

LETTER TO THE EDITOR

An Anti-Stokes Vibronic Line in the Emission Spectrum of $\text{LaF}_3:\text{Gd}$

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The emission spectrum of $\text{LaF}_3:\text{Gd}$ shows an anti-Stokes vibronic line coupled to the ${}^6P_{7/2} \rightarrow {}^8S$ transition. © 1989 Academic Press, Inc.

The optical spectra of transitions within the $4f^n$ configuration of rare-earth ions are dominated by pure electronic (zero-phonon) transitions. The vibronic side lines are weak; their intensity amounts characteristically to 1% of that of the corresponding electronic transition (1). The temperature dependence of the intensity of these vibronic transitions is well understood (see, e.g., (2)), and has been studied especially on transitions within the $3d$ shell with strong zero-phonon lines. Examples are $\text{MgO}:\text{V}^{3+}$ (2) and Cr^{3+} in several hosts (for a recent example, see (3)). The optical transition involved is ${}^2E \rightarrow {}^4A_2$.

The temperature dependence of the intensity of the Stokes vibronic lines is given by $1 + n$ and that of the anti-Stokes vibronic lines by n , where $n = [\exp(h\nu/kT) - 1]^{-1}$ (2). The vibrational frequency involved is given by ν .

Recently we have shown that X-ray excitation of Gd^{3+} -containing compositions can yield very efficient Gd^{3+} emission (4, 5). In this way it is possible to study vibronic transitions in the Gd^{3+} emission spectra. The fact that the ground state (8S) of the Gd^{3+} ion is not split makes it easy to observe and interpret these spectra. In view of our results with Stokes vibronics on the ${}^6P_{7/2} \rightarrow {}^8S$ electronic transition of the Gd^{3+} ion, we tried to observe also the anti-Stokes emission.

A serious problem, however, is the ${}^6P_{5/2} \rightarrow {}^8S$ emission transition which is located at $\cong 600 \text{ cm}^{-1}$ higher energy than the ${}^6P_{7/2} \rightarrow {}^8S$ transition. This will overlap vibronics with frequencies equal to that energy difference. Anti-Stokes vibronics with still higher frequency will not have high enough intensity at 300 K to allow observation: for $\nu = 1000 \text{ cm}^{-1}$ the intensity ratio of anti-

Stokes and Stokes vibronics at 300 K is less than 1%. This follows from the ratio $n/(1+n)$ which will be a good approximation.

The most suitable frequency for our purpose is $\nu = 300 \text{ cm}^{-1}$. The corresponding vibronic line will be between the ${}^6P_{5/2} \rightarrow {}^8S$ and ${}^6P_{7/2} \rightarrow {}^8S$ emission lines and yield 22% for the anti-Stokes/Stokes intensity ratio at 300 K. We found that $\text{LaF}_3:\text{Gd}$ shows a ${}^6P_{7/2} \rightarrow {}^8S$ Gd^{3+} emission line with a Stokes side line at 320 cm^{-1} (Fig. 1, Table I). Instrumental details have been given in Ref. (6). The ${}^6P_{5/2}$ - ${}^6P_{7/2}$ energy difference is 605 cm^{-1} (Table I). There is a weak feature at 308.5 nm between the two electronic lines (Fig. 1). This is at 340 cm^{-1} higher energy than the ${}^6P_{7/2} \rightarrow {}^8S$ transition.

There are two reasons why the 308.5-nm feature should not be correlated to the ${}^6P_{5/2} \rightarrow {}^8S$ transition:

(i) its intensity is too high to be a Stokes side line of ${}^6P_{5/2} \rightarrow {}^8S$. The expected intensity is 1% or less of the electronic ${}^6P_{5/2} \rightarrow {}^8S$ emission line (as for ${}^6P_{7/2} \rightarrow {}^8S$); the observed intensity is more than 10% of the ${}^6P_{5/2} \rightarrow {}^8S$ transition.

(ii) the vibrational frequency relative to ${}^6P_{5/2} \rightarrow {}^8S$ is 265 cm^{-1} which is too low a value in comparison with the ${}^6P_{7/2} \rightarrow {}^8S$ side line.

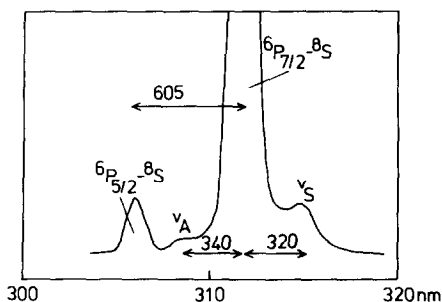


Fig. 1. Emission spectrum in the ${}^6P \rightarrow {}^8S$ region of a $\text{LaF}_3:\text{Gd}$ crystal at 300 K under X-ray excitation. The Stokes and anti-Stokes vibronic lines are indicated by ν_S and ν_A , respectively. Energy differences are indicated between arrows in cm^{-1} .

TABLE I

ANALYSIS OF THE EMISSION LINES IN THE 300- TO 320-nm REGION OF THE EMISSION SPECTRUM OF A $\text{LaF}_3:\text{Gd}$ CRYSTAL UNDER X-RAY EXCITATION AT 300 K (COMPARE FIG. 1)

Position		Assignment
nm	cm^{-1}	
306.0	32.680	${}^6P_{5/2} \rightarrow {}^8S$ (electronic)
308.5	32.415	${}^6P_{7/2} \rightarrow {}^8S + 340 \text{ cm}^{-1}$
311.75	32.075	${}^6P_{7/2} \rightarrow {}^8S$ (electronic)
314.9	31.755	${}^6P_{7/2} \rightarrow {}^8S - 320 \text{ cm}^{-1}$

The intensity ratio of the anti-Stokes and the Stokes side lines of ${}^6P_{7/2} \rightarrow {}^8S$ is found to be 0.2; the value of $n/(1+n)$ at 300 K for $\nu = 330 \text{ cm}^{-1}$ amounts to 0.19. This good agreement shows that the 308.5-nm feature is the anti-Stokes side line of the ${}^6P_{7/2} \rightarrow {}^8S$ transition on Gd^{3+} in LaF_3 .

An obvious way to check our interpretation is to repeat the measurements at low temperatures, since the anti-Stokes line should disappear under these conditions. Therefore, the X-ray excited emission spectrum of $\text{LaF}_3:\text{Gd}$ was measured at 10 K. Unfortunately, many changes take place in the emission spectrum upon cooling. A broad emission band with a maximum at about 280 nm occurs. It is ascribed to V_K center emission because of its striking similarity with the ultraviolet V_K emission band of BaF_2 under high-energy excitation (7, 8) and of a BaFX ($X = \text{Cl}, \text{Br}$) (9). However, it makes observation of weaker features more difficult than at room temperature. Nevertheless, the ${}^6I \rightarrow {}^8S$ emission at 10 K becomes considerably stronger at the cost of the ${}^6P \rightarrow {}^8S$ emission due to the lower rate of the nonradiative ${}^6I \rightarrow {}^6P$ transition. At the same time, however, the ${}^6P_{5/2} \rightarrow {}^8S$ emission together with the anti-Stokes line disappear within the accuracy of our measurements. This agrees with the expectation, although it must be realized that any

Stokes lines belonging to ${}^6P_{5/2} \rightarrow {}^8S$ have also disappeared.

The infrared spectrum of LaF_3 shows as the highest absorption transition an intense band around 350 cm^{-1} (10). This is in good agreement with the observed frequency from the vibronic lines. The vibration will have rare-earth vs fluorine stretching character.

Recently Richardson *et al.* (11) reported anti-Stokes vibronic lines in the emission spectra of $\text{Eu}(\text{AP})_6\text{I}_3$ and $\text{Eu}(\text{AP})_6(\text{ClO}_4)_3$ (AP = antipyrine). We found that their intensities agree with the expression $n/(1+n)$ within the accuracy of the data.

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