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Polarized Emission of $[Ru(bpy)_3](PF_6)_2$ Single Crystals

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Abstract: Polarized emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ are reported for the first time. The spectra are recorded in the temperature range from $T = 243$ to 343 K. A new **E**$\parallel$**c**-polarized emisson band is found, situated 650 cm^{-1} ± 20% above the main emission peak maximum. The corresponding emitting state is assigned to A_2' (in D_3'). The **E**$\perp$**c**-polarized emission results from one or more E′ states and is by a factor of about 20 more intense than the **E**$\parallel$**c**-polarized emission.

The excited electronic states of $[Ru(bpy)_3]^{2+}$ compounds (with bpy = 2,2′-bipyridine) have been analyzed intensively during the past decade, since these compounds might be of importance in a water-splitting process through electron-transfer reactions, induced by solar energy.[1-4] However, up until now there is no agreement in the assignment of the lowest excited states, which determine the emission spectrum. But just these states are of importance in the observed electron-transfer processes.

It has been shown that especially the polarized single-crystal spectroscopy represents a very useful technique for the identification and assignment of electronic states, if the relevant structure data of the crystals are available.[5] Polarized absorption spectra of $[Ru(bpy)_3]^{2+}$ doped in $[Zn(bpy)_3]X_2{\cdot}nH_2O$ (with X = Br or $^1/_2SO_4$) have already been published.[6,7] Yet, pure single-crystal spectra of $[Ru(bpy)_3]^{2+}$ compounds are not known, either in absorption or in emission. The subject of this paper is to present, for the first time, spectra of the polarized emission of single-crystal $[Ru(bpy)_3](PF_6)_2$. This is, to our knowledge, the only $[Ru(bpy)_3]^{2+}$ compound for which the structure has been determined.[8] We are further interested in discussing the observed spectra in the scope of selection rules determined by group theory.

Experimental Section

Standard literature methods[6] were employed for preparing $[Ru(bpy)_3]Cl_2$ which was the starting material for the synthesis of $[Ru(bpy)_3](PF_6)_2$ by the mutual exchange reaction of $[Ru(bpy)_3]Cl_2$ with $AgPF_6$ in ethanol. The crude material was washed several times with ethanol. Further purification was obtained by recrystallization from solutions in acetone. Single crystals of $[Ru(bpy)_3](PF_6)_2$ were grown by slow evaporation in ethanol–acetonitrile (1:1 v/v) solutions at room temperature. Crystals of good quality were selected under a polarization microscope. The typical crystal size was about 1 × 0.3 × 0.3 mm^3.

Polarized emission measurements were carried out with a microspectrophotometer described elsewhere.[9,10] The crystals were excited with the 488.0-nm line of an argon ion laser (Spectra Physics, Model 165). The attenuated laser beam was focused onto the crystal surface. Only a small area of high optical quality was selected by a diaphragm and used for recording. Care was taken to ensure the comparability of intensities of the spectra.

Results

Figure 1 reproduces the polarized emission spectra (at 290 K) of single-crystal $[Ru(bpy)_3](PF_6)_2$. The observed emission is polarized with the electric field vector **E** either perpendicularly or parallel to the crystal needle axis (**c** axis). It is evident that the spectra for the two polarizations are distinctly different. The intensity of the **E**$\parallel$**c**-polarized transition is weaker by a factor of about 20 than that of the **E**$\perp$**c**-polarized emission. Moreover, a new **E**$\parallel$**c**-polarized transition is observed at the high-energy side of the spectrum. If one crudely estimates the energy difference between the **E**$\perp$**c**-polarized maximum and the blue-side **E**$\parallel$**c**-polarized shoulder, one obtains ΔE(emission spectra) ≈ 700 cm^{-1}.

We have further recorded the differently polarized emission spectra in the temperature range from $T = 243$ to 343 K. It is found that the blue-side shoulder of the **E**$\parallel$**c**-polarized emission can be frozen out. From these measurements one can independently estimate a mean activation energy if one assumes that the corresponding states are in thermal equilibrium and that the separation of the low energetic states is small compared to the activation energy (see also below). From a $\ln (I_\parallel/I_\perp)$ vs. $1/T$ plot we determined ΔE(activation) = 650 cm^{-1} ± 20%, where $I_\parallel$ and $I_\perp$ are the intensitites of the **E**$\parallel$**c**-polarized blue-side shoulder and the **E**$\perp$**c**-polarized peak, respectively. This value is in good agreement with the energy difference, which is determined directly from the spectra.

Discussion

According to the structure determination the space group of $[Ru(bpy)_3](PF_6)_2$ is $P\bar{3}c$ (with $Z = 2$, $a = 10.760$ Å, and $c = 16.391$ Å). The Ru complex lies at a special position, having a D_3 point symmetry with the C_3 axis in the direction of the **c** axis.[8] The assignment of polarized absorption spectra should be accomplished in this D_3 symmetry, since, because of the Franck–Condon principle, the ground-state symmetry is retained during the absorption process. Indeed, the published absorption spectra have been classified group theoretically in the D_3 (or D_3') point symmetry.[7,11,12]

On the other hand, there are several indications that if the lowest excited states are occupied, the $[Ru(bpy)_3]^{2+}$ complex has a reduced point symmetry, which presumably is C_2.[13-15] Consequently, one should classify the emitting states according to the reduced symmetry. However, up to now there is no information available about the size of the electronic-state splitting due to this symmetry reduction. If the splitting of degenerate states (in D_3) is much less than the thermal energy (≈200 cm^{-1} at 300 K), and this is very probable, then on the basis of our actual high-temperature data we cannot decide whether the excited-state point symmetry of the complex is D_3 or C_2. The transitions are simply smeared out. Therefore, we use a first-order assignment in the D_3' parentage double group.

It is well established that the ground state is a singlet A_1' (in D_3') and the lowest excited states are mainly of triplet character as indicated by the long emission lifetime.[11,16-19] The corresponding

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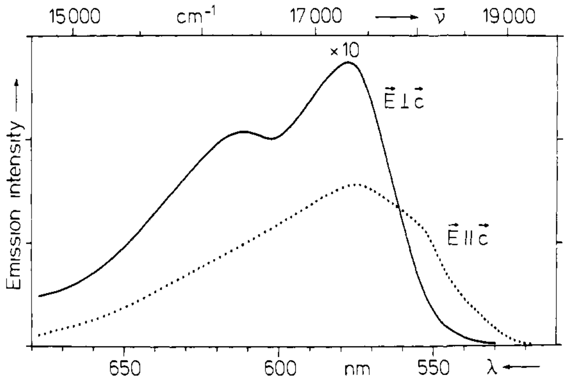

Figure 1. Polarized emission spectra of $[Ru(bpy)_3](PF_6)_2$ single crystals at $T = 290$ K. Note that for comparison of the intensities the $E \perp c$-polarized spectrum has to be enhanced by a factor of 10. The absolute error of peak height is ±10%. The spectra are not corrected due to the response of the detector system. Excitation wavelength (and polarization) = 488 nm ($E \parallel c$).

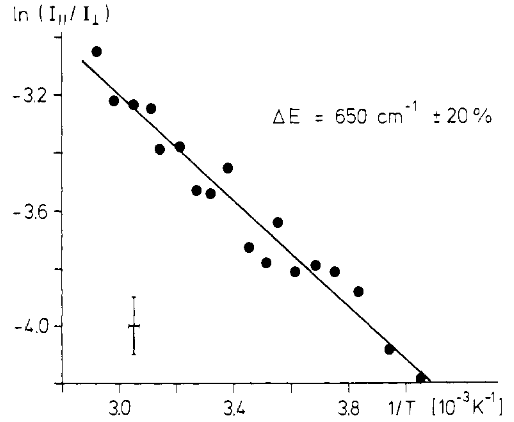

Figure 2. Temperature dependence of the intensity ratio $I_\parallel/I_\perp$. $I_\parallel$ and $I_\perp$ are the intensities of the $E \parallel c$-polarized blue-side shoulder and the $E \perp c$-polarized peak, respectively. The plot of ln $(I_\parallel/I_\perp)$ vs. $1/T$ is drawn to determine the activation energy ΔE.

transitions are allowed through mixing of appropriate wave functions of singlet character to the excited triplet states by spin-orbit coupling ($\xi(Ru^{2+}) \approx 1200$ cm^{-1}).[11]

The $E \perp c$-polarized emission is assigned to originate mainly from E' states (selection rules in D_3': $A_1' \leftrightarrow E'$: $E \perp c$; $A_1' \leftrightarrow A_2'$: $E \parallel c$; $A_1' \leftrightarrow A_1'$: forbidden). The required singlet character will be supplied from singlet states of the same symmetry. There are several strongly allowed $E \perp c$-polarized absorption peaks above $\approx 21\,000$ cm^{-1}.[7]

The $E \parallel c$-polarized blue-side shoulder results from a A_2' state. This is concluded from the selection rules. The A_2' state has not been observed up until now. The corresponding transition seems to acquire its intensity through mixing, for example, with Ru 5p or higher lying bpy π^* states. Mixing with these states of higher energy is small and therefore has explicitly been omitted in recent theoretical papers.[11,12,16] This interpretation is consistent with the fact that the $E \perp c$-polarized emission is more intense by a factor of about 20 than the $E \parallel c$-polarized one.

It is evident from low-temperature investigations, accomplished by Crosby and co-workers,[16-18] that there are further states that are not resolved by our high-temperature emission measurements. These low-temperature investigations show that the emission has to be ascribed to at least three electronically excited states, lying in a small energy range of less than 100 cm^{-1}. This energetic separation is smaller than the experimental error (±130 cm^{-1}) in our determination of the energetic position of the A_2' state. Consequently, our simple method of evaluating the activation energy seems to be justified.

Conclusion

Polarized emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ have been recorded for the first time. A new $E \parallel c$-polarized transition is observed, situated 650 cm^{-1} ± 20% above the main emission peak maximum. In the D_3' symmetry group the new emission peak is assigned to a $A_2' \rightarrow A_1'$ transition. The main emission intensity, however, is $E \perp c$ polarized. It results from one or more E' states. Since the $E \perp c$-polarized intensity is higher by a factor of about 20 than the parallel-polarized one, the unpolarized spectrum is very similar to the $E \perp c$-polarized one.

The results given in this paper are not sufficient to present a complete energy level diagram for the emitting states. But they demonstrate that the models presented up until now have to be refined.

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