The Vibronic and Infrared Spectra of Europium Dibenzoylmethane Chelate with Piperidine

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The vibronic spectra of europium dibenzoylmethane chelate with piperidine in the neighbourhood of the $^5D_0 \to {}^7F_0$ line at 293 K and 77 K and the infrared absorption spectra in the region of $20-200$ cm^{-1} at various temperatures have been studied. It is shown that all vibrational frequencies obtained from the vibronic spectrum at 77 K can be observed in the infrared spectrum at the same temperature. For the above frequencies we assign some vibrations as belonging to irreducible representations of S_4 point group symmetry.

Introduction

The spectra of the crystalline complex of europium with β-diketone show line structure. Weissman pointed out that these lines belong to transitions between electronic states of Eu^{3+} [1]. Apart from the pure electronic lines the spectra also contain some vibronic peaks which involve a simultaneous change in both electronic states of the molecule and vibrational states of either the molecule or a mode of the crystal [2]. The vibronic lines observed in the fluorescence spectra are mainly due to transitions between the lowest excited level $^5D_0$ and the vibrational levels of the fine structure ^7F_J states [3, 4].

Until now the interpretation of fluorescence vibronic spectra based on the study of infrared (IR) absorption spectra has been given only in the range above 200 cm^{-1} [5, 6, 7]. In particular, IR work in this range on the rare earth dibenzoylmethane chelate has been reported in Ref. [8, 9]. The present work reports on the vibronic spectra of the dibenzoylmethane (DBM) europium complex with piperidine (P)-chemical formula Eu(DBM)$_4$HP. Special attention is given to the low vibrational frequencies and their description based on the IR spectra in the range of $20-200$ cm^{-1}. For such an analysis the fluorescence spectra including the $^5D_0 \to {}^7F_0$ transition are most convenient since the $^5D_0$ and $^7F_0$ levels are not degenerate [10, 11, 12].

Experimentel

It has been found that Eu(DBM)$_4$HP can appear in three different forms depending on the crystallization conditions [13, 14]. Among these three forms, according ot our previous paper [15], only one form has a recognized symmetry, namely S_4. The crystalline form of Eu(DBM)$_4$HP chelate showing the S_4 symmetry was used in the present investigations. Molecular crystals were obtained from methanol solution in the same way as in [13]. In this solution the molar ratio of europium : dibenzoylmethane : piperidine was 1 : 5 : 100. The europium complex was obtained in a microcrystalline powder form.

The vibronic spectra of the chelate were measured using an ISP-51 spectrograph with a photoelectric recording system. The fluorescence spectra were measured at room and liquid nitrogen temperatures. The microcrystalline powder was excited in the cryostat by a mercury HBO-50 lamp followed by an absorption filter with $\lambda_{\max} = 365$ nm.

The far IR spectra of the europium chelate in the region from 20 to 200 cm^{-1} were obtained at 293 K, 145 K and 77 K on Nujol mulls using the Grubb Parsons IRIS Fourier spectrophotometer. The frequencies were determined to an accuracy of 1 cm^{-1}.

Results and Discussion

Figure 1 shows the vibronic spectra of the Eu(DBM)$_4$HP chelate in the neighbourhood of the $^5D_0 \to {}^7F_0$ line of Eu^{3+}. For brevity this line will be quoted as the $0-0$ transition. As one can see, these spectra consist of the sharp $0-0$ pure electronic line and may broadened satellite lines
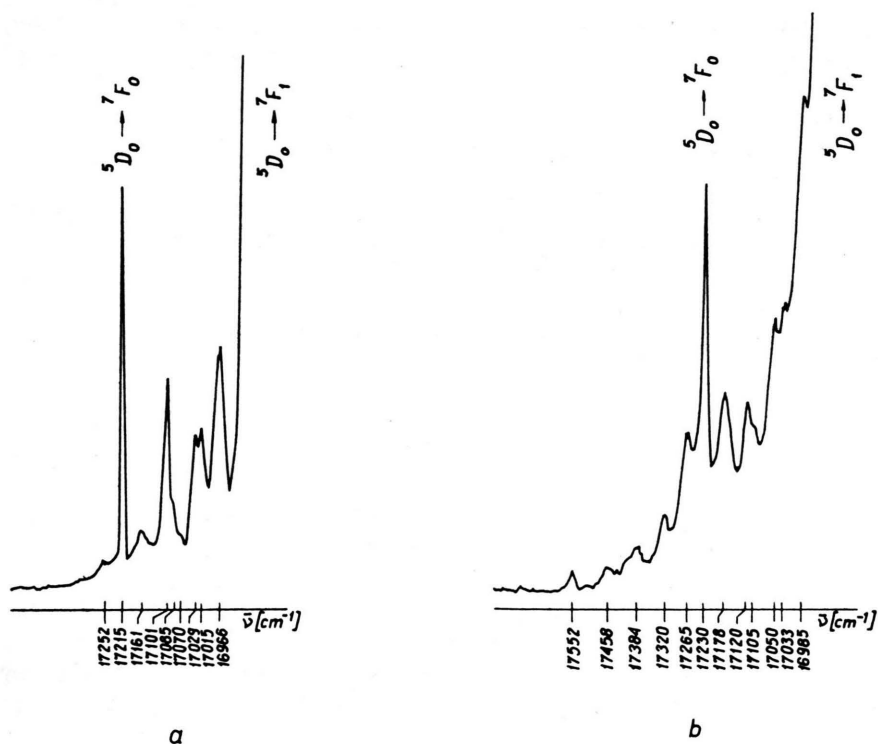
Fig. 1. The vibronic spectra of europium dibenzoylmethane chelate in the neighbourhood of the $^5D_0 \rightarrow {^7F_0}$ line at 77 K (a) and 293 K (b).
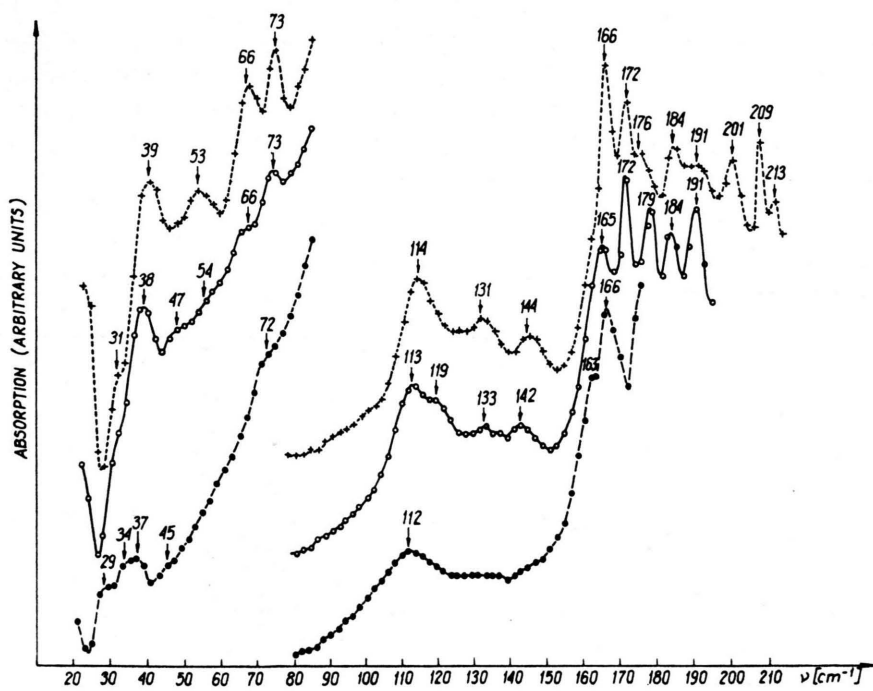

Fig. 2. The intrared absorption spectra of europium dibenzoylmethane chelate at different temperatures;
−+−−+−   77 K,
−○−−○−   145 K   and
−●−−●−   293 K.

arising from electronic-vibrational transitions. At 77 K the spectrum consists mainly of satellite lines appearing in the long-wavelength part of the 0—0 parent line (17215 cm^{-1}). This implies that at this temperature the observed satellite lines are due to transitions from the excited $^5D_0$ level to the oscillation levels of the $^7F_0$ state. These lines belong to one-phonon transitions [3]. On the short-wavelength side of the 0—0 line there appears a single line at 17252 cm^{-1}. The presence of this line, which corresponds to the anti-Stokes transition, proves that the lowest vibrational level of the $^5D_0$ term is also populated. At room temperature the vibronic lines appear in fluorescence as long- and short-wavelength satellites of the 0—0 parent line at 17230 cm^{-1}, see Figure 1 b. This is expected since the Boltzmann distribution ensures that at room temperature the higher vibrational levels of the $^5D_0$ state are also populated. It is worth noticing that the study of the vibronic spectrum at room temperature permits one to determine not only the vibrational frequencies of the ground state but also the vibrational frequencies of the excited $^5D_0$ state [4].

Figure 2 shows the complicated structure of the far IR spectra. The peaks in these spectra correspond to normal vibrations of the molecular complex as well as to certain vibrational modes of the crystal lattice. As can be seen in Fig. 2 the width of the peaks increases with temperature. This is due to line broadening caused by the overlap of low energy acoustic mode phonon frequencies with frequencies of internal modes. The observed line broadening increases at higher temperatures.

Table 1 lists the wavenumbers of vibronic lines and the values of vibronic frequencies connected with the vibrational levels of the ground $^7F_0$ and excited $^5D_0$ states of Eu^{3+}. As one can see from columns 3 and 4 in Table 1, all the vibrational frequencies at 77 K obtained from the fluorescence spectrum as the difference between frequencies of pure electronic and accompanying vibronic transitions are also observed in the far IR spectrum.

The vibronic transitions appears as result of electronic-vibrational interaction [2]. The changes of the position of atoms surrounding the Eu^{3+} ion in the organic complex cause a dynamic crystalline field which interacts with the shielded electrons of the central ion. This interaction depends on the symmetry of the electronic states and the type of vibrations. Since the $^5D_0$ and $^7F_0$ states belong to the same irreducible representation they interact with the same normal vibrations. From this one may be conclude that absorbed or emitted vibrational quanta connected with both the anti-Stokes and Stokes transitions are associated with the same type of vibrations in the $^5D_0$ and $^7F_0$ states. Hence our measurements show that the vibrational frequencies of the $^5D_0$ state are lower than those of the $^7F_0$ state. This means that the interaction of the Eu^{3+} ion with its surroundings is stronger in the ground state than in the excited state.

Table 1. The wavenumbers of vibronic lines and frequencies of the vibrations at 77 K and 293 K.

	77 K			293 K			
	Wavenumber of vibronic line [cm^{-1}]	Frequency of the vibration [cm^{-1}]		Wavenumber of vibronic line [cm^{-1}]	Frequency of the vibration [cm^{-1}]		Symmetry of the normal vibration
		Vib. spec.	IR		Vib. spec.	IR	
Anti-Stokes line				17552	322		
				17458	228		
				17384	154		
				17320	90		
	17252	37		17265	35		
0—0 line	17215			17230			
Stokes line	17161	54	53	17178	52	—	A
	17101	114	114	17120	110	112	B or E
	17085	130	131	17105	125	—	A
	17070	145	144	—	—	—	A
	17029	186	184	17050	180	—	B or E
	17015	200	201	17033	197	—	B or E
	16966	249		16985	245		B or E

The vibronic peaks can be assigned using the selection rules [2, 10] if we assume that these vibrational levels belong to normal vibrations of the molecular complex and that the symmetry of the crystalline field operating at the central ion shows the symmetry of the molecular complex. Let us consider transitions from the $^5D_0$ level to the vibrational levels of the $^7F_0$ term. Since it is known that the $^5D_0$ and $^7F_0$ states for the S_4 point group appropriate to the europium chelate belong to the A irreducible representation and the components of the electric dipole moment belong to the B and E irreducible representations, one can find the vibronic selection rules using the Born-Oppenheimer approximation without knowing the detailed characteristics of the normal mode displacements [10]. Thus it is only necessary to determine for which vibrations the transition probability does not vanish. In this case the transitions are allowed when the symmetry of the normal co-ordinates have the same symmetry as that of the components of the electric dipole moment, i.e. the irreducible representation B or E. From the assumption that the strongest lines appearing in the vibronic spectra correspond to allowed transitions it is to be concluded that the lines at 17101, 17029, 17015 and 16966 cm^{-1} (Fig. 1a) are connected with the normal vibrations described by B or E representations. On the other hand the weak lines should correspond to forbidden transitions. Thus the lines at 17161, 17085 and 17070 cm^{-1} are probably connected with the normal vibrations which belong to the A irre-

ducible representation of the S_4 point group. The values of vibrational modes are relevant in the treatment of radiationless transitions of excited rare earth ions [11, 16, 17]. However, their symmetry typs are needed (among other things) to describe the interaction between the vibrational modes and near lying 4f Stark levels leading to "borrowing" of intensity [3]. From this it would seem reasonable to suppose that the strong line at 16966 cm^{-1} can rather correspond to the normal vibration as belonging to the E irreducible representation. At this symmetry the above line can "borrow" the intensity from the $^5D_0 \rightarrow {}^7F_1$ transitions. Because all the vibrational frequencies have small values, they are assigned as metal-ligand bond stretching and bending vibrations. These vibrations are due to positional changes and librations of ligands or groups of atoms within ligands [3, 8, 9, 12].

It is worth noticing that in the range of the vibronic spectrum at 77 K all the lines have corresponding peaks in the far IR spectrum. Therefore it can be concluded that all lines appearing in the vibronic spectrum of the europium chelate are electronic-vibrational lines. In the fluorescence spectrum we found no peaks which could be described as the $^5D_1 \rightarrow {}^7F_3$ transition. This confirms that the probability of the $^5D_1 \rightarrow {}^7F_3$ transition is small.

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