

Vibronic Emission Transitions of Gadolinium(III) in Sodium Lanthanum Sulfate Hydrate

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Abstract

Cooperative vibronic emission transitions are reported for Gd^{3+} in $\text{NaLa}(\text{SO}_4)_2\text{H}_2\text{O}$. They involve the electronic ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition on the Gd^{3+} ion and the asymmetric-valence–vibrational transition on the SO_4^{2-} anion and the H_2O molecule which are both coordinated to the Gd^{3+} ion.

Stavola and coworkers have reported and discussed cooperative vibronic spectra involving the trivalent rare-earth ions [1, 2]. The luminescence spectra of these ions consist for the greater part of purely electronic transitions within the 4f subshell (with the exception of Ce^{3+}). Sometimes, however, weak vibronic features are also observed. When the vibronic transition involves a rare-earth ion and a nearby molecule, Stavola *et al.* have proposed to call these transitions cooperative vibronic. We will follow this proposal here.

The quantitative model given in ref. 1 assumes dipole–dipole interaction as the coupling mechanism between electronic and vibrational excitation. This falls off like R^6 , so that the contribution from molecules coordinated to the rare-earth ion dominates. The vibronic intensity is proportional to the infrared oscillator strength of the vibrational transition involved. The model predicts the intensity of the vibronic transition to be about 1% of that of the electronic transition [1]. The agreement with experimental results is satisfying.

Hao *et al.* [3] have reported on the luminescence properties of several rare-earth ions in $\text{NaLa}(\text{SO}_4)_2\text{H}_2\text{O}$. In this crystal lattice the rare-earth ion has a peculiar coordination. It is coordinated by nine oxygen atoms; eight of these are sulfate oxygen and one a water molecule. Four oxygens belong to different sulfate groups, the other four belong to two sulfate groups (two oxygens belong to the same sulfate group) [4]. Therefore the rare-earth ion is coordinated by one water molecule and six sulfate groups. The distances between the central ion and the different surrounding groups are similar.

It seemed interesting to reinvestigate the rare-earth emission for cooperative vibronic transitions. Two of these are to be expected, *viz.* one by coupling with the H_2O stretching vibration, and another by coupling with the SO_4^{2-} stretching vibration.

Samples were prepared and measured as reported in ref. 3. For our purpose we selected the Gd^{3+} ion which has only one emission line, *viz.* ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ at about 311 nm. In this way the vibronic transitions to be expected are not overlapped by other electronic lines which will be more intense. The sample composition was $\text{NaLa}_{0.5}\text{Gd}_{0.5}(\text{SO}_4)_2\text{H}_2\text{O}$, concentration quenching of the Gd^{3+} emission being rather weak in this lattice [3].

Figure 1 shows the emission spectrum at 300 K. Clearly the ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ electronic transition (1 in Fig. 1) dominates. However, two weak features were observed at lower energy. Feature 2 lies at 1150 cm^{-1} lower energy and feature 3 at 3550 cm^{-1} lower energy. These values agree very well with the asymmetric stretching frequency of the SO_4^{2-} group and the H_2O molecule, respectively. Therefore, these features are assigned as cooperative vibronic transitions involving the electronic ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition on the Gd^{3+} ion and the vibrational modes mentioned. Actually Stavola *et al.* [2] have reported such spectra for Gd^{3+} in aqueous solution.

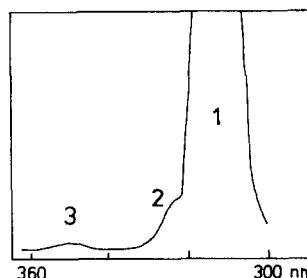


Fig. 1. Spectral energy distribution of the emission of Gd^{3+} in $\text{NaLa}_{0.5}\text{Gd}_{0.5}(\text{SO}_4)_2\text{H}_2\text{O}$ at 300 K. Excitation is at 279 nm (${}^8\text{S}_{7/2} \rightarrow {}^6\text{I}$ transitions on Gd^{3+}). Feature 1 relates to the electronic ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ transition, features 2 and 3 are the vibronic emissions due to coupling with the SO_4^{2-} and H_2O stretching vibrations, respectively.

The interesting aspect is that in our case the Gd^{3+} ion is surrounded by two different molecular groups which both turn up in the vibronic spectrum. The ratio of the integrated emission intensities of the features 1, 2 and 3 in Fig. 1 is as follows: (1):(2):(3) = 100:2.5:0.5. We note that the total intensity of the vibronic lines is again two orders of magnitude less than that of the electronic transition. The intensity ratio of the two vibronic features (~ 5) is, within the experimental error, equal to the ratio of sulfate and water oscillators. Since both groups are at comparable distance from the Gd^{3+} ion and have a high oscillator strength in the infrared spectrum, this observation is not unexpected.

The value of the H_2O vibrational frequency in the sulfate hydrate is higher than observed for bulk water (3400 cm^{-1}) or for water molecules surrounding Gd^{3+} in aqueous solution (3315 cm^{-1}) [2]. This suggests that the hydrogen bonding between the water molecule and the sulfate groups in the solid sulfate hydrate [4] is weaker than in liquid water.

Let us now compare the intensity of the vibronic line involving the water vibration with that observed in aqueous solution. According to ref. 1 this ratio is about 45. There are eight water molecules in the first coordination sphere of Gd^{3+} in solution. If we reduce this to one water molecule, the ratio is expected to increase to 360. Although the accuracy of our experimental value ($100/0.5 = 200$) is not large, the intensity of the vibronic feature due to coupling with the water vibration is certainly higher in $Na(La, Gd)-(SO_4)_2H_2O$ than in liquid water (after correction for the number of water molecules). From this we conclude that the coupling between the electronic and vibrational excitations is stronger in the sulfate hydrate than in water.

The luminescence of Tb^{3+} , but especially of Eu^{3+} , is strongly quenched in the host lattice $NaLa(SO_4)_2 \cdot H_2O$ [3]. This was ascribed to the presence of the water molecule. However, Blasse and Sabbatini [5, 6] have shown that this quenching is unexpectedly strong for one water molecule. This is another and completely independent way to conclude that the coupling between the electronic transitions on the rare-earth ion and the vibrational transition on the water molecule is relatively large in the case of the $NaLa(SO_4)_2H_2O$ lattice. It is an example of the relation between the intensity of vibronic side bands and the rate of radiationless transitions [7].

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