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SPECTROPHOTOMETRIC STUDIES OF HOLMIUM(III)
CHLORIDE-ALUMINUM(III) CHLORIDE VAPOR COMPLEXES

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SPECTROPHOTOMETRIC STUDIES OF HOLMIUM(III)
CHLORIDE-ALUMINUM(III) CHLORIDE VAPOR COMPLEXES[†]

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Abstract

The gas complexation reactions between LnCl_3 and Al_2Cl_6 to yield molecular species of the form $\text{LnCl}_3(\text{Al}_2\text{Cl}_6)_x$ have been studied for a number of years. The spectrophotometric technique has been used to deduce the thermodynamic properties of the molecular species. We have studied the $\text{HoCl}_3(\text{Al}_2\text{Cl}_6)_x$ system from 600 to 900 K and at Al_2Cl_6 pressures between 1 and 7 atm. The Ho^{3+} hypersensitive transition between $^5\text{I}_8$ and $^5\text{G}_6$ at 456 nm has been used to measure the complex vapor densities as a function of pressure and temperature. A temperature-dependence of the optical absorption spectrum was observed in samples with a constant Ho^{3+} ion density. These data cannot be understood in terms of the generally used treatment of molar absorptivity, but requires the introduction of an effective oscillator strength. A temperature-dependent oscillator effect is also observed and this is interpreted as evidence for the presence of multiple species with differing oscillator strengths. The consequence of these observations for the determination of equilibrium constants for the different species will be discussed.

Introduction

Experiments have been undertaken to characterize lanthanide vapor complexes for potential use in high-power vapor phase laser systems - such as those required to drive laser fusion.

Neodymium glass lasers are currently employed in feasibility studies of laser fusion, however, it is generally accepted that these lasers will not be suitable for use in practical power plants. For future laser fusion application volatile complexes of lanthanides constitute one type of gas-phase laser medium which could alleviate problems of low repetition rate, optical non-linearity, permanent damage potential, and high fabrication costs associated with solid-state lasers.¹

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Complex formation resulting in increased vapor-phase density is a relatively common phenomenon among metal halides.² The binary lanthanide halides have low volatility even at relatively high temperatures (~900°C), however, appreciable concentrations of lanthanides in the gas phase can be achieved at much lower temperatures by formation of the more volatile vapor complexes, such as those resulting from the interaction between lanthanide halide and the corresponding aluminum halide. Early studies by Øye and Gruen³ indicated that the apparent vapor pressure of NdCl₃ was increased by a factor of 3×10^7 in the presence of 1 atm Al₂Cl₆ at 800 K. In their study of the NdCl₃-AlCl₃ system and in subsequent investigations of other LnCl₃-AlCl₃ complex systems, ion densities were calculated from spectroscopic (absorbance) measurements. When utilizing this technique one must assume that either the molar absorptivity is independent of temperature or derive an expression which relates absorbance to temperature in cells where all of the Ln³⁺ ions are in the vapor phase. In the present investigation of the HoCl₃(AlCl₃)_x system, a temperature dependence of the optical absorption spectrum and a temperature-dependent oscillator strength is observed which we interpret as evidence for the presence of a multi-species system with differing oscillator strengths. In view of these observations, the treatment of spectrophotometric data has been reformulated to properly account for temperature-dependent effects and multi-species systems.

New spectrophotometric formulation:

Several methods have been used to determine vapor densities of complexed metal ions of transition metal systems, however, the spectrophotometric technique has been used exclusively for the actinide and lanthanide systems. This method relates the optical absorbance at a given wavelength, λ , to the vapor density of the complex. In general, the treatment assumes Beer's law to be obeyed over the range of temperature and pressure studied. This technique utilizes the relationships

$$\epsilon(\lambda) = \frac{A(\lambda)V}{n\ell} \quad (1)$$

and

$$P_C = \frac{A(\lambda)RT}{\epsilon(\lambda)\ell} \quad (2)$$

The molar absorptivity, $\epsilon(\lambda)$, at a specific wavelength, λ , is measured by using a known molar density, n/V , of the lanthanide halide in a pathlength, ℓ , and volume, V . The absorbance, $A(\lambda) \equiv -\log I(\lambda)/I_0(\lambda)$, is measured at the peak of a suitably intense transition from which the complex pressure, P_C , is calculated using equation (2) where R is the gas constant.

In several lanthanide chloride-aluminum chloride vapor complex systems a temperature-dependent molar absorptivity has been reported.^{4,5,6} The partial pressure of the complex, P_c , was then calculated from an empirically-derived equation which expresses this temperature dependence. Although the concept of molar absorptivity measured at a specific wavelength is sometimes useful, it fails to describe the spectral behavior of multi-species systems whose apparent molar absorptivities are temperature-dependent. To overcome these effects we analyzed the system in terms of an effective oscillator strength⁷ given by

$$f^* \approx \frac{v}{n\lambda} \frac{mc^2}{\pi e^2} \frac{\ln 10}{\lambda^2} \int_{\text{band}} A(\lambda) d\lambda \quad (3)$$

where $\bar{\lambda}$ is the central wavelength of the band, m and e are the mass and charge of the electron, and c is the velocity of light.

Experimental

Anhydrous holmium chloride was prepared in gram quantities from 99.9% Ho_2O_3 using a procedure in which the sesquioxide was dissolved in 6 M HCl, six moles of NH_4Cl per mole of Ho were added and the resultant solution evaporated to dryness. The solid $\text{NH}_4\text{Cl}\cdot\text{HoCl}_3\cdot 6\text{H}_2\text{O}$ mixture was then heated slowly under vacuum to 500°C over a period of eight hours to dehydrate the salt.⁸ Aluminum chloride was synthesized by reacting 99.999% Al disks with HCl gas generated in a H_2SO_4 -NaCl reactor. All sample handling was carried out in a dry atmosphere box.

Spectrophotometer cells of fused silica (~ 10 cm path-length) were thoroughly cleaned in a 50% 6N hydrochloric acid-50% ethanol solution, washed repeatedly in triply distilled water, then dried 48 hours in air at 1000°C and finally heated in vacuo for 12 hours at 900°C before the HoCl_3 samples were introduced. Access to moisture was minimized by subliming the aluminum chloride into evacuated cells. The cells were sealed off under vacuum. Absorption spectra were recorded in a prism-grating double beam spectrophotometer modified for use with samples of high temperature.³ The general furnace design and procedures developed by Øye and Gruen³ were used to heat the sample cells. Condensation of HoCl_3 and AlCl_3 on the end windows was prevented by maintaining the ends of the cells $\sim 20^\circ$ hotter than their mid-point.

Results and Conclusion

The absorption spectrum of the $\text{HoCl}_3(\text{AlCl}_3)_x$ vapor system is shown in Fig. 1. We used the hypersensitive transition between $^5\text{I}_8$ and $^5\text{G}_6$ at 440-480 nm to measure the absorbance from Ho^{3+} ions. The absorption spectrum of this transition is shown in Fig. 2 for two temperatures. The effective oscillator strengths for the observed band (440-480 nm) was computed from the results of two separate experiments given in Table I. Milligram quantities of HoCl_3 and sufficient AlCl_3 to insure complexing of all of the HoCl_3 were loaded into cells of known volume. Absorption spectra were then taken as a function of temperature. A plot of $\ln f^*$ vs T^{-1} yielded two distinct regions. At high temperature $\ln f^*$ was a weak function of T^{-1} and at low temperature a strong function of T^{-1} . The critical point is the temperature at which all of the HoCl_3 was complexed and therefore in the vapor phase. After determining the weight of HoCl_3 present by analytical methods subsequent to completion of each experiment, the effective oscillator strength, f^* , in terms of the integrated band intensity of the given absorption band was calculated. A plot of $\ln(10^6 \times f^*)$ vs T^{-1} shown in Fig. 3 indicates a definite temperature dependence of the oscillator strength. The solid line is the result of a least squares fit of the data given in Table I. The result is

$$f^* = 89.33 \times 10^{-6} \exp (-305/T(\text{K})).$$

It appears that within experimental error there is no dependence of f^* on Al_2Cl_6 concentration.

A detailed investigation of the unsaturated $\text{HoCl}_3(\text{AlCl}_3)_x$ system is currently being made using the reformulated spectrophotometric technique to establish the temperature and $\text{Al}_2\text{Cl}_6(\text{g})$ pressure dependence of the complex metal ion density. Vapor density measurements have been made in the region of 1 atm to 7 atm. $\text{Al}_2\text{Cl}_6(\text{g})$ pressure and 600 K to 900 K. Analysis of the dimer pressure dependence of the complex vapor pressure on isotherms revealed that the system is best described by a model which requires three vapor species. In addition to the two species that Øye and Gruen³ proposed for the Nd^{3+} system, LnAl_4Cl_5 and $\text{LnAl}_3\text{Cl}_{12}$, there is indication of a third, lower molecular weight species, HoAl_2Cl_9 , being formed at higher temperature.

Since all of the reactions and their equilibrium expressions are interrelated, the system may be described by a series of simultaneous solid-gas and gas-gas equilibrium reactions. The vapor density of the complexed lanthanide ion due to each species will go through a maximum at some temperature depending upon the thermodynamics of formation of the complex species and the temperature dependent equilibrium

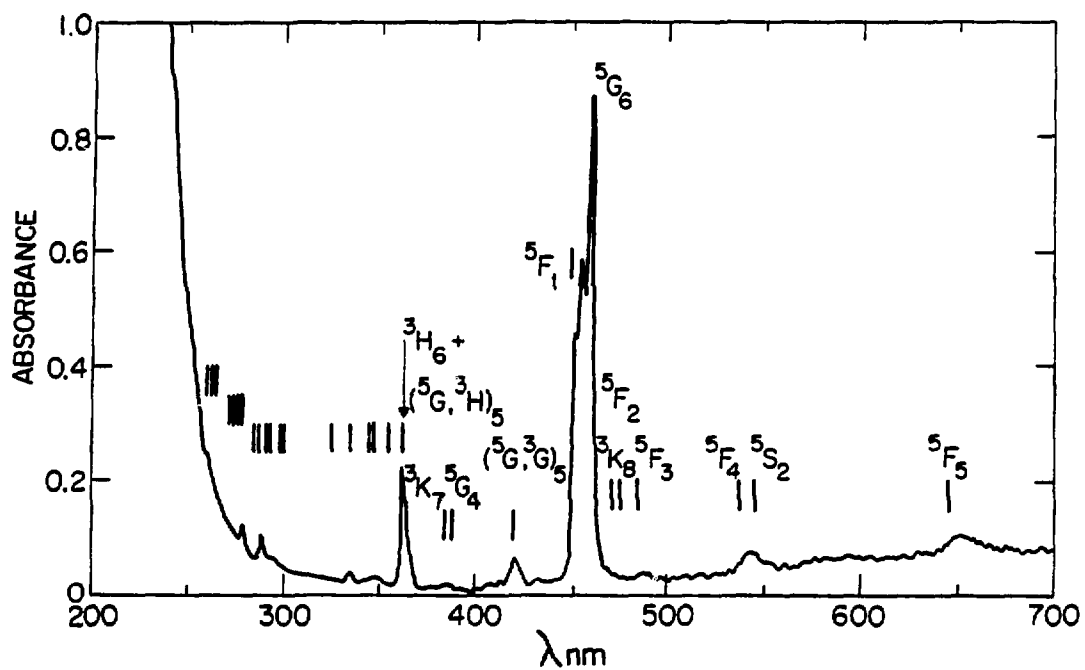


Fig. 1. Absorption spectrum of $\text{HoCl}_3(\text{Al}_2\text{Cl}_6)_x$ vapor complex system at 820 K. The vertical lines are the calculated positions of the free-ion manifolds.

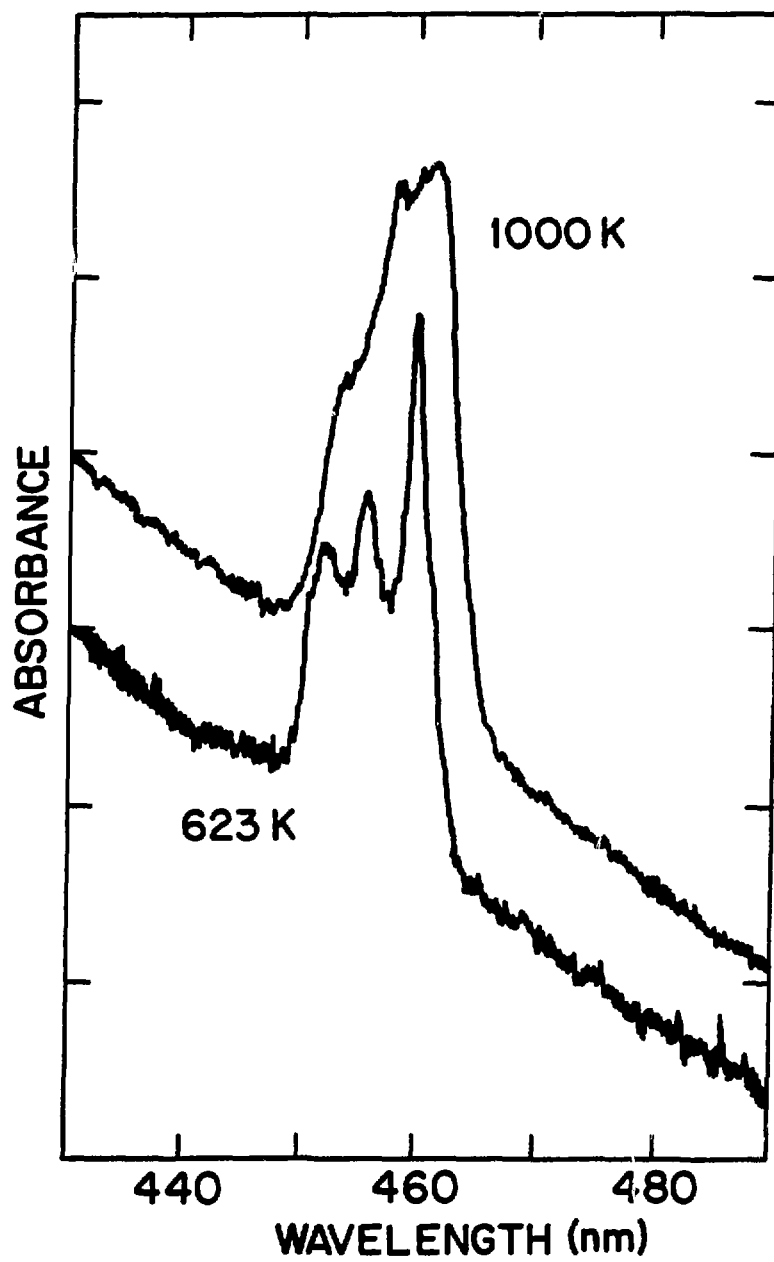


Fig. 2. Absorption spectra of the ${}^5\text{I}_8$ to ${}^5\text{G}_6$ hypersensitive transition at different temperatures.

TABLE I. Effective Oscillator Strength Data.

Experimental Parameters	T(K)	T^{-1} (K ⁻¹)	$\int A(\lambda) d\lambda$ (nm)	$10^6 \times f^*$
<u>Run #2</u>				
	825	1.212	$3.801 \pm .056$	$61.63 \pm .91$
$c(\text{Ho}^{3+}) = 1.282 \text{ mol/m}^3$	756	1.323	$3.625 \pm .038$	$58.78 \pm .62$
$V_{\text{cell}} = 29.1 \times 10^{-6} \text{ m}^3$	736	1.360	$3.609 \pm .029$	$58.52 \pm .47$
$l = 0.10 \text{ m}$	675	1.481	$3.464 \pm .106$	56.17 ± 1.72
$c(\text{Al}_2\text{Cl}_6) = 78.9 \text{ mol/m}^3$	617	1.621	$3.390 \pm .031$	$54.97 \pm .50$
	565 ^a	1.769	$2.420 \pm .068$	39.20
<u>Run #4</u>				
$c(\text{Ho}^{3+}) = .686 \text{ mol/m}^3$	835	1.198	$2.079 \pm .016$	$62.95 \pm .48$
$V_{\text{cell}} = 25.5 \times 10^{-6} \text{ m}^3$	788	1.268	$2.024 \pm .027$	$61.29 \pm .82$
$l = .10 \text{ m}$	738	1.354	$1.944 \pm .016$	$58.88 \pm .41$
$c(\text{Al}_2\text{Cl}_6) = 47.3 \text{ mol/m}^3$	692	1.446	$1.903 \pm .004$	$57.62 \pm .13$
	638	1.568	$1.844 \pm .011$	$55.83 \pm .35$
	585 ^a	1.709	$1.589 \pm .016$	48.12
	550 ^a	1.819	$0.815 \pm .016$	24.68

^aLiquid phase presentLeast squares fit for two runs: $10^6 \times f^* = 89.33 \exp(-305/T(K))$.

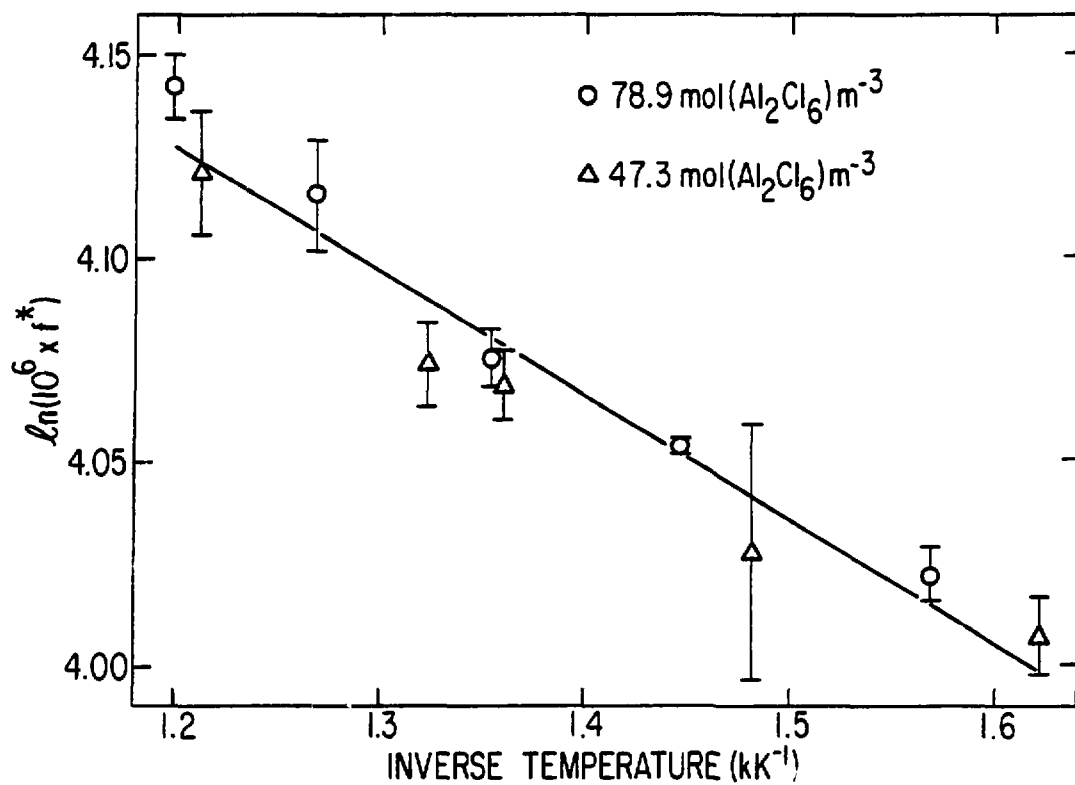


Fig. 3. Temperature dependence of the effective oscillator strength of the $^5\text{I}_8$ to $^5\text{G}_6$ transition in $\text{HoCl}_3(\text{Al}_2\text{Cl}_6)_x$ vapor complex. The two cells had different Al_2Cl_6 concentrations.

expression behavior of the monomer-dimer couple $\text{Al}_2\text{Cl}_6(\text{g}) \rightleftharpoons 2\text{AlCl}_3(\text{g})$. (However, this does not imply that the total complexed metal ion density will decrease in a region where one molecular species is becoming less significant.)

Preliminary analysis resulting from optical absorption spectra are consistent with the three species interpretation of the vapor density information. The temperature dependent changes in the visible spectrum are consistent with the change in coordination number which is expected when going from $\text{HoAl}_3\text{Cl}_{12}$ to HoAl_2Cl_9 , $(\text{Ho}(\text{AlCl}_4)_3$ to $\text{HoCl}(\text{AlCl}_4)_2$). In the spectra reported above it is apparent that the high temperature spectrum is really the linear superposition of the low temperature spectrum and an almost identical spectrum with a slight red shift. Thus these spectra are consistent with formation of a species with a different local environment at higher temperatures.

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