LETTER TO THE EDITOR

The Electronic and Vibronic Transitions in the Emission Spectrum of Gd³⁺ in the Yttrium Hydroxide Structure

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The luminescence of the Gd³⁺ ion in a hydroxide is reported for the first time. The X-ray excited emission spectrum is discussed with special attention to the vibronic transitions. © 1989 Academic Press, Inc.

Introduction

Recently it has been shown that the emission of the Gd³⁺ ion can be successfully studied using X-ray excitation. Not only did we observe many higher level emissions (*1*), but vibronic transitions were also seen (*2*). A special case of these vibronic transitions are the cooperative transitions in which the electronic transition occurs on the rare-earth ion (Gd³⁺) and the vibrational transition on a coordinating molecular group (*3*). We observed these transitions for the Gd³⁺ ion in many compounds, such as $Gd_2(SO_4)_3 \cdot 8H_2O$ (*4*), $Gd(ClO_4)_3 \cdot 6H_2O$ (*5*), and Gd acetate tetrahydrate (*6*).

In the present study we tried to observe cooperative vibronic transitions involving the Gd³⁺ ion and the hydroxyl group. The host lattice used was $Y(OH)_3$. In the crystal structure of $Y(OH)_3$ (*9, 10*) each Y³⁺ ion is coordinated by nine OH⁻ ions. Six of these form a trigonal prism. These prisms share the triangular faces forming linear rows with shortest Y–Y distances equal to the value of the *c* axis (3.53 Å). Each O is coordinated by three Y and one H. The OH⁻ ions do not form hydrogen bonds.
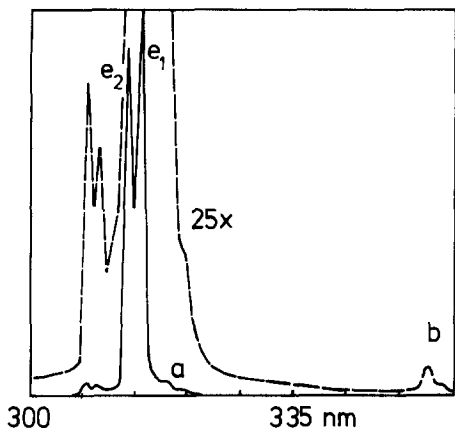
The results of this study are remarkable, since two types of vibronic transitions are observed with strikingly different intensities. One is a purely cooperative vibronic transition, the intensity of which can be readily accounted for.

Experimental

Samples of well-defined single crystalline needles of several millimeters in length were obtained hydrothermally at 400°C and 15,000 atm in Ag tubes. Their X-ray patterns were in excellent agreement with ASTM File Card No. 24,1422. For more details on the preparation we refer to Ref. (7).

The apparatus for measuring the X-ray excited emission spectra has been described elsewhere (8). Measurements were performed at 300 K. The needles were pressed into ½-in.-diameter self-supporting pellets without any binder.

Results

The X-ray excited emission of nominally pure Gd(OH)₃ at 300 K consists mainly of

Tb^{3+} emission which is obviously present as an impurity in the starting material.

The X-ray excited emission of Y(OH)₃:Gd at 300 K has a reasonable efficiency. It consists of the $^6P_{7/2} \to {}^8S$ emission of the Gd^{3+} ion. Figure 1 shows the emission spectrum. The dominating line is the $^6P_{7/2} \to {}^8S$ transition which is split by the crystal field. The splitting is 175 cm⁻¹. The weaker transition on the shorter wavelength side is the $^6P_{5/2} \to {}^8S$ transition which is thermally activated. It is also split by the crystal field. On the longer wavelength side there are some vibronic transitions. Their total integrated intensity is about 8% relative to that of the electronic $^6P_{7/2} \to {}^8S$ transition. Under strong magnification another weak vibronic transition is observed at about 353 nm. Its integrated intensity is much lower and only about 0.2% of the parent transition. Table 1 gives an assignment of the emission spectrum.

The diffuse reflection spectrum of Y(OH)₃ at 300 K shows the following features:

(i) a strong band at 200 nm which is ascribed to a transition on oxygen (comparable to Y_2O_3) (11);

TABLE I

EMISSION TRANSITIONS IN THE SPECTRUM OF Y(OH)₃:Gd AT 300 K UNDER X-RAY EXCITATION

Position		Assignment
nm	cm⁻¹	
307.5	32520	$^6P_{5/2} \to {}^8S$
309.0	32360	$^6P_{5/2} \to {}^8S$
313.0	31950	$^6P_{7/2} \to {}^8S$ (e_2)
314.7	31775	$^6P_{7/2} \to {}^8S$ (e_1)
318.2	31425	$e_2 - 525$ cm⁻¹[a]
320.3	31220	$e_1 - 555$ cm⁻¹[a]
352.5	28370	$e_2 - 3580$ cm⁻¹[b]
354.5	28210	$e_1 - 3564$ cm⁻¹[b]

[a] Gd–(OH)⁻ stretching mode.
[b] OH⁻ stretching mode.

(ii) a weaker band at 235 nm ascribed to a singlet–singlet transition on the OH⁻ group;

(iii) an even weaker band at about 320 nm ascribed to the corresponding singlet–triplet transition. The two latter assignments agree with the excitation spectra of OH⁻ luminescence reported before (12). The latter band does not seem to hamper the Gd^{3+} emission. This is probably related to its very low oscillator strength.

Discussion

(a) Gd(OH)₃

The compound Gd(OH)₃, which is isomorphous with Y(OH)₃, shows mainly Tb^{3+} emission under X-ray excitation. Obviously Tb^{3+} is present as an impurity in the starting materials. The Tb^{3+} ions capture the charge carries preferentially as can be seen from the following argument. If the Gd^{3+} ions capture the excitation energy, energy migration to Tb^{3+} will occur (13). In view of the short Gd–Gd distances in Gd(OH)₃, this migration is expected to be so efficient that the following relation holds:

$$\frac{I(\text{Gd})}{I(\text{Tb})} = \frac{P_\text{r}}{C_\text{Tb} \cdot P_\text{tr}}.$$

Here $I(M)$ is the intensity of the M emission, P_r the radiative rate of Gd^{3+}, P_tr the $Gd^{3+} \rightarrow Tb^{3+}$ transfer rate, and C_Tb the Tb^{3+} concentration relative to the Gd^{3+} concentration. Experimentally $I(\text{Gd})/I(\text{Tb}) \simeq 0.05$. Further we take $P_\text{r} = 500 \text{ sec}^{-1}$ and $P_\text{tr} = 5 \times 10^6 \text{ sec}^{-1}$ (13). In this way we estimate $C_\text{Tb} \simeq 0.2\%$. Since this seems high for the starting material used, part of the excitation energy must be trapped preferentially by terbium.

Since we are interested in the Gd^{3+} emission, the investigations were continued with Y(OH)₃ : Gd.

b. Y(OH)₃ : Gd

The X-ray excited emission spectrum of Y(OH)₃ : Gd is very simple (Fig. 1). It consists of the $^6P_{5/2}$ and $^6P_{7/2} \rightarrow {}^8S$ emission lines. The latter is accompanied by relatively strong vibronic lines with a maximum at $\sim 540 \text{ cm}^{-1}$ from the parent electronic lines. These vibronic lines can only be due to coupling with the Gd–(OH)⁻ vibrations.

Surprisingly enough there is at first sight no vibronic feature due to coupling with the OH⁻ group. Under high magnification a weak feature could be observed at 353 nm. Its intensity is very low. It is situated at $\sim 3570 \text{ cm}^{-1}$ from the electronic origin. Therefore this feature must be due to coupling with the OH⁻ stretching vibration. Reference (9) gives $(3500 \pm 50) \text{ cm}^{-1}$ for this vibration in the infrared spectrum. This is the first example of a vibronic transition involving Gd^{3+} and OH⁻.

In previous papers we reported on the vibronic transition involving Gd^{3+} and H_2O (4–6). Its intensity is an order of magnitude higher than that of the present cooperative vibronic transition. The Gd^{3+}–OH⁻ vibronic transition seems, therefore, unique.

The system Y(OH)₃ : Gd is very suitable for the study of Gd^{3+} vibronic lines. Only two vibronic lines are observed relative to the two electronic lines. The frequencies of the vibrations involved differ nearly an order of magnitude, so that mixing can be neglected. Further the OH⁻ vibration is not coupled to other hydroxyl groups due to the absence of H-bonding. This means that the OH⁻ vibration in Y(OH)₃ is located in the OH⁻ group, and that the Gd–(OH)⁻ vibration in Y(OH)₃ : Gd is a vibration of Gd relative to the OH⁻ group.

The vibronic line due to OH⁻ is, therefore, a real cooperative vibronic line (3), whereas the other one is a regular vibronic feature. This will be of importance in the considerations below.

Stavola et al. (3) performed a quantitative calculation of the OH⁻ vibronic transition belonging to the $^6P_{7/2} \rightarrow {}^8S$ transition, but compared the results to experiments where H_2O is used as a ligand. They

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showed that the vibronic intensity is proportional to the oscillator strength of the molecular vibration in the infrared spectrum. The infrared oscillator strength of the OH^- ion amounts to $(1-6) \times 10^{-3}$ (*14*). With this value they arrived at a radiative rate for coupling with one OH^- group of 0.08 sec^{-1} (*3*). For nine OH^- groups (as in $Y(OH)_3$: Gd) this yields 0.7 sec^{-1}.

From the spectra of this vibronic transition we find a relative integrated intensity of 0.2%. If we estimate the total radiative rate to be 300 sec^{-1} (a reasonable value for Gd^{3+} on a site without inversion symmetry), the OH^- vibronic rate is about 0.6 sec^{-1}. This is in very good agreement with the prediction by Stavola *et al.* (*3*), where it should be remembered that $Y(OH)_3$: Gd is a perfect system to apply the theory.

For the stretching vibration of H_2O the oscillator strength in the infrared is an order of magnitude larger than for OH^- (*15*), especially if hydrogen bonding occurs (see, e.g., (*16*)). In fact the relative intensity of H_2O vibronic lines due to coupling of the stretching mode with the $^6P_{7/2} \rightarrow {}^8S$ transition is also an order of magnitude larger for the OH^- stretching vibration. Examples are $[Gd \subset 2.2.1]Cl_3 \cdot 2H_2O$ (*17*), $Gd_2(SO_4)_3 \cdot 8H_2O$ (*4*), $NaGd(SO_4)_2 \cdot H_2O$ (*18*), and $Gd(ClO_4) \cdot 6H_2O$ (*5*).

The coupling with the $Gd-(OH)^-$ vibration in $Y(OH)_3$: Gd is much stronger (relative intensity 8%). This is ascribed to a large value of the ligand polarizability due to the fact that the ligand absorption is situated near the frequency of the vibronic transition. This was discussed before (*6*). In a forthcoming paper the intensity of many different Gd^{3+} vibronic transitions will be compared and discussed (*19*).

Here we have convincingly shown that the intensity of the OH^- vibronic transition in the emission spectrum of the Gd^{3+} ion has an unexpectedly low value. This effect has to be related to the intensity of the infrared active OH^- stretching vibration.

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