Relative Contributions of Odd Vibrations to the Intensity of the First Band of $Co(NH_3)_6^{3+}$

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Without actually evaluating the integrals involved, an experimental technique and a mode of analysis have been developed to quantitatively verify van Vleck's theory of vibronic interactions. The success of the analysis suggests that errors introduced by the computational approximations far outweight those introduced by the partial breakdown of the assumptions upon which the theory is constructed. Specifically, the vibronic transition at 21 200 cm^{-1} of $Co(NH_3)_6^{3+}$ has been used to discuss the techniques developed. Furthermore, it has been established that at all temperatures from 293 °K down to 83 °K the $\tilde{\nu}_6$ vibrational mode of the MX_6 entity is primarily responsible (60%) for the admixture of odd parity in the ground and the first excited states of $Co(NH_3)_6^{3+}$.

Introduction

The theory of vibronic interactions, which was first proposed by VAN VLECK [1], has been discussed by several investigators [2–8], while empirical fits for temperature dependent vibronic oscillator strengths have been proposed by others [9–11]. In the present paper we report our study of the temperature dependence of the so-called first band [12] of $Co(NH_3)_6^{3+}$, which from symmetry considerations is Laporte forbidden.

Experimental

Our attempts to obtain KBr, KCl and NaCl pellets as well as fluorolube mulls of $Co(NH_3)_6Cl_3$ resulted in total failure. The problem of obtaining a suitable matrix material was solved by mulling the sample with DuPont's Duco and pressing it into a thin film which could then be removed as a sheet after the solvent evaporated. The recommended procedure for preparing such a sample is to place about 80 mg of the sample in a stainless steel Wig-1-Bug capsule and pulverize it for approximately two minutes, after which approximately 500 mg of Duco is added and the resulting mixture mulled for about 4 minutes. The mull is then removed and pressed into a ring which is constructed so as to yield samples whose average thickness is about 0.066 mm. Allowing five minutes for polymerization to occur, the sample is then carefully removed and allowed to solidify for approximately one hour while being pressed between two glass plates. The sample is then cut to the desired dimensions and checked for its acceptability which of course depends upon the band and the region of the spectrum to be studied.

All spectra were obtained by using a Cary Model 14 spectrophotometer and all optical parts consisted of Optosil *. Since the optical density of the samples used (usual concentrations were about 17% by weight) was greater than 2, a diaphragm was used to adjust the reference beam. The spectra of the pure matrix (Duco) were obtained at room temperature as well as 80 °K to determine any temperature effects, and none were observed. Furthermore, dilute disks of the matrix and $Co(NH_3)_6Cl_3$ were run at various temperatures to determine temperature effects on scattering. Spectra at other than room temperature were obtained by (i) the addition of liquid nitrogen, (ii) then using a slush of n-pentane and liquid nitrogen, and finally (iii) after removal of the n-pentane the addition of a chloroform-liquid nitrogen slush. As a check for the technique used

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* Optosil, Engelhard Industries, Inc., Amerosil Quarz Division.

for the analysis of our data, two additional temperatures were obtained using slushes of carbon tetrachloride and toluene with liquid nitrogen respectively. The actual temperature attained by the sample for each bath was measured with a Cu-constantan thermocouple placed in Duco between the optosil disks. The temperatures obtained by the baths appear in Table 1. The accuracy of the thermocouple was estimated in each region by checking the *actual* temperature of the respective baths as reported by JOLLY [13]. Table 1 gives also the relative intensities which were estimated by weighing the areas under thet appropriate curves and then finding their ratios. Several runs were made with different films and the ratios obtained were almost identical.

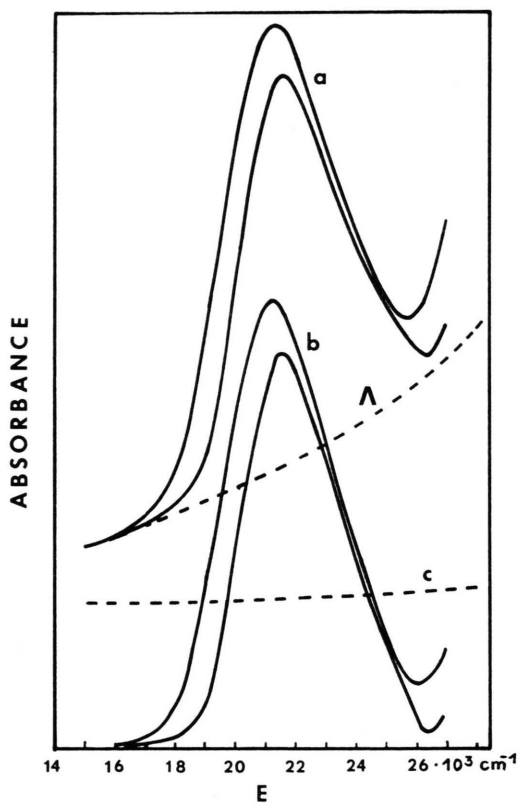

Fig. 1. Spectra of the 21.2 kK band of solid $Co(NH_3)_6Cl_3$ at 298 °K and 83 °K. (a) Spectra before the subtraction of the baseline Λ, (b) Spectra after the subtraction of Λ, and (c) Spectrum of the pure matrix (Duco).

To reduce kaleidoscopic confusion, on the other hand, Fig. 1 shows only the spectra obtained at 298 °K and and 83 °K. The scattering baseline Λ was obtained by trying to coincide the *positions* of the first two spin-allowed transitions of $Co(NH_3)_6^{3+}$ in the solid state with those of the solution spectrum (both at 298 °K). It is indeed encouraging to note that after the subtraction of the baseline, the *positions* as well as *the relative intensities* of the said bands in both the solid and the solution remained unchanged (see Fig. 2). The final expression for the baseline was found to be

$$\Lambda = 0.8504 \exp(-8.57 \times 10^{-5} \lambda) + 9 \exp(-10^{-3} \lambda) + 4 \exp(-2 \times 10^{-3} \lambda)$$

where λ is the wavelength in Å.

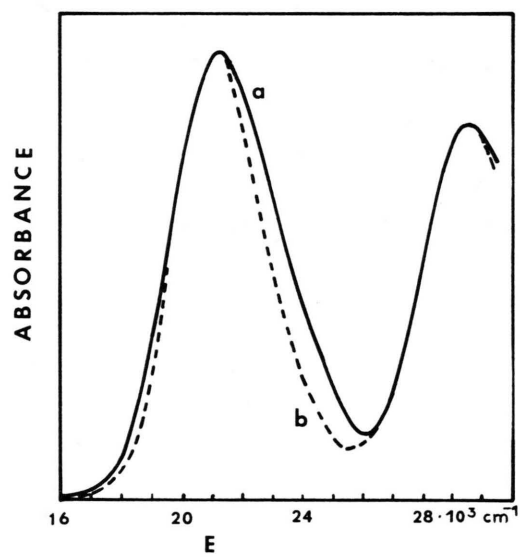

Fig. 2. Near U.V. spectra of Solid (a) and Solution (b) $Co(NH_3)_6Cl_3$ at 298 °K.

Analysis of Data and Discussion

At any given temperature T (°K), the theoretical oscillator strength of a vibronic transition between the electronic states $\boldsymbol{k}$ and $\boldsymbol{k'}$ is given by [8]

$$f^T_{k\to k'} = 1.085 \times 10^{11}\, \tilde{\nu}_{kk'}\, G_{k'} \sum_{\gamma} \frac{\hbar}{4\pi c \tilde{\nu}_\gamma} \operatorname{ctnh}\left(\frac{h c \tilde{\nu}_\gamma}{2 k T}\right) \left[\sum_{s\neq k}\left(\frac{\partial \lambda_{ks}}{\partial Q_\gamma}\right)_0 \cdot M_{sk'}(0) + \sum_{s\neq k'}\left(\frac{\partial \lambda_{k's}}{\partial Q_\gamma}\right)_0 \cdot M_{ks}(0)\right]^2$$

where $\tilde{\nu}_{kk'}$ is the energy separation of the levels $\boldsymbol{k}$ and $\boldsymbol{k'}$ in cm^{-1}, $G_{k'}$ is the degeneracy of the upper level $\boldsymbol{k'}$, $\tilde{\nu}_\gamma$ is the frequency of the vibration in cm^{-1} which induces the vibronic transition, $M_{st}(0)$ is the transition moment * between the levels $\boldsymbol{s}$ and $\boldsymbol{t}$ in the equilibrium configuration, and $(\partial\lambda_{st}/\partial Q_\gamma)_0$ is

[13] W. L. JOLLY, Synthetic Inorganic Chemistry, Prentice-Hall, Inc., New Jersey 1961.

the vibronic perturbation per unit displacement in the s and t.

Now, if all the assumptions considered in the derivation of $f^T_{k\to k'}$ were to hold, the latter could be separated into two parts. One being temperature dependent, and the other temperature independent. That is, one could write

$$f^T_{k\to k'} = \sum_\gamma A_\gamma(T) \cdot X_\gamma'$$

where

$$A_\gamma(T) = \tilde{\nu}_{kk'}\,\tilde{\nu}_\gamma^{-1}\,\mathrm{ctnh}\left(\frac{h\,c\,\tilde{\nu}}{2\,k\,T}\right)$$

and

$$X_\gamma' = 1.085 \times 10^{11}\,\frac{\hbar\,G_{k'}}{4\,\pi\,c} \cdot \left[\sum_{s\neq k}\left(\frac{\partial\lambda_{ks}}{\partial Q_\gamma}\right)_0 \cdot M_{sk'}(0) + \sum_{s\neq k'}\left(\frac{\partial\lambda_{k's}}{\partial Q_\gamma}\right)_0 \cdot M_{ks}(0)\right]^2$$

which, if one assumes that the internuclear distances do not appreciably change with temperature can be taken as constant.

Furthermore, since in our case there were three equivalent normal modes [14] for each inducing vibration, the expression for $f^T_{k\to k'}$, reduced to

$$f^T_{k\to k'} = \sum_{i=1}^{3} X_i \cdot A_i(T)$$

and the best set of X_i's was computed by using $f^T_{k\to k'}$ values at four different temperatures. Naturally, once the X_i's were determined it was easy to compute the vibronic oscillator strength an any other temperature. The frequencies of the $\tilde{\nu}_3$ and $\tilde{\nu}_4$ vibrations, on the other hand, were obtained from SHIMANOUCHI and NAKAGAWA [15], while the approximate value of $\tilde{\nu}_6$ was determined by a normal coordinate analysis [16] which considered the $Co(NH_3)_6^{3+}$ ion as a seven body problem. Table 1 shows that the calculated test cases, f^{253} and f^{180} are within 2% of the experimental values.

Another exciting outcome of our method of analysis was the ability of estimating, at any temperature, the relative contributions of the different modes of vibrations to the total vibronic oscillator strength. The insert in Fig. 3, for instance, gives the per cent contributions at 298° and 83 °K, while the figure itself depicts graphically their absolute contributions from 293 °K to 83°. It is indeed interesting to note that at all temperatures the $\tilde{\nu}_6$ mode is the primary mechanism of admixing odd parity in the ground and first states of $Co(NH_3)_6^{3+}$.

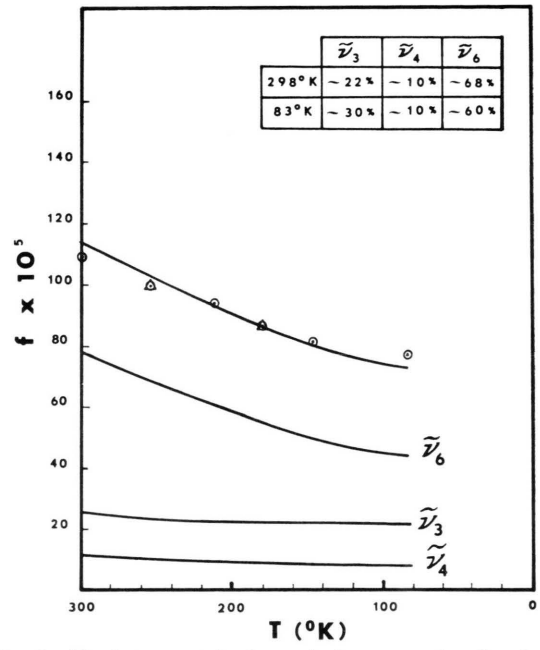

Fig. 3. Absolute contributions of the ungerade vibrational modes to the total vibronic oscillator strength as a function of temperature. The insert indicates the percent contributions to the oscillator strength at 293 °K and 83 °K.

Working Temperatures (°K) This work	Reported by JOLLY [13]	Baths (Liq. N_2 slushes)	f^T/f^{298}	Osc. Strength * $f^T \times 10^5$ obs.	calc.	Absolute % error
298	298.0	(Room temp.)	1.000	109	114	4.5
253	250.1	Carbon tetrachloride	0.945	100	102	2
211	209.5	Chloroform	0.860	93	92	1
180	178.0	toluene	0.783	85	86	1
146	143.0	n-pentane	0.743	81	80	1
83	77.0	(Liq. N_2)	0.710	77	73	5

* Calculated on the basis of the oscillator strength in the solution spectrum ($f^{298} = 90 \times 10^{-5}$).

Table 1. Calculated and observed vibronic oscillator strength as a function of temperature.

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