VAPOR PHASE SPECTROSCOPY OF COMPLEX LANTHANUM HALIDE--ALUMINUM HALIDE MOLECULAR SPECIES

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Chemistry Division
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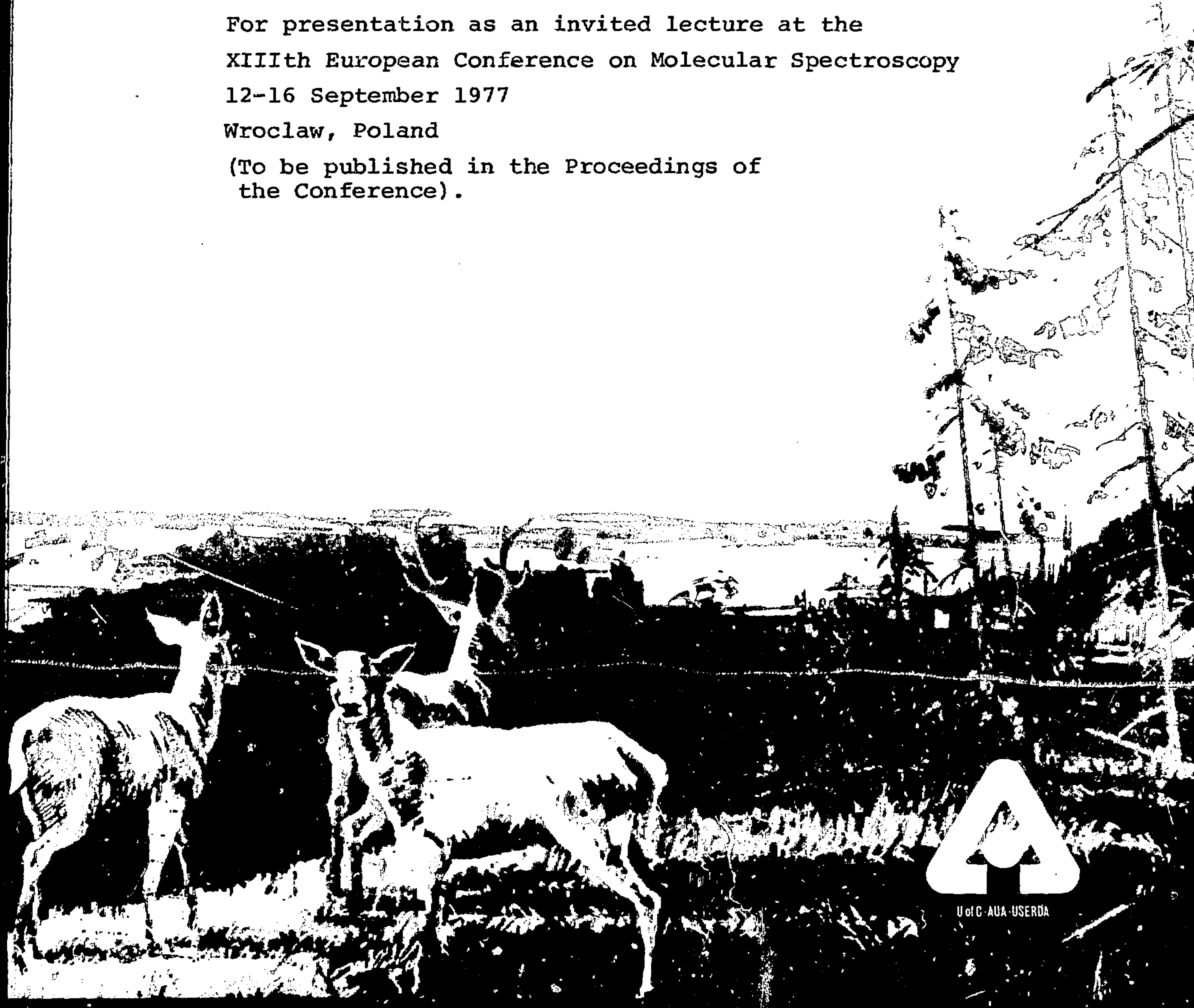

Vapor phase spectroscopy of complex lanthanide halide-aluminum halide molecular species*

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The vapor pressure of many binary metal halides at elevated temperatures can be greatly enhanced by the formation of complexes with a second more volatile metal halide. Thus, for example, the volatility of $ErCl_3(s)$ at 966°K is increased by a factor of 10^4 in the presence of excess $AlCl_3$:

$$ErCl_3(s) + x/2\ Al_2Cl_6(g) \rightleftarrows ErCl_3(AlCl_3)_x \qquad (1)$$

There has been considerable recent interest in the nature and thermodynamic properties of vapor complexes of this type, and in their use for novel inorganic syntheses and single crystal growth.[1,2] Reaction (1) is quite general, involving many different reaction pairs over the periodic table, although most such complexes are very weak, and exist only in the vapor phase.

Our interest in these systems stems from the fact that they constitute a means of achieving significant concentrations of lanthanides in the vapor phase at rather moderate temperatures. They are therefore conducive to fundamental studies of the mechanisms of absorption of radiation and of excited state

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relaxation processes in gases. They are also of importance as potential optical gain media in very high power laser applications such as those associated with laser fusion.[3] The present paper summarizes some of our recent work on the spectroscopic properties of lanthanide chloride vapor complexes with $AlCl_3$.

1. EXPERIMENTAL

Absorption spectra were recorded in a prism-grating double beam spectrophotometer (Cary 14H) modified for measurement of samples at high temperature. The spectrophotometer and furnace designs have been described previously.[4] Sample cells were fabricated from fused silica and were 10 cm or 20 cm in path length. The anhydrous lanthanide and aluminum halides were prepared using standard vacuum system techniques and all sample handling was carried out in dry atmosphere glove boxes. For the fluorescence studies the excitation source was a xenon lamp. Fluorescence was monitored by a 1 meter monochromator equipped with a photomultiplier tube and lifetimes were measured using a Tektronics 7904 oscilloscope.[5]

2. ABSORPTION SPECTRUM OF $ErCl_3(AlCl_3)_x$

Without the loss of any generality, we use here the specific example of the $ErCl_3(AlCl_3)_x$ vapor complex. For present purposes, where the temperature range of interest is ∿300-500°C, the equilibrium reaction is between a solid phase of low volatility (1) and the gas phase comprised primarily of the aluminum chloride dimer, $Al_2Cl_6(g)$.[6]

With $P_{Al_2Cl_6} >> P_{complex}$, we recognize that several different vapor complexes may exist at any given temperature (and $AlCl_3$ pressure) and use the expression $ErCl_3(AlCl_3)_x$ to represent their total concentration. The absorption spectra of systems of this type reveal the sharp f → f transitions characteristic of trivalent lanthanide ions (Ln^{3+}), and can be used to deduce the number density of these ions after appropriate calibration experiments have been completed.[4] The spectrum of the $ErCl_3(AlCl_3)_x$ vapor complex, shown in Fig. 1, is dominated by intense bands due to hypersensitive transitions[7] to the ${}^2H_{11/2}$ and ${}^4G_{11/2}$ states. These will be mentioned later. The absorption due to the Al_2Cl_6 host gas in the visible-ultraviolet range occurs at $>42000\ cm^{-1}$. In order to facilitate the comparison of intensities of bands observed in the gas phase to those reported in other phases, it is advantageous to determine the parameters of the Judd-Ofelt theory.

3. JUDD-OFELT ANALYSIS OF BAND INTENSITIES

The process of absorption of radiation by a lanthanide ion at $\sigma(cm^{-1})$ can be expressed quantitatively in terms of the area under a normalized absorption band:

$$f_{EXPT} = \frac{1}{\eta \ell} \frac{mc^2}{\pi e^2} \int_{band} A(\sigma)\, d\sigma \qquad (2)$$

where A is the absorptivity at $\sigma(\mathrm{cm}^{-1})$, η is the number density of lanthanide ions $(\mathrm{number/cm}^3)$, ℓ is the optical path (cm) and the other constants have their usual meaning. This normalized band area can then be related to the computed band intensity where absorption of radiation occurs via electric and magnetic dipole mechanisms, $f_{EXPT} = f_{ED} + f_{MD}$. This yields the expression:

$$f_{EXPT} = \frac{8\pi^2 mc\sigma}{3he^2(2J+1)} [\chi\ S_{ED} + n\ S_{MD}] \qquad (3)$$

where n is the refractive index of the medium, $\chi = (n^2+2)^2/9n$, and S_{ED} and S_{MD} are the electric and magnetic dipole line strengths, respectively.

Following the Judd-Ofelt analysis[8,9] of electric dipole transitions, we can express S_{ED} for the transition from an initial state ψJ to a final state $\psi'J'$ in the form[10]

$$S_{ED} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda (\psi J||U^{(\lambda)}||\psi'J')^2 \qquad (4)$$

where the quantities Ω_λ are treated as adjustable parameters related to the environment of the ion, and $\underset{\sim}{U}^{(\lambda)}$ is a unit tensor operator of rank λ. Experimentally we observe that the energies characteristic of absorption bands in the spectra of $LnCl_3(AlCl_3)_x$ vapor complexes are only slightly perturbed from those in well analyzed systems such as Ln^{3+}(aquo).[11] As a consequence, the matrix elements of $\underset{\sim}{U}^{(\lambda)}$ which have been computed based on the energy level analyses of the aquo ion spectra can also be used for the vapor complex spectra. The magnetic dipole line strength,

$$S_{MD} = e^2(\psi J||L+2S||\psi'J')^2/4m^2c^2 \qquad (5)$$

for those few transitions where the contribution is significant, can be evaluated exactly from matrix elements computed for Ln^{3+}(aquo). The value of f_{EXPT} is then corrected prior to determining the values of Ω_λ via a least squares fitting process. Details of the band analysis have been published.[11]

The results of the intensity analysis of the spectrum of $ErCl_3(AlCl_3)_x$ are given in Table I. A good fit to the experimental data for bands with widely different intensities was achieved. The resulting parameters Ω_λ can then be compared to those determined for Er^{3+} in a variety of other hosts and at other temperatures, as shown in Table II.

The values of Ω_4 and Ω_6 are found to vary only slightly with phase and host, whereas Ω_2 shows a significant change. Based on this comparison of parameters, we can exclude any point symmetry for Er^{3+} in the vapor complex that possesses an inversion operator. In such a case the absorption bands would diminish greatly in intensity and the values of Ω_λ would be much less than those for, as an example, Er^{3+}(aquo).

The large values of Ω_2 for Er^{3+} in molten $LiNO_3$-KNO_3 eutectic[12] (molten LiCl-KCl host would show similar results[13]), as well as for the vapor phase species cited in Table II reflect very intense bands associated with certain (hypersensitive) transitions, $^4I_{15/2} \rightarrow {}^2H_{11/2}$ and $^4G_{11/2}$. Several groups have made important contributions to the theoretical understanding of these transitions,[14-16] and point symmetry of the Ln^{3+} is an element in some of these treatments. However, there is no basis at present for unique identification of the point symmetry based only on the observation of intense bands corresponding to hypersensitive transitions.

4. STRUCTURAL CORRELATIONS IN OTHER $AlCl_3$ VAPOR COMPLEXES

In contemplating the types of structures that might be ascribed to the $LnCl_3(AlCl_3)_x$ vapor complexes, there appears to be very little direct evidence on which to base the models. The published work has primarily been concerned with d-transition metal complexes, and some of the proposed structures are indicated in Fig. 2. Much of the thinking has been influenced by single crystal x-ray investigations, but such solid state ordering may have little relevance to the gas phase. Recurring structural elements are, of course, $AlCl_4^-$, which can bond via two-bridging Cl atoms ($FeCl_3 \cdot AlCl_3$),[17] and $Al_2Cl_7^-$, which in one proposed type of structure for $CuCl_2 \cdot 2AlCl_3$[18] forms a six member ring. Finally, octahedral complexing in transition metal vapor complexes has been suggested based on the intensities of bands observed in absorption spectra,[19] but there is no indication of this type of configuration in the lanthanide vapor complexes.

Evidence was obtained in the $NdCl_3(AlCl_3)_x$ system[4] for $x = 3.46$ in (1), which suggests the presence of at least two species. Possible combinations would include $NdCl_3(AlCl_3)_3$ and $NdCl_3(AlCl_3)_4$. Both could be formulated in terms of $AlCl_4^-$ and $Al_2Cl_7^-$ bonding groups. We note that in the case of our investigation of the $ErCl_3(AlCl_3)_x$ system, several of the more intense bands were monitored as a function of $AlCl_3$ pressure and system temperature. The linear changes in band intensities under these conditions suggested minimal modification of the immediate environment of the Er^{3+} ions.

The temperature dependence of the fluorescence lifetime of the $^5D_4$ state in $TbCl_3(AlCl_3)_x$,[5] to be discussed later, can on the other hand be taken as evidence that changes in the immediate environment of the Ln^{3+} do occur with increasing temperature. This situation has its analog in the solution spectra of the lanthanides where there are a number of examples of the insensitivity of absorption spectra to changes in the hydration sphere occasioned by the substitution of H_2O for D_2O.[20] The fluorescence lifetimes of excited states, on the contrary, vary significantly under such substitution.

As cited earlier, octahedral coordination of Ln^{3+} similar to that proposed in the structure of the $CrCl_3(AlCl_3)_3$ vapor complex[21] is excluded by the observation of normal intensities for the f → f transitions. The recent study of the laser Raman spectrum of the $CuCl_2(AlCl_3)_2$ vapor complex,[18] which could be interpreted in terms of the existence of a ring structure $Al_2Cl_7^-$ (Fig. 2), provides a reasonable basis for accommodating the bond angles to the larger Ln^{3+} ion. It remains to obtain direct experimental evidence for the lanthanide complex structures. It is useful to further point out that the Raman spectrum of the $CuCl_2(AlCl_3)_2$ vapor complex[18] was interpreted as consistent with a coordination number of 3 or less for Cu^{2+}--not the type of strucutre that would have been postulated based on solid state models.

5. EMISSION OF RADIATION

Following absorption of energy by the Ln^{3+} ion, excited state relaxation can occur by both radiative and non-radiative modes. The total lifetime of any excited state, τ_T, can therefore be expressed as

$$\tau_T = [A_T(\psi J) + W_T(\psi J)]^{-1} \tag{6}$$

where $A_T(\psi J)$ is the total radiative relaxation rate and $W_T(\psi J)$ is the total rate due to non-radiative processes. The quantitative treatment of the absorption process (3), which made it possible to determine the Judd-Ofelt parameters, Ω_λ, is directly related to the expression for radiative relaxation of an excited state (ψJ) to a particular lower-lying state $(\psi' J')$;[10]

$$A(\psi J,\psi' J') = \frac{64\pi^4\sigma^3 e^2}{3h(2J+1)}\,[\chi' S_{ED} + n^3\, S_{MD}] \tag{7}$$

where $\sigma(\mathrm{cm}^{-1})$ is the energy of the transition. The evaluation of the line strengths, S_{ED} and S_{MD}, (4) and (5), follows from the known values of Ω_λ and matrix elements of $\underset{\sim}{U}^{(\lambda)}$ calculated between the interacting states, and $\chi' = n^2\,\chi$, (3).

In general the observed lifetime of a state may be strongly dependent on non-radiative processes which greatly increase the relaxation rate compared to the purely radiative process. Thus, the total radiative lifetime $\tau_R(\psi T) = [\sum_i [A(\psi J,\psi' J')]_i]^{-1} = [A_T(\psi J)]^{-1}$, the sum running over all states lower in energy than ψJ, represents the maximum lifetime of an excited state. Computation of the radiative lifetimes for several states in Er^{3+} that have been observed to fluoresce in other hosts, is shown in Table III where the branching ratio to any one state, β_R, is given by $\beta_R = A(\psi J, \psi' J')/A_T(\psi J)$.

Since non-radiative processes are strongly dependent on the energy gap between an excited state and that state immediately lower in energy, only those excited states separated from lower-lying levels by large energy gaps may approach the purely radiative relaxation rate. The uniformly relatively narrow energy gap between excited free-ion states in Er^{3+} insures that even in the most favorable circumstances, lifetimes in the vapor complexes will be short. Much more favorable circumstances are present in the case of the $TbCl_3(AlCl_3)_x$ vapor complex.

6. FLUORESCENCE FROM THE $TbCl_3(AlCl_3)_x$ VAPOR COMPLEX

Recent investigations[5] of excited state relaxation in $TbCl_3(AlCl_3)_x$ following excitation with a xenon lamp source revealed the fluorescence spectrum indicated in Fig. 3. The fluorescence wavelengths are in good agreement with those expected for transitions from $^5D_4$ to states in the ground term (^7F) multiplet. It is of particular interest that the most intense band in the fluorescence spectrum is associated with the $^5D_4 \rightarrow {}^5F_5$ transition. An analysis of the predicted branching ratios from the $^5D_4$ state based on intensity parameters extrapolated from data on the $ErCl_3(AlCl_3)_x$ and $HoCl_3(AlCl_3)_x$ systems[22] shows good agreement with the observed strength of the ${}^5D_4 \rightarrow {}^5F_5$ transition. Examination of the matrix elements of $\underset{\sim}{U}^{(\lambda)}$, also identifies this as a hypersensitive transition which is strongly dependent on the expected large value of Ω_2. The transition also has a significant magnetic dipole character, which would not vary with host. The observed lifetime of ∿2.5 ms between 450 and 510°K may be compared to a computed value of 2.3 ms.[5]

As the temperature is increased in the range 510-550°K the excited state decay is resolvable into two decay rates, the lower temperature rate cited and a second lifetime (∿460 μsec) characteristic of the higher temperature region. The nature of the temperature dependence suggests that non-radiative mechanisms are not involved so that both of the indicated lifetimes are purely radiative. A significant change in the Ω_λ parameters would be required to account for the lifetime differences.

Recently, we have detected fluorescence from the ${}^5D_3$ state to the ${}^7F$ manifold using pulsed excitation techniques, and have also been able to demonstrate the rapid growth in intensity of the daughter ${}^5D_4$ state due to radiative relaxation of the ${}^5D_3$ state.[23] Studies of the temperature dependence of excited state lifetimes and of non-radiative relaxation mechanisms are in progress.

7. FLUORESCENCE IN THE $NdCl_3(AlCl_3)_x$ SYSTEM

Since interest in high power solid state lasers for fusion energy applications has been centered on Nd^{3+} glass systems, work was undertaken jointly with R. R. Jacobs and W. F. Krupke to investigate possible fluorescence in the $NdCl_3(AlCl_3)_x$ system.[24] The absorption spectrum of $NdCl_3(AlCl_3)_x$[4] is also dominated by an intense absorption band, corresponding to a hypersensitive transition from the ground state to the $^4G_{5/2}$ state. Laser operation is associated with the transitions $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1.06 μ) and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (0.88 μ).

In an experiment with the $NdCl_3(AlCl_3)_x$ system in which excitation was achieved using a Nd^{3+}:YAG laser doubled in frequency to 531 nm, it was observed that the $^4F_{3/2}$ state was populated via rapid non-radiative relaxation, and fluorescence from the $^4F_{3/2}$ to the $^4I_{11/2}$ and $^4I_{9/2}$ states was detected. A lower temperature range lifetime of ~0.8 ms compared to a computed value of 1.4 ms was observed. At higher temperatures the lifetime decreased exponentially as a function of increasing temperature. Possible non-radiative processes consistent with the observed results have been examined and resonant dipole-dipole interaction was indicated as a possible important relaxation mode.

Recently, Krupke and Jacobs succeeded in observing optical gain in an optical cell containing $NdCl_3(AlCl_3)_x$ prepared by the Argonne group.[25] These results further stimulate our interest in the basic mechanisms of energy transfer in those systems, and in a broad range of physical properties.

TABLE I. Oscillator strengths for the $ErCl_3(AlCl_3)_x$ vapor complex

Spectral Range (cm^{-1})	Excited State (S'L'J')	$f \times 10^6$	
		EXPT	CALC[a]
6400- 6800	$^4I_{13/2}$	1.7	1.8
9090-10500	$^4I_{11/2}$	1.2	1.1
14100-15600	$^4F_{9/2}$	2.3	2.8
17700-18300	$^4S_{3/2}$	1.3	0.61
18300-19500	$^2H_{11/2}$	26.9	27.1
19800-20700	$^4F_{7/2}$	2.1	2.5
21400-22600	$^4F_{5/2} + {}^4F_{3/2}$	1.0	1.2
23800-24800	$({}^2G, {}^4F, {}^2H)_{9/2}$	1.2	0.92
25300-26700	$^4G_{11/2}$	48.3	48.2
26700-28200	$^4G_{9/2} + {}^2K_{15/2} + {}^2G_{7/2}$	4.7	0.04 MD[b] 3.9 ED
37700-39700	$^2D_{5/2} + {}^4D_{7/2}$	20.7	7.7[c]

[a] $\Omega_2 = 28.5$, $\Omega_4 = 4.38$, $\Omega_6 = 2.09$ (all $\times 10^{-20}$ cm^2)

[b] Magnetic dipole contribution.

[c] Not included in parameter fit.

TABLE II. Values of Ω_λ for Er^{3+} in various host systems.

			$(\times 10^{-20}$ cm)		
System	Phase	T°C	Ω_2	Ω_4	Ω_6
Er^{3+}(aquo)	liquid	25	1.59	1.95	1.90
Er^{3+}:$YAlO_3$[a]	solid	25	1.06	2.63	0.78
Er^{3+}:$LiNO_3$-KNO_3	liquid	200	15.8	1.84	1.39
$NdCl_3(AlCl_3)_x$[b]	vapor	∿400	18.0	4.8	3.9
$ErCl_3(AlCl_3)_x$	vapor	∿400	28.5	4.38	2.09
$Er(thd)_3$[c,d]	vapor	288	46	2.7	3.7
$ErBr_3$[d]	vapor	1105	60	1.47	1.66

[a] M. J. Weber, Proc. 10th R.E. Conference.

[b] Computed from data in reference 4.

[c] 2,2,6,6-tetramethyl-3,5 heptanedionate

[d] D. M. Gruen, C. W. DeKock, R. L. McBeth, Adv. Chem. Ser. **71**, 102 (1967).

TABLE III. Calculated matrix elements of $[\underset{\sim}{U}^{(\lambda)}]^2$, branching ratios, and lifetimes associated with certain excited states of $ErCl_3(AlCl_3)_x$.

ψJ	$\psi'J'$	Initial State	Final State	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$	β_R	$\tau_R(\psi J)$ (msec)
$^4S_{3/2}$	$^4F_{9/2}$	18200	15200	0	.0001	.0228	~ 0	1.19
	$^4I_{9/2}$		12400	0	.0766	.2569	.04	
	$^4I_{11/2}$		10200	0	.0046	.0773	.02	
	$^4I_{13/2}$		6500	0	0	.3419	.28	
	$^4I_{15/2}$		0	0	0	.2225	.66	
$^4F_{9/2}$	$^4I_{9/2}$	15200	12400	.1220	.0061	.0203	.01	1.24
	$^4I_{11/2}$		10200	.0715	.0101	1.2671	.06	
	$^4I_{13/2}$		6500	.0109	.1533	.0828	.06	
	$^4I_{15/2}$		0	0	.5512	.4622	.87	
$^4I_{9/2}$	$^4I_{11/2}$	12400	10200	.0021	.0690	.1520	.01	10.5
	$^4I_{13/2}$		6500	.0003	.0087	.7100	.25	
	$^4I_{15/2}$		0	0	.1588	.9972	.74	

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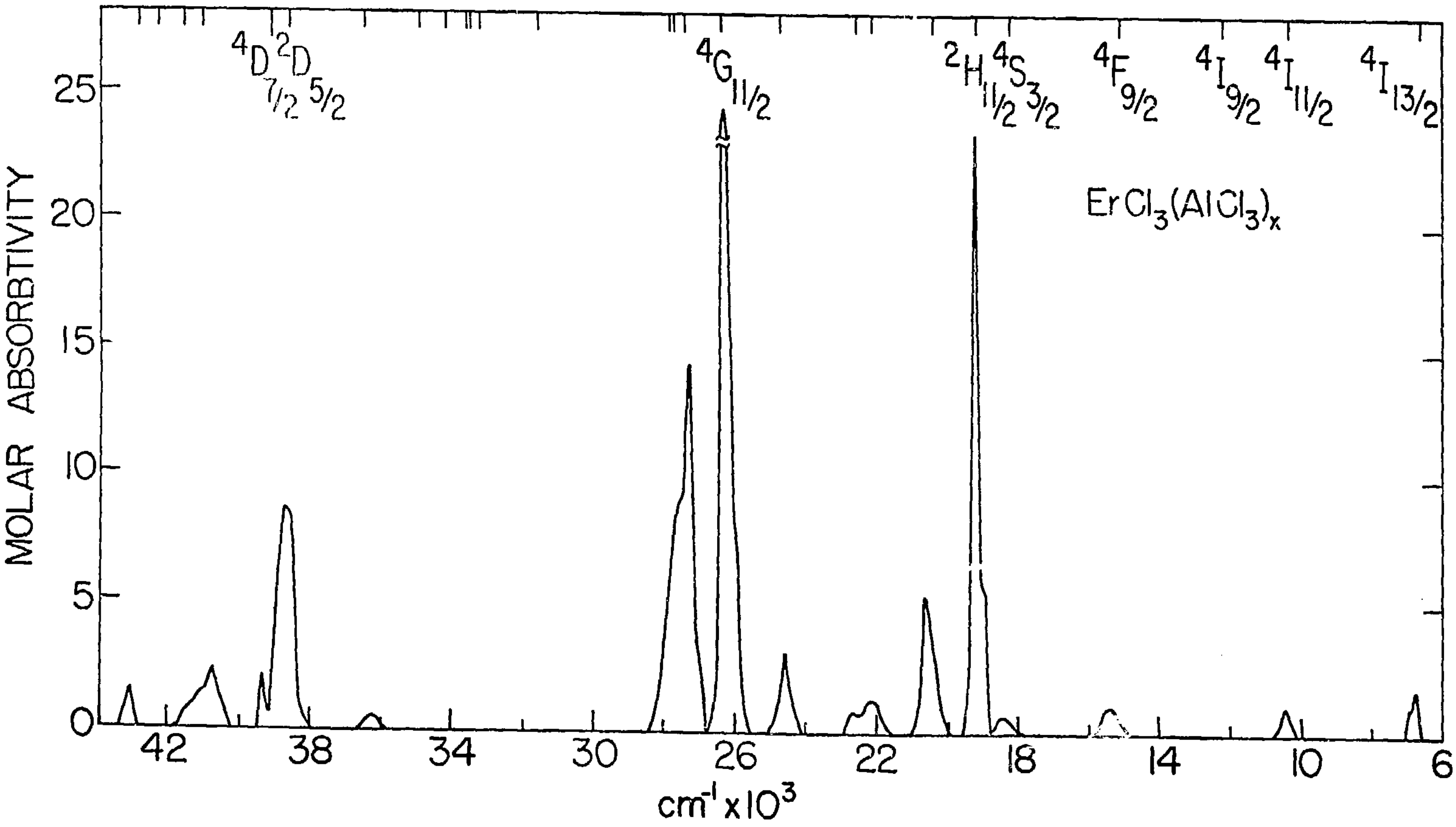
FIGURE CAPTIONS

Fig. 1. The absorption spectrum of the $ErCl_3(AlCl_3)_x$ vapor complex in the range 6000-44000 cm^{-1}.

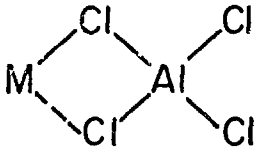
Fig. 2. Structural models for $AlCl_3$ vapor complexes.

Fig. 3. Fluorescence spectrum of the $^5D_4$ state of the $TbCl_3(AlCl_3)_x$ vapor complex at 535°K.

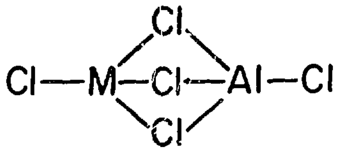


MOLAR ABSORBTIVITY
25
20
15
10
5
0
42
38
34
30
26
22
18
14
10
6
cm⁻¹ x10³
$^4D_{7/2}$ $^2D_{5/2}$
$^4G_{11/2}$
$^2H_{11/2}$ $^4S_{3/2}$
$^4F_{9/2}$
$^4I_{9/2}$
$^4I_{11/2}$
$^4I_{13/2}$
$ErCl_3(AlCl_3)_x$

STRUCTURAL MODELS FOR $AlCl_3$ VAPOR COMPLEXES



$NaCl \cdot AlCl_3$



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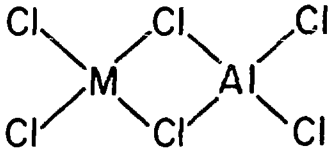

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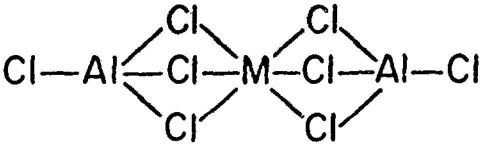

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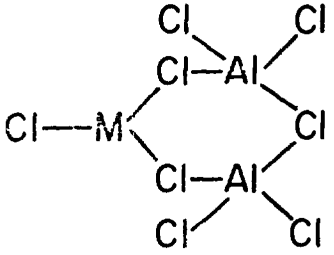
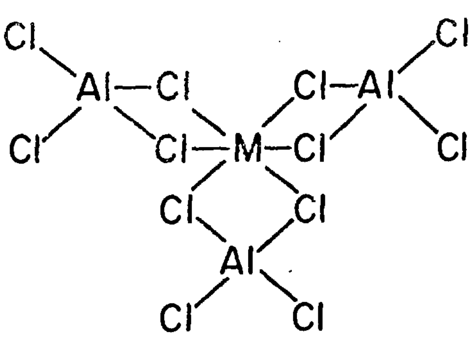
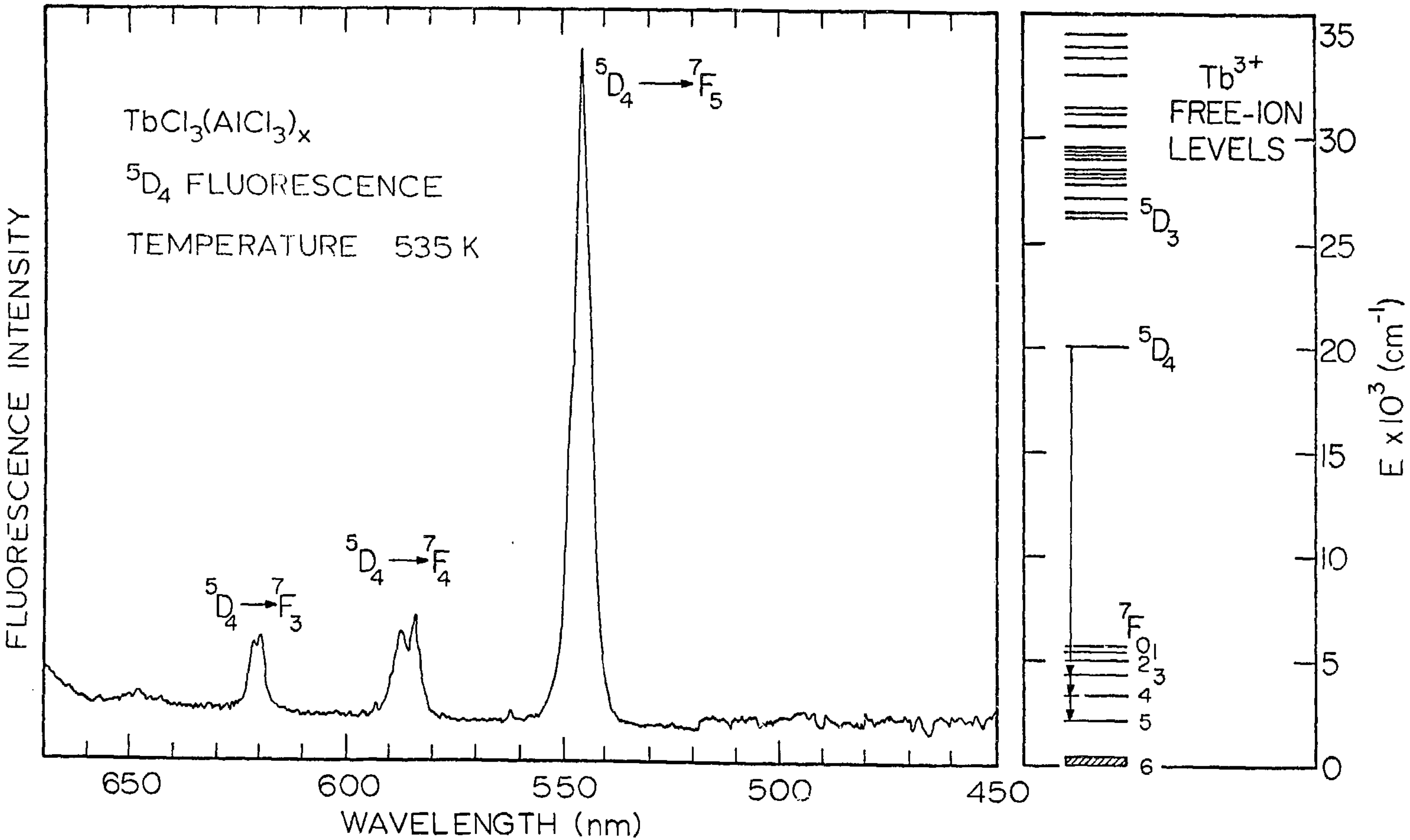


$CuCl_2 \cdot 2\,AlCl_3$



$CrCl_3 \cdot 3\,AlCl_3$



$TbCl_3(AlCl_3)_x$
$^5D_4$ FLUORESCENCE
TEMPERATURE 535 K
$^5D_4 \rightarrow {}^7F_5$
$^5D_4 \rightarrow {}^7F_4$
$^5D_4 \rightarrow {}^7F_3$
FLUORESCENCE INTENSITY
650
600
550
500
450
WAVELENGTH (nm)
Tb^{3+}
FREE-ION
LEVELS
$^5D_3$
$^5D_4$
^7F
0
1
2
3
4
5
6
35
30
25
20
15
10
5
0
E x 10^3 (cm^{-1})