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Fine Structure in the Emission Spectrum of $[Ru(bpy)_3](PF_6)_2$ Single Crystals

GEROLD HENSLER, ERICH GALLHUBER and HARTMUT YERSIN*

Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-8400 Regensburg, F.R.G.

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Abstract

For the first time, highly resolved polarized emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ are presented. At low temperatures ($T < 20$ K) we observed fine structure on the blue side of the emission spectrum with a typical halfwidth of $\leqslant 5$ cm^{-1}. The spectral properties of the sharp emission lines and their temperature dependences allow us to assign two zero-phonon lines corresponding to $1E' \rightarrow A_1'$ at 17 809 cm^{-1} and to $2E' \rightarrow A_1'$ at 17 816 cm^{-1} in the D_3' symmetry group.

Introduction

The photophysical and photochemical characterization of the lowest excited states of $[Ru(bpy)_3]^{2+}$ compounds is an area which has received increasing attention during the past decade. The early works of Crosby *et al.* [1–3] were followed by an accelerating interest in the investigation of this material by various spectroscopic methods [4–8]. However, there is no general agreement, either about the group-theoretical assignment of the lowest excited states or about the energetic positions of the purely electronic transitions [1–5, 7–10]. It has been shown that the polarized single-crystal spectroscopy is a very useful method for the identification and characterization of electronic states [11–14]. However, as all $[Ru(bpy)_3]^{2+}$ spectra published hitherto are several hundreds of wavenumbers broad, the available spectroscopic information is restricted. Therefore, it is of interest, and thus the subject of this investigation, to measure carefully the spectra of single crystals at very low temperatures under conditions of high spectroscopic resolution.

Experimental

$[Ru(bpy)_3](PF_6)_2$ was prepared metathetically from the corresponding chloride salt, which was synthetized following published procedures [14, 15], and $AgPF_6$. Crystals were grown at room temperature by slow evaporation of a solution of the complex in acetonitrile/ethyleneglycol. $[Ru(bpy)_3](PF_6)_2$ crystallizes in hexagonal needles with the crystallographic $\vec{c}$ axis (≡ needle axis) parallel to the molecular C_3 axis [16]. We selected crystals of good quality using a polarization microscope. The typical crystal thickness was 50 to 100 μm. The polarized emission spectra were recorded with the electric field vector $\vec{E}$ either parallel ($\vec{E} \| \vec{c}$) or perpendicular ($\vec{E} \perp \vec{c}$) to the needle axis using a micro-spectrometer constructed as described in earlier publications [17, 18]. For excitation, different lines of an argon ion laser were selected (polarization of the excitation $\vec{E} \| \vec{c}$). The excitation at 561.5 nm ($\hat{=}$17 809 cm^{-1}) and at 561.3nm ($\hat{=}$17 816 cm^{-1}) was achieved with a dye laser (Rhodamine 110). Care was taken to attenuate the laser beam sufficiently to avoid sample heating. The sample was placed into a liquid helium dewar. The temperature was determined with a resistor for $T > 4.2$ K, and with a He vapor pressure manometer for lower temperatures, respectively. The temperature was held constant to ±0.05 K for $T < 2.1$ K and ±0.5 K for $T > 2.1$ K, respectively. The absolute error of the monochromator read-out was ±3 cm^{-1}; the spectral resolution was about 4 cm^{-1}. The spectra were not corrected for the spectral response of the apparatus.

Results

Figure 1 shows the $\vec{E} \perp \vec{c}$-polarized emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ between 1.6 and 10 K. At the right-hand side of Fig. 1 we reproduced the spectra which cover (nearly) the whole range of emission. The spectra and their temperature dependence correspond to the results presented in ref. 13. The left-hand side of Fig. 1 shows part of the blue flank of the emission spectra, highly enlarged (marked by arrows at the right-hand side) and with higher spectroscopic resolution. An important result of this investigation is that one can observe a sharp line structure consisting of a pair of narrow lines (half widths ≈5 cm^{-1}) at 17 809 cm^{-1} and 17 816

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*Author to whom correspondence should be addressed.

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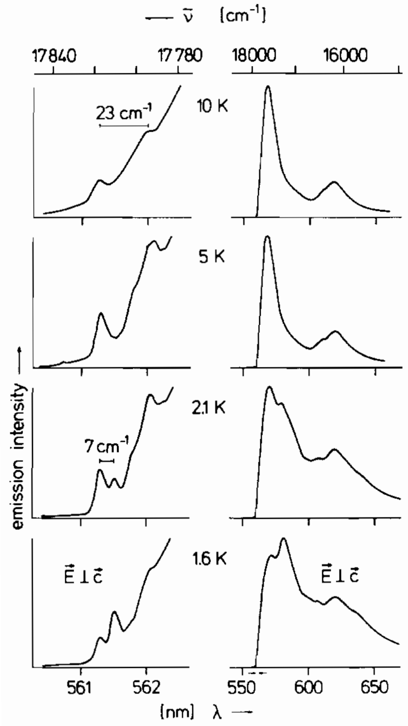

Fig. 1. $\vec{E} \perp \vec{c}$ polarized emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ at different temperatures. (Intensities are not comparable.) The spectra at the left-hand side represent an enlarged and highly resolved section of the total emission spectra, marked by arrows at the right side. The maximum of the total emission spectrum is higher by a factor of about twenty than the peaks of the fine structure. The $\vec{E} \parallel \vec{c}$-polarized highly resolved emission exhibits the same fine structure as the $\vec{E} \perp \vec{c}$-polarized one but is more than twenty times less intense.

cm^{-1} and a progression of (23 ± 2) cm^{-1}. Three vibronic components of this progression are resolved, and are only partially reproduced in Fig. 1. With increasing temperature the high-energy emission peak (at 17 816 cm^{-1}) grows out at the expense of the low-energy one. This temperature behavior is quantified in Fig. 2 by plotting $\ln\{I(17\,816\ cm^{-1})/I(17\,809\ cm^{-1})\}$ *vs.* $1/kT$, and it results in a slope of (7 ± 1) cm^{-1}. (The corresponding intensities are corrected taking into account the background features from the neighbouring peak and the broad band emission.) Near $T \approx 20$ K the fine structure vanishes. Furthermore, we observed the $\vec{E} \parallel \vec{c}$ polarized emission in the energy range of the fine structure; we found the same features at the same energy positions as in $\vec{E} \perp \vec{c}$, but the $\vec{E} \parallel \vec{c}$-emission intensity is smaller by a factor of about 20. The emission spectra were found to be independent of the excitation wavelengths (458, 488, 514 nm). Especially, the results (T = 4.2 K) show that excitation at 17 816 cm^{-1} also leads to the same spectrum, whereas only very weak emission intensity is observed when exciting at 17 809 cm^{-1}.

Discussion

In a recent publication [13], the polarized broad band emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ have been reported; it has been shown that, for these single crystals, no compelling reasons require the assumption of a complex symmetry lower than D_3 for an assignment of the very lowest excited states. Further, it was possible to work out a more comprehensive energy level diagram using mainly the temperature dependence of the spectra. The following emitting states were classified (in D_3'): 1E′, 2E′ (5 to 10 cm^{-1} above 1E′), $1A_2'$ (30 to 40 cm^{-1}), 3E′ (100 to 200 cm^{-1}), $2A_2'$ (≈800 cm^{-1}).

The electronic properties of the two very lowest excited states and their energy difference determine mainly the emission behavior for $T \lesssim 10$ K. The energy separation between these states was estimated in ref. 13 from the temperature-dependent development of the spectra. The obtained energy difference of 5 to 10 cm^{-1} (but not the group-theoretical assignment) is in agreement with the value determined by Crosby *et al.* [1–3], who used temperature-dependent lifetime and quantum efficiency measurements. From these data, it was further concluded that the oscillator strength from the second lowest excited state (to the ground state) is substantially higher than from the very lowest excited one (presumably due to different amounts of singlet admixture [9, 13]). Since these transitions are connected to different vibrations of the ground state, temperature reduction from 5 to 1.6 K leads to a red-shift of ≈350 cm^{-1} of the maximum of the broad band emission spectra ([1–3], see also Fig. 1, right part).

The discovery of fine structures (Fig. 1) brings about a more definite description of the properties of the lowest excited states. The two sharp lines detected on the blue side of the emission band at 17 809 cm^{-1} and 17 816 cm^{-1} are, as is explained below, classified as 0–0-transitions, corresponding to $1E' \rightarrow A_1'$ and $2E' \rightarrow A_1'$, respectively.

The point group chosen for the assignment is D_3' for the complex in the ground state [16] and for the lowest excited states, since the results found for single-crystal $[Ru(bpy)_3](PF_6)_2$ can be described consistently without any need of assuming a symmetry reduction. This is in accordance with the conclusions outlined in ref. 13. The experimental ratio of the emission intensities $I(\vec{E} \perp \vec{c})/I(\vec{E} \parallel \vec{c})$ for both of the high-energy sharp lines is at least as high as twenty. (This is a lower limit since the experimental polarization error is about 5%). Further, no extra lines could be detected in this high-energy range of the $\vec{E} \parallel \vec{c}$-polarization. Therefore, the excited states are assigned to E′ representations. It is worthwhile to emphasize that both 0–0-transitions exhibit the same experimental polarization ratio. Thus, it is very unlikely that the corresponding excited states belong to different group theoretical representations, as has been assumed in earlier papers [1–3]. This implies, for example, that the two states cannot be assigned to A′ and B′ representations which might result from a splitting of a degenerate E′ state (in D'_3) caused by a C_2 perturbation.

The following arguments support the interpretation that the 17 809 cm^{-1} and 17 816 cm^{-1} lines represent zero-phonon lines:

– At very low temperatures ($T < 5$ K) the two emission lines are the features of highest energies (Fig. 1).

– The energy separation between the two emission lines is 7 cm^{-1}. For 0–0-transitions, this should be the energy difference between the two very lowest excited states 1E′ and 2E′. Under the assumption of a thermal equilibrium, the intensity ratio I (17 816 cm^{-1})/I(17 809 cm^{-1}) should be governed by a Boltzmann factor. Indeed, this behavior is found, and the activation energy of $\Delta E = (7 \pm 1)$ cm^{-1} fits perfectly (see Fig. 2).

– The temperature dependence of the emission intensities of the zero-phonon lines should also be displayed in the broad band part (vibronic part) of the spectra. In fact, with a temperature increase from 1.6 K to 10 K (Fig. 1), the disappearance of the 17 809 cm^{-1} line ($1E' \rightarrow A'_1$) is parallel to the vanishing of the red peak maximum of the broad band spectrum (at ≈17 200 cm^{-1}). This latter effect has been used by Crosby *et al.* [1–3] and by the authors [13] to determine the energy difference between the two very lowest excited states (1E′ and 2E′) before the fine structure had been discovered.

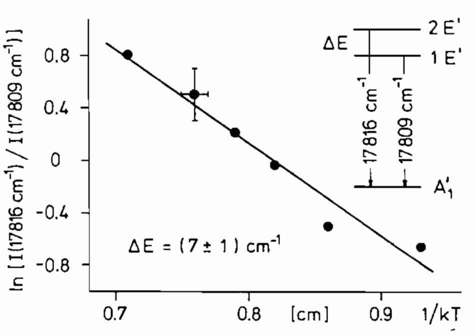

Fig. 2. Temperature dependence of the ratio of the $\vec{E} \perp \vec{c}$-polarized emission intensities ln{I(17 816 cm^{-1})/I(17 809 cm^{-1})} for the temperature range T = 1.5–2.1 K. ΔE is the activation energy between the two lowest excited states of single-crystal $[Ru(bpy)_3](PF_6)_2$. The inset shows the deduced energy level diagram and the observed zero-phonon transitions.

It could be argued that impurities are responsible for the appearance of the fine structure. But this possibility is excluded by the observation that excitation into the sharp line at 17 816 cm^{-1} produces the same spectrum (zero-phonon-lines and broad emission band) as for higher energy excitations. However excitation into the sharp line at 17 809 cm^{-1} leads to only very weak emission intensity, thus the low extinction coefficient of the $1E' \rightarrow A_1$ transition is clearly demonstrated, as expected [3]. Further, the conclusion that the sharp lines might be artefacts can be rigorously rejected since the two lines have just the expected energetic separation for this compound [1–3]; and they show a temperature-dependent development in exact correlation to the broad-band emission of $[Ru(bpy_3)]^{2+}$ and the lines are totally $\vec{E} \perp \vec{c}$-polarized. Moreover, $[Ru(bpy)_3](ClO_4)_2$ which was prepared in an equivalent procedure and thus should contain the same impurities also exhibits a fine structure which is distinctly different while other salts (e.g. X = Cl, Br, I) do not show any fine structure at all [19, 20]. For the $[Ru(bpy)_3](ClO_4)_2$ compound, the fine structure is observed over the entire emission spectrum. The sharp lines can definitely be interpreted as vibrational satellites of the zero-phonon transition, since the energetic distances of the various sharp lines from the zero-phonon line agree with the frequencies of those vibrations of $[Ru(bpy)_3]^{2+}$ enhanced by the resonance Raman effect [20].

The simultaneous appearance of sharp lines and broad bands in the emission spectrum is a common phenomenon in low-temperature solid-state spectroscopy [21, 22]. The sharp lines come from zero-phonon transitions or represent a progression of the dominant deactivating phonon, whereas the broad emission bands result from the corresponding multi-phonon transitions. The relative intensity of the zero-phonon line is given by the electron-phonon coupling strength [21], which commonly is characterized by the Huang–Rhys factor S. S can be evaluated from the emission spectrum at low temperatures using the expression [21]

$$\frac{I_z}{I_t} \approx e^{-S}$$

wherein I_z is the intensity of the zero-phonon line and I_t the total intensity of the corresponding broad multi-phonon emission band plus phonon progression plus zero-phonon line. Thus, at T = 2 K for $[Ru(bpy)_3](PF_6)_2$ a Huang–Rhys factor of 6 to 7 is calculated. This means that the electron-phonon coupling is quite strong for this compound, which is not surprising due to the fact that the emission spectrum stems from a charge-transfer transition.

Conclusion

Fine structure has been observed in the emission spectra of crystalline $[Ru(bpy)_3](PF_6)_2$ at low temperatures. The total halfwidths of these sharp lines are of the order of only 5 cm^{-1}. This is less by a factor of about 100 than the halfwidths of the hitherto known spectra of best resolution. Due to thermal broadening effects, the structure is only observed for $T \lesssim 20$ K. The fine structure consists of a 23 cm^{-1} progression built upon two lines, being separated by 7 cm^{-1}. These are identified as zero-phonon lines, corresponding to the two lowest excited states. Since all results found for the two lowest excited states of single-crystal $[Ru(bpy)_3](PF_6)_2$ can be explained on the basis of a D_3 point group symmetry, both O–O-transitions are assigned to E′ states due to group-theoretical arguments. Furthermore, it is worth mentioning that the thermal behavior of the two zero-phonon lines suggests the existence of a thermal equilibrium between the two lowest excited states. However, in contrast to this, the next higher lying state, $1A_2'$, which is responsible for the $\vec{E} \parallel \vec{c}$ polarized emission between 10 and 100 K [13], yields a delayed emission (delay time $\approx$ 1 μs), indicating the existence of an energy barrier between 1E′, 2E′ on the one hand and $1A_2'$ on the other [23].

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