at wave number  $\sigma$  (cm<sup>-1</sup>), m and e are the mass and charge of the electron, c is the velocity of light, n is the number density of lanthanide ions (number/cm<sup>3</sup>), and l is the optical path length (cm). The transitions are attributed to absorption of energy via electric and magnetic dipole mechanisms,  $f = f_{\rm ED} + f_{\rm MD}$ , using the expression<sup>22</sup>

$$f = \frac{8\pi^2 m c \sigma}{3he^2(2J+1)} \left[\chi_{S} + n\mathfrak{M}\right],\tag{2}$$

where  $\chi = (n^2 + 2)^2/9n$ , *n* is the bulk index of refraction at  $\sigma$ , and \$ and  $\mathfrak{M}$  represent the matrix elements of the electric and magnetic dipole operators, respectively, joining an initial state *J* to an excited state *J'*. \$ can be expressed in the form

$$S = e^2 \sum_{\lambda=2, 4, 6} \Omega_{\lambda}(\psi J \mid |\mathbf{U}^{(\lambda)}| \mid \psi' J')^2, \qquad (3)$$

and  $\mathfrak{M}$  is given by<sup>23</sup>

$$\mathfrak{M} = e^2 / 4m^2 c^2 (\psi J | |\mathbf{L} + 2\mathbf{S} | |\psi' J')^2.$$
(4)

The quantities  $\Omega_{\lambda}$  are treated as adjustable parameters to be evaluated from a fit to experimental data. The matrix elements of  $\mathbf{U}^{(\lambda)}$  recently computed for  $\mathrm{Er}^{3*}$ :  $\mathrm{LaF}_3^{-1}$ : were used in the calculations. Details of the calculations have already been discussed.<sup>11</sup> A comparison of the experimental oscillator strengths for the  $\mathrm{ErCl}_3(\mathrm{AlCl}_3)_x$ vapor complex to those computed using an optimized set of  $\Omega_{\lambda}$  values is given in Table II. Data for the band near 38900 cm<sup>-1</sup> was not included in the fit since, as was the case for  $\mathrm{Er}^{3*}(\mathrm{aquo})$ ,<sup>11</sup> the calculated oscillator strength is only approximately one half that actually observed. No explanation is offered.

The values of  $\Omega_{\lambda}$  determined for the ErCl<sub>3</sub>(AlCl<sub>3</sub>)<sub>x</sub> vapor complex are intermediate between those for  $Er^{3+}$ in molten  $LiNO_3$ -KNO<sub>3</sub> eutetic at 200 °C,<sup>23</sup> and those reported by Gruen, DeKock, and McBeth for binary erbium halide vapors.<sup>24</sup> In both the latter cases, intense bands were observed corresponding to the transitions to the  $^{2}H_{11/2}$  and  $^{4}G_{11/2}$  states. The  $\Omega_{\lambda}$  values for ErCl<sub>3</sub>(AlCl<sub>3</sub>)<sub>x</sub> are similar in magnitude to those derived by Krupke<sup>3</sup> from an intensity analysis of the published spectrum of  $NdCl_3(AlCl_3)_r$ . <sup>7</sup> Values of  $\Omega_1$  for several Er-containing systems are shown in Table III. They reflect mainly the sensitivity of  $\Omega_2$  to the oscillator strengths of the hypersensitive transitions whereas relatively small changes in  $\Omega_4$  and  $\Omega_6$  show the consistency in oscillator strengths of nonhypersensitive transitions regardless of phase. The apparent increase in values of  $\Omega_4$  and  $\Omega_6$  in the gas phase compared to condensed phases is in part a function of the refractive index correction which is  $\sim 1$  for vapors and > 1 for condensed phases.

It should be pointed out that one of the assumptions of the Judd-Ofelt theory is that all of the crystal-field components of the ground state are equally populated. Thus, the results obtained with the vapors much more closely approach the conditions of the theory than those usually reported for systems at room temperature.

### C. Excited state relaxation and possibilities for optical pumping

In evaluating the  $LnCl_3(AlCl_3)_x$  vapor complexes as potential optical gain media it is important to establish the paths of excited state relaxation. Based on the analysis of the absorption of radiant energy by the complex, we can compute the radiative lifetime of any excited state and the branching ratios to all states lower in energy than the fluorescing state. Following

TABLE III. Values of  $\Omega_{\lambda}$  for  $Er^{3+}$  in various systems.

×10 <sup>-20</sup> cr					$n^2$	
System	Phase	<b>T</b> °C	$\Omega_2$	$\Omega_4$	$\Omega_6$	Ref.
Er <sup>3+</sup> (aquo)	Liquid	25	1.59	1.95	1.90	11
Er <sup>3+</sup> : YAlO <sub>3</sub>	Solid	25	1.06	2.63	0.78	a
Er <sup>3+</sup> : LiNO <sub>3</sub> – KNO <sub>3</sub>	Liquid	200	15.8	1.84	1.39	23
NdCl <sub>3</sub> (AlCl <sub>3</sub> ) <sub>x</sub>	Vapor	$\sim 400$	18.0	4.80	3.90	3,7
$ErCl_3(AlCl_3)_x$	Vapor	~400	25.8	2.70	2.01	Present work
Er(thd)3 <sup>b</sup>	Vapor	288	46	2.70	3.70	24
ErBr <sub>3</sub>	Vapor	1105	60	1.47	1.66	24

<sup>a</sup>M. J. Weber, Proceedings of the 10th Rare Earth Research Conference (Tech. Information Center, Oak Ridge, TN, 1973), Vol. 2.

<sup>b</sup>2, 2, 6, 6-tetramethyl-3, 5-heptanedionate.

Krupke,<sup>22</sup> the rate of radiative relaxation of an excited state  $\psi J$  to a particular lower-lying state  $\psi' J'$  is

$$A(\psi J, \psi' J') = \frac{64\pi^4 \sigma^3}{3h(2J+1)} [\chi' s + n^3 \mathfrak{M}], \qquad (5)$$

where  $\sigma$  (cm<sup>-1</sup>) is the wave number gap between  $\psi J$  and  $\psi'J'$ ,  $\chi' = n(n^2 + 2)^2/9$ , and the expressions for s and  $\mathfrak{M}$  are those given in Eqs. (3) and (4). Since excited state relaxation in general involves transitions to several lower-lying states, the total radiative relaxation rate  $A_T(\psi J)$  is given by

$$A_T(\psi J) = \sum A(\psi J, \psi' J'),$$

where the sum runs over all states with energy less than  $(\psi J)$ . The branching ratio to a particular state is defined by

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

and the total radiative lifetime of a state  $\tau_R(\psi J) = 1/A_T(\psi J)$ .

As a result of experimental lifetime studies with  $NdCl_{3}(AlCl_{3})_{x}^{4}$  and  $TbCl_{3}(AlCl_{3})_{x}^{5}$  we can predict that when the energy gap between adjacent energy levels in this type of vapor complex is less than 4000 cm<sup>-1</sup>, nonradiative mechanisms (similar to multiphonon mechanisms in solids) will be an important mode for depopulating the excited state. The free-ion energy level scheme indicated in Fig. 2 shows that the largest energy gaps in the visible near-infrared range for which fluorescent radiation to lower energy states may be detectable are associated with the  ${}^{4}S_{3/2}$  (18200 cm<sup>-1</sup>),  ${}^{4}F_{9/2}$  (15400 cm<sup>-1</sup>),  ${}^{4}I_{11/2}$  (10200 cm<sup>-1</sup>), and  ${}^{4}I_{13/2}$  (6500 cm<sup>-1</sup>) states. The radiative lifetimes and branching ratios computed for these states are summarized in Table IV, The observed lifetimes of these states except that for  ${}^{4}I_{13/2}$ , are expected to be controlled by nonradiative relaxation processes, and thus will lie at most in the microsecond range.

Calculations describing the radiative relaxation of the  ${}^{4}S_{3/2}$  state are of interest since they indicate strong branching to the  ${}^{4}I_{13/2}$  and  ${}^{4}I_{15/2}$  states which would re-

sult in detectable fluorescence at ~ 12000 and 18000 cm<sup>-1</sup>, respectively. In principle it should be possible to optically pump the intense  ${}^{2}H_{11/2}$  state with a narrow band laser at ~ 19100 cm<sup>-1</sup>, and observe the indicated fluorescence. There will be no magnetic dipole contribution to these transitions, nor is the magnitude of  $\Omega_{2}$  a factor, since  $|\Delta J| = 5$  and 6. As can be seen from the data given in Table IV, radiative relaxation of the other states cited will be sensitive to the value of  $\Omega_{2}$ , which is very large in this case, and will also have magnetic dipole contributions.

We have already referred to the possibility for optical pumping presented by the existence of intense hypersensitive transitions in the  $ErCl_3(AlCl_3)_x$  vapor complex. Much more attractive possibilities for pumping could be associated with the presence of accessible Rydberg  $(4f^n - 4f^{n-1}5d)$  or charge transfer states (CTS). Systematics make it possible to predict that the lowest free-ion state in the next higher Er<sup>3+</sup> configuration  $(4f^{10}5d, {}^{6}L_{17/2})$  will lie near 83000 cm<sup>-1</sup>.<sup>25</sup> Assuming a stabilization energy in the  $ErCl_3(AlCl_3)_x$  complex of ~2.48 eV based on the observation of  $f^7d$  states in the  $\text{TbCl}_3(\text{AlCl}_3)_x$  vapor complex,<sup>26</sup> the  ${}^6L_{17/2}$  state of the  $f^{10}d$  configuration in  $Er^{3+}$  would lie near 63000 cm<sup>-1</sup>. Thus we would not expect Rydberg states of  $Er^{3+}$  to be accessible within the energy range of interest here (< 50000  $\,{\rm cm^{-1}})$  . However, evidence indicates that charge transfer absorption does occur at  $< 50000 \text{ cm}^{-1}$ .

An absorption that increases rapidly with wavelength in the high energy range for the  $\text{ErCl}_3(\text{AlCl}_3)_x$  vapor complex was cited earlier and the absorption bands indicated in Fig. 2 were corrected for this background. Typical results are shown in Fig. 3 in which uncorrected absorption spectra taken with the same cell at different temperatures are superimposed. Comparison of the absorption edges in the vapor complex with similar edges in pure  $\text{Al}_2\text{Cl}_6$  vapor, revealed an apparent red shift of the complex with respect to the  $\text{Al}_2\text{Cl}_6$  of approximately 10–15 nm at each temperature shown.

TABLE IV. Calculated reduced matrix elements of  $[U^{(k)}]^2$ , branching ratios, and radiative lifetimes associated with certain excited states of  $\operatorname{ErCl}_3(\operatorname{AlCl}_3)_x$ .

ψJ	<b>∉'J'</b>	Initial state	Final state	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$	β <sub>R</sub>	$ au_R(\psi J)$ (ms)
4S3/2	${}^{4}\!F_{9/2}$	18200	15400	0	0.0001	0.0217	0	1.31
-, -	4I3/2		12400	0	0.0766	0,2580	0.04	
	${}^{4}I_{11/2}$		10200	0	0.0047	0.0776	0.02	
	$4I_{13/2}$		6500	0	0	0.3428	0.28	
	4/15/2		0	0	0	0.2231	0.66	
${}^{4}\!F_{9/2}$	419/2	15400	12400	0,1190	0,0060	0.0175	0.02	1.34
	$4I_{11/2}$		10200	0.0719	0,0096	1.2578	0.08	
	$4I_{13/2}$		6500	0,0110	0,1543	0.0874	0.06	
	4/15/2		0	0	0,5587	0,4634	0.84	
4/9/2	<sup>4</sup> <i>I</i> <sub>11/2</sub>	12400	10200	0,0020	0,0692	0.1579	0.05	11.9ª
	4/13/2		6500	0,0003	0.0083	0.7073	0.25	
	4/15/2		. 0	0	0.1549	0,0061	0.70	
4111/2	$4I_{13/2}$	10200	6500	0,0333	0,1706	1,0877	0.25	7.81ª
	4/15/2		0	0.0282	0,0003	0.3963	0.75	_
4113/2	<sup>4</sup> / <sub>15/2</sub>	6500	0	0,0195	0.1172	1,4301	1.0	6.54 <sup>a</sup>

<sup>a</sup>Significant magnetic dipole contribution.

#### J. Chem. Phys., Vol. 68, No. 9, 1 May 1978



FIG. 3. Absorption spectrum of  $\text{ErCl}_3(\text{AlCl}_3)_x$  vapor in the ultraviolet range. *A*, cell background at 25 °C due to absorption of silica windows only. *B*, *C*, and *D*, vapor complex spectra at 249, 311, and 400 °C, respectively.

In both pure  $Al_2Cl_6$  and the vapor complex we attribute the absorption edges to a transfer of charge from filled molecular orbitals associated primarily with the Cl<sup>-</sup> ligands to the metal ion. That intense CTS characteristic of Er-Cl bonds could have their actual maxima at somewhat higher energies and show tailing effects into the 40-45000 cm<sup>-1</sup> range is consistent with observations of this type of absorption edge in the spectra of the lanthanides in molten LiCl-KCl eutectic at ~400 °C,<sup>27</sup> as well as with the systematics of CTS deduced by Jørgensen.<sup>28</sup> The results indicate that at a given temperature there exists a limited region in the ultraviolet in which it would be possible to preferentially excite the CTS of the complex. At higher energies essentially all radiation would be absorbed by the Al<sub>2</sub>Cl<sub>6</sub>.

The transfer of energy from excited CTS to states within the  $4f^n$  configuration has been explored in lanthanide doped solid state host lattices<sup>29,30</sup> and recently reviewed by Blasse.<sup>31</sup> The excitation of CTS is established as a viable mechanism for optically pumping  $f^n$  states in condensed phases, but does not appear to have been studied in vapor phase compounds of the lanthanides. We are currently exploring the relaxation dynamics of such systems.

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