The ${}^2E \rightarrow {}^4A_2$ Spectra of Hexaquo Chromium (III) Crystals *

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Spectra of Hexaquo Chromium (III) Crystals

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Abstract

The emission spectra of $\text{C}(\text{NH}_2)_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (GASH), $\text{C}(\text{NH}_2)_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{D}_2\text{O}$ (GASD), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$ doped with Cr^{3+} have been recorded at 4 and 77°K. The two R lines are intense in both the 4 and 77°K spectra of Cr^{3+} : GASH and Cr^{3+} : GASD, negating an interpretation in which the R lines are ascribed to the components of ${}^2\text{E} \leftarrow {}^4\text{A}_2$ from a single species.

The vibronic intervals within 350 cm^{-1} of the origin are only slightly changed when H_2O is replaced by D_2O , whereas the energies of most vibrations in the $400\text{-}1000 \text{ cm}^{-1}$ range are much reduced by deuteration.

INTRODUCTION

The ${}^2E \leftarrow {}^4A_2$ absorption spectra of hexaquo chromium (III) ions in the crystalline hosts $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ (GASH) and $AlCl_3 \cdot 6H_2O$ have been described in some detail (1, 2). The two strong absorption lines in the pure GCrSH spectrum were assigned to the split components of ${}^2E \leftarrow {}^4A_2$ (R lines), in conflict with the interpretation of Martin-Brunetiere and Couture wherein these lines were ascribed to the unsplit ${}^2E \leftarrow {}^4A_2$ transitions arising from Cr^{3+} ions in two different sites (3). The ${}^2E \rightarrow {}^4A_2$ emission, which is weak but detectable in Cr^{3+} :GASH, is much more intense in the D_2O analog, Cr^{3+} :GASD (4). One purpose of the present work is the resolution of the aforementioned conflict.

The ${}^2E \rightarrow {}^4A_2$ emission from Cr^{3+} : $KAl(SO_4)_2 \cdot 12D_2O$ has been reported but no vibronic analysis was attempted (5). The second aim of this study is to consider the effect of deuteration and environment on the vibronic transitions of the $Cr(H_2O)_6^{3+}$ moiety. Preliminary vibronic assignments are made, but a complete description of the vibrations coupled to ${}^2E \rightarrow {}^4A_2$ is not yet possible.

EXPERIMENTAL

Doped (10%) crystals of Cr^{3+} :GASH were obtained by evaporation of aqueous solutions containing guanidine, aluminium, and chromium sulfates in the appropriate mole ratios. The Cr^{3+} :GASD was prepared by dissolving Cr^{3+} :GASH in D_2O and removing the solvent. At least two such exchanges were performed. The Cr^{3+} : $AlCl_3 \cdot 6H_2O$ was obtained by saturating an aqueous solution of aluminium chloride and blue-gray chromium chloride

with gaseous HCl at 15°. The D₂O analog was prepared in a like fashion; DCl was generated by the reaction of POCl₃ and D₂O.

Emission spectra were recorded on Kodak I-N plates with a grating spectrograph (90 Å/mm). Calibration was made with a neon discharge lamp and the sharp line positions were determined both with a recording microdensitometer and visually with a travelling microscope. In all cases the samples were immersed directly in the coolant and the emission was excited by radiation from a 500 W Hg lamp, filtered through 9782 and 3387 Corning glasses and a short pass interference filter rejecting radiation > 610 mμ. The luminescence passed through a Corning 2403 filter before entering the spectrograph. Prolonged exposure of Cr³⁺:GASH to the Hg lamp produced an impurity which emitted a spurious sharp doublet at about 6915 Å.

RESULTS

Cr³⁺:GASH and Cr³⁺:GASD

The 4°K emission spectra are displayed in Figs. 1 and 2. Except for a shift of 5 cm⁻¹ to lower energy, broadening, and the appearance of hot bands, the 77°K spectra closely resemble those at 4°K. In particular, the intensities of both R lines are nearly the same at each temperature. In pure GCrSH, the R lines occur in absorption at 14 133 and 14 114 cm⁻¹, but upon dilution to 50% Cr³⁺:GASH, these lines shift to 14 108 and 14 092 cm⁻¹ (1). In the 4°K emission from 10% Cr³⁺:GASH, the intense lines are located at 14 109 and 14 092 cm⁻¹. The close coincidence between these lines in absorption and emission confirms the assignment as the O-O transitions.

If a Boltzmann distribution (thermalization) obtains between the ${}^2\text{E}$ components, emission from the higher energy component will be quenched at sufficiently low temperatures. A large number of ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission spectra have been recorded and in no case has nonthermalization between ${}^2\text{E}$ components been observed. The persistence of two intense R lines, separated by 17 cm^{-1} , at 4°K provides strong support for the two site interpretation of the $\text{Cr}^{3+}:\text{GASH}$ spectrum (3).

The O-O lines are shifted 13 cm^{-1} to the red when H_2O is replaced by D_2O and the splitting is reduced by about 1 cm^{-1} .

As indicated above, the O-O doublet cannot be ascribed to the ${}^2\text{E}$ splitting but rather results from complexes at different symmetry sites, C_3 and C_{3i} . The apparent absence of the doubling in some of the vibronic bands e. g., $13\,888\text{ cm}^{-1}$, is unexpected. It is reasonable that the vibrations be coupled to ${}^2\text{E} \rightarrow {}^4\text{A}_2$ in both environments, and in fact this may be the case, with one component somewhat weaker and hidden in the broad vibronic bands.

Two weak lines appear at O-O-2198 and O-O-2283 cm^{-1} in the $\text{Cr}^{3+}:\text{GASD}$ emission spectrum.

$\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$

The 4°K emission spectra are shown in Figs. 3 and 4. The O-O lines are unsplit and the 14555 cm^{-1} line in $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ coincides, within 7 cm^{-1} , with the apparent ${}^2\text{E} \rightarrow {}^4\text{A}_2$ origin of pure $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Fig. 5),

confirming the assignment of the origin (1). The temperature effect is about the same as in $\text{Cr}^{3+}:\text{GASD}$, a shift of 6 cm^{-1} to lower energy as the temperature is increased from 4° to 77°K . The deuteration shift is in the opposite direction of that in GASH , *viz.*, 5 cm^{-1} to the blue when H_2O is replaced by D_2O . The weak lines at O-O-2253 , O-O-2297 , and O-O-2320 cm^{-1} in $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$ are barely detectable in $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, but are definitely shifted to the region of O-O-3000 cm^{-1} .

DISCUSSION

R Lines in GASH

The rejection of the two-site interpretation and the assignment of the $14\,109$ and $14\,092 \text{ cm}^{-1}$ lines to the components of ${}^2\text{E} \leftarrow {}^4\text{A}_2$ was made on the basis of a simple axial ligand field model (1). In this model the ${}^4\text{T}_2$ splitting, as measured by the separation of the band maxima of ${}^4\text{A}_1({}^4\text{T}_2) \leftarrow {}^4\text{A}_2$ and ${}^4\text{E}({}^4\text{T}_2) \leftarrow {}^4\text{A}_2$, and the ${}^2\text{E}$ splitting are both proportional to the same trigonal field parameter, $\underline{v}$ (6). From the ${}^4\text{T}_2 \leftarrow {}^4\text{A}_2$ band splitting at 20°K , $\underline{v}$ is estimated as 640 cm^{-1} (1). The Sugano and Tanabe expression (7) for the ${}^2\text{E}$ splitting, $\lambda = -4/3 \underline{v} \mathcal{J} / [W({}^2\text{E}) - W({}^2\text{T}_2)]$, is nearly correct (8) and when $\underline{v} = 640 \text{ cm}^{-1}$ a ${}^2\text{E}$ splitting of some 20 cm^{-1} is computed for any reasonable value of the spin-orbit coupling constant, $\mathcal{J}$. That the actual splitting for an ion in a given site is less than one cm^{-1} illustrates the inadequacy of a model in which a single $\underline{v}$ parameter describes both the ${}^2\text{E}$ and ${}^4\text{T}_2$ splittings. These splittings are not in general, related by a simple proportionality (9), but it is

noteworthy that in $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, both ${}^4\text{T}_2$ and ${}^2\text{E}$ are unsplit (1).

Vibronic Assignments

The analysis of Nakagawa and Shimanouchi provides a useful basis for this discussion (10). The 51 normal modes of $\text{M}(\text{H}_2\text{O})_6$ complexes in T_h symmetry are classified as a_g (3), a_u (1), e_g (3), e_u (1), t_g (5), and t_u (8). In T_h only t_u modes are infrared active and Nakagawa and Shimanouchi indicate that the H_2O librational and M-O stretching modes should appear in the $270\text{-}1000\text{ cm}^{-1}$ region while O-M-O deformation should lie below 250 cm^{-1} . The M-O and O-M-O frequencies will not be changed very much when H_2O is replaced by D_2O , but the water librational energies are very sensitive to deuteration. For example, the 541 cm^{-1} transition in $\text{Zn}(\text{H}_2\text{O})_6^{3+}$ is found at 392 cm^{-1} in $\text{Zn}(\text{D}_2\text{O})_6^{3+}$ (10). The ratio of librational energies, $\nu(\text{H}_2\text{O})/\nu(\text{D}_2\text{O})$, ranges from 1.2 to 1.4 (10, 11).

Comparison of the emission spectra of each $\text{H}_2\text{O} - \text{D}_2\text{O}$ pair (Figs. 1 and 2; Figs 3 and 4) permits the classification of the participating vibrations into deuterium-sensitive and deuterium-insensitive types. The low-frequency modes (within 350 cm^{-1} of the origin) fall into the deuterium-insensitive category, while most of the higher-frequency vibrations are sensitive to deuteration with $\nu_{\text{H}_2\text{O}}/\nu_{\text{D}_2\text{O}}$ of 1.3 - 1.4 (Table 1).

In $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, the site symmetry of the trivalent ion is C_{3i} (12). Upon reduction of the symmetry from T_h to C_{3i} only the

t_u and t_g modes are split into two components. In the $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$ spectra where the lines are narrow, the results of this splitting are evident (Figs. 3 and 4). Upon exchange of D_2O for H_2O , not only are the energies but the splitting patterns of vibronic transitions involving low energy ($< 350 \text{ cm}^{-1}$) vibrations are the same, and the correlation of these vibrations in the two systems is evident. The correspondence of the deuterium-sensitive bands is less obvious and the correlations in Table I are only suggestive. ^{Three bands in the} IR spectrum of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ have been assigned: 800 cm^{-1} , H_2O rock; 541 cm^{-1} , H_2O wag; and 490 cm^{-1} M-O stretch (10). These can also be identified in the $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ emission spectrum. The weak infrared band at $\sim 370 \text{ cm}^{-1}$ has not been assigned, the 364 cm^{-1} shoulder may be the counterpart in the emission spectrum. The M-O stretch frequency should not be changed much by deuteration and the 476 cm^{-1} ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and 491 cm^{-1} ($\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$) lines may arise from this vibration.

In a like manner, the spectra of $\text{Cr}^{3+}:\text{GASH}$ and $\text{Cr}^{3+}:\text{GASD}$ are analyzed. A one-to-one correspondence can be made for the low frequency modes ($< 350 \text{ cm}^{-1}$) which are deuterium-insensitive, but the correlations of the high frequency deuterium-sensitive vibration are again uncertain.

The absorption spectra of GCrSH (1) and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Fig. 5) have been determined at 20°K . A number of the prominent vibrations are found in both the absorption and emission spectra. A possible correlation between the intervals in the several hosts is presented in Table I. The $\text{Cr}^{3+}:\text{GASH}$ absorption and emission spectra are more nearly mirror images than is sometimes the case (13) but there are some notable

differences. For example, the $\text{Cr}^{3+}:\text{GASH}$ 329 cm^{-1} vibration is relatively more intense in absorption than in emission.

If we compare the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission spectra of Cr^{3+} in GASD, $\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$, and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$ (5), some similarities as well as some differences are noticable. In all three hosts there is a strong band around 200 cm^{-1} , which is not much shifted by deuteration. By assuming an analogous small deuterium shift in all hosts, the 273 cm^{-1} ($\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$) and 306 cm^{-1} (GASD) bands can be correlated. These in turn probably correspond to the 307 cm^{-1} vibration in $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$. The 550 and 674 cm^{-1} $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$ bands are also present in the GASD and $\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$ spectra. The markedly different intensity distribution in the emission spectra are apparent. The ratio of the $\underline{\text{R}}$ line intensity to the total intensity ($\eta_{\underline{\text{R}}}$) is a measure of the "allowedness" of the transition (14). The ${}^2\text{E} \rightarrow {}^4\text{A}_2$ $\underline{\text{R}}$ line in $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is magnetic dipole, but the nature of the transition in $\text{Cr}^{3+}:\text{GASH}$ is uncertain (1). The $\eta_{\underline{\text{R}}}$ values are 0.07 and 0.27 in $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$ and $\text{Cr}^{3+}:\text{GASD}$, respectively (4), indicating a much greater contribution of vibrationally induced intensity in the former. The intensities of vibrationally induced components will be more sensitive to environment than those of "allowed" components.

In addition to the different intensity distributions, there is a significant difference between the $\text{Cr}^{3+}:\text{GASD}$ and $\text{Cr}^{3+}:\text{AlCl}_3 \cdot \text{D}_2\text{O}$ spectra, viz., an additional deuterium-insensitive band is observed in $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$. It is conceivable that the 169 and 121 cm^{-1} $\text{Cr}^{3+}:\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$ bands are components of the 141 cm^{-1} GASD transition, but the IR and Raman spectra of $\text{CrCl}_3 \cdot 6\text{D}_2\text{O}$, GCrSH and GCrSD will be required to settle this question and

to make more definitive assignments. Inasmuch as we are interested in the intramolecular $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and $\text{Cr}(\text{D}_2\text{O})_6^{3+}$ modes, the vibrational spectra of the host crystals are not sufficient for this purpose.

The data in Table I qualitatively support the conclusions of Nakagawa and Shimanouchi (10). The O-M-O deformations fall below 350 cm^{-1} and the bulk of the vibrations in the $350\text{-}1000\text{ cm}^{-1}$ region are deuterium shifted and consequently water librations. The weak bands near 3000 cm^{-1} (H_2O) and 2200 cm^{-1} (D_2O) are the localized water stretching modes. The vibrations below 100 cm^{-1} may be lattice modes, but a vibration around 50 cm^{-1} is found in five different hosts, suggesting an intramolecular assignment.

Legends

Fig. 1. ${}^2E \rightarrow {}^4A_2$ emission spectrum of 10% Cr^{3+} :GASH at 4°K.

Fig. 2. ${}^2E \rightarrow {}^4A_2$ emission spectrum of 10% Cr^{3+} :GASD at 4°K. Curve (b) was taken with a long exposure. Two weak bands at 11 899 and 11 814 cm^{-1} are not shown.

Fig. 3. ${}^2E \rightarrow {}^4A_2$ emission spectrum of 10% Cr^{3+} : $AlCl_3 \cdot 6H_2O$ at 4°K. A weak feature near 11 500 cm^{-1} is not shown.

Fig. 4. ${}^2E \rightarrow {}^4A_2$ emission spectrum of 10% Cr^{3+} : $AlCl_3 \cdot 6D_2O$ at 4°K. Weak lines at 12 307, 11 263, and 11 240 cm^{-1} are not shown.

Fig. 5. ${}^2E \leftarrow {}^4A_2$ absorption spectrum of $CrCl_3 \cdot 6H_2O$ (redrawn from ref. (2)). The polarizations are referred to the crystal c axis.

Table I. Correlation of ${}^2E \rightarrow {}^4A_2$ Vibrations (cm^{-1})

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$			$\text{AlCl}_3 \cdot 6\text{D}_2\text{O}$		GASH		GASD	$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$	
Emission	Absorption ^a	I.R. ^b	Emission	Emission	Absorption ^c	Emission	Emission	Emission	Emission ^d
46	44		37-62	51	40-60		49		
82	89		82						
122	123		121						
				144	151		141		
160+173	166		155+169						
219	219		214	214	204		209		188
253	256			254	254		248		
293	298		273	329	333		306		307
444	450			445	450				
476	484	490	491	479	489		490		
544+570	558	541	393+408	569	566		415		
614+628	629		445+459	606+641	626		452		
692	677		517+537	667			518		
731	731			714	716				
769	778		564	769	756		547		550
817	825	800	608+627	797			574		
885			672				673		674
951			725				732		

a. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (fig. 5)

b. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, ref. (10)

c. GCrSH , ref. (2)

d. ref. (5)

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Fig. 1

Fig. 2

Fig. 3

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Fig 5