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Vibronic Lines in the Gd^{3+} Emission Spectrum due to Coupling with the Second Coordination Sphere: $Gd(ClO_4)_3 \cdot 6H_2O$

G. BLASSE

Debye Research Institute, University of Utrecht,
P.O. Box 80.000, 3508 TA Utrecht (The Netherlands)

and L. H. BRIXNER

E. I. du Pont de Nemours and Company, Central Research
and Development Department, Experimental Station,
P.O. Box 80356, Wilmington, DE 19880-0356 (U.S.A.)

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Recently we have shown the potential of X-ray excitation to obtain Gd^{3+} emission spectra showing considerable detail [1–3]. Especially the vibronic lines yield information on the coupling with and the nature of the surroundings of the Gd^{3+} ion. In this note we report on the emission of $Gd(ClO_4)_3 \cdot 6H_2O$ under X-ray excitation.

The perchlorate hexahydrates of the lanthanides have a peculiar crystal structure [4]. The Gd^{3+} ion is octahedrally coordinated by six water molecules. The $[Gd(H_2O)_6]^{3+}$ species form a cubic close packing. The ClO_4^- ions fill all the available octahedral and tetrahedral holes in the close packing. If we assume that the distances for $Tb(ClO_4)_3 \cdot 6H_2O$ [4] may also be used in good approximation for $Gd(ClO_4)_3 \cdot 6H_2O$, we arrive at the following data:

- shortest Gd–Gd distance: 8.4 Å; this excludes Gd^{3+}–Gd^{3+} energy transfer [5];
- Gd–O(water) distance: 6 X 2.35 Å;
- Gd–Cl(2) (centre of perchlorate ion in tetrahedral hole): 4 X 4.22 Å;
- Gd–Cl(1) (centre of perchlorate ion in octahedral hole): 6 X 5.96 Å.

Samples of $Gd(ClO_4)_3 \cdot 6H_2O$ were of 99.9% purity from AESAR division of Johnson Matthey Incorporated. The instrumentation to record the X-ray excited emission spectra has been described before [6]. Measurements were made using Mo Kα radiation (45 mA, 40 kVp).

Figure 1 shows the emission spectrum of X-ray excited $Gd(ClO_4)_3 \cdot 6H_2O$ at 300 K. The electronic $^6P_{7/2} \rightarrow {}^8S$ transition is dominating. At shorter wavelength the thermally excited $^6P_{5/2} \rightarrow {}^8S$ transition occurs; at longer wavelength a number of vibronic lines are observed. Table 1 gives the exact data and an assignment.

The occurrence of vibronic lines due to coupling with the bending and stretching modes of the water molecules which form the first coordination sphere is not surprising in view of our earlier work [7, 8]. However, the occurrence of vibrations due to coupling with the perchlorate ion of the second coordination sphere is a unique observation. First, we note that this is the only assignment possible. Second, Fig. 1 shows that the perchlorate vibronics are not much weaker than the water vibronics.

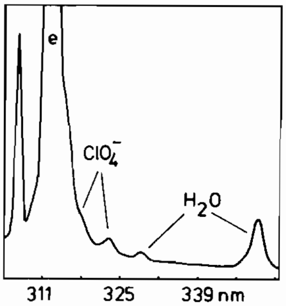

Fig. 1. The X-ray excited emission spectrum of $Gd(ClO_4)_3 \cdot 6H_2O$ at 300 K (compare Table 1). The ClO_4^- and H_2O vibronics are marked. The electronic origin $^6P_{7/2} \rightarrow {}^8S$ is indicated as e. The sharp line on the left-hand side is $^6P_{5/2} \rightarrow {}^8S$.

TABLE 1. Emission spectrum of $Gd(ClO_4)_3 \cdot 6H_2O$ at 300 K under X-ray excitation

Spectral position		Assignment[a]	
(nm)	(cm^{-1})		
306.5	32.625	$^6P_{5/2} \rightarrow {}^8S$	
312.0	32.050	$^6P_{7/2} \rightarrow {}^8S$ (e)	
315.5	31.695	e–355 cm^{-1}	ν(Gd–O)
318.0	31.445	e–605 cm^{-1}	$\nu_4(ClO_4^-)$
323.0	30.960	e–1090 cm^{-1}	$\nu_3(ClO_4^-)$
329.0	30.395	e–1655 cm^{-1}	$\nu_b(H_2O)$
350.0	28.570	e–3480 cm^{-1}	$\nu_s(H_2O)$

[a] Infrared data: $\nu_3(ClO_4^-)$, 1120 cm^{-1}; $\nu_4(ClO_4^-)$, 625 cm^{-1} [10].

According to Stavola *et al.* [9], the intensity of these cooperative vibronic lines varies as R^{-6} where R is the rare-earth to vibrational-centre distance. If we assume that all other factors are equal for H_2O and ClO_4^- (for example, the oscillator strength of the vibrational mode), that R for Gd^{3+}–H_2O is 3.50 Å (since the O–H vibration has its centre of gravity near H, we take the estimated Gd^{3+}–H distance), that R for Gd^{3+}–$[Cl(2)O_4]^-$ is 4.22 Å, and consider that there are six H_2O and four $[Cl(2)O_4]^-$ species around the Gd^{3+} ion, the intensity ratio of the water and the perchlorate vibronic lines is $6/4 \cdot (4.22/3.50)^6 = 4.5$. For the stretching vibrations the experimental ratio is about 4. The agreement is excellent. The contribution of the $[Cl(1)O_4]^-$ ions in the octa-

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hedral holes is only some 10% of that of the tetrahedral ones due to the considerably larger distance.

In conclusion, we have shown the first example of a vibronic line in a trivalent lanthanide ion emission spectrum which is due to coupling with the second coordination sphere.

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