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On the Lowest Excited States 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 temperature range from 1.6 to 300 K. A detailed energy-level diagram for the emitting states including hitherto unresolved states is presented. The assignment of the excited states is accomplished within the D_3' symmetry group. The very lowest excited states being only 5–10 cm^{-1} apart are both of E′ character, however, exhibiting different amounts of singlet admixture. They are responsible for the drastic change of the emission properties between 1.6 and 4.2 K. According to their E′ character, the $\mathbf{E}\perp\mathbf{c}$-polarized emission component is far more intense than the $\mathbf{E}\parallel\mathbf{c}$-polarized one. With increasing temperature a $\mathbf{E}\parallel\mathbf{c}$-polarized transition appears which emerges from a higher lying A_2' state. This transition carries at about 70 K more than half of the total emission intensity. For higher temperatures ($T \gtrsim 100$ K) an emission from a third E′ state becomes important and dominates at room temperature. Thus, at 300 K, the $\mathbf{E}\perp\mathbf{c}$-polarized component delivers the major part of the emission intensity (about 95%). Another emission band appears in the $\mathbf{E}\parallel\mathbf{c}$-polarized spectrum for $T \gtrsim 250$ K. This band results, as has been assigned previously, from a further A_2' state. The presented polarized emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ deliver no compelling reason to assume a reduced symmetry of the emitting states compared to the ground-state symmetry. It is proposed that the symmetry reduction in the excited states of $[Ru(bpy)_3]^{2+}$ as observed by other authors is not an intrinsic property of the complex but occurs through an interaction with the solvent sphere.

$[Ru(bpy)_3]^{2+}$ (with bpy = 2,2′-bipyridine) and related compounds have attracted widespread interest due to their photochemical and photophysical properties.[1-3] However, up until now a widely accepted and detailed group-theoretical and quantum-mechanical description of the lowest lying charge-transfer excited states of $[Ru(bpy)_3]^{2+}$ is not available. Crosby and co-workers developed a model[4] to rationalize the low-temperature dependence of the spectroscopic properties of $[Ru(bpy)_3]^{2+}$ and related compounds.[5] The authors proposed an energy-level diagram for the lowest excited states comprising a manifold of three close-lying emitting states. In two recent studies Kober and Meyer[6] and independently Ferguson and Herren[7] presented a more comprehensive electronic structural investigation. But although these authors tried a complete assignment of the charge-transfer absorption spectra of $[M(bpy)_3]^{2+}$ (with M = Fe, Ru, Os),[8] there is still little understanding concerning the relative ordering, the lifetimes, and the intensities of the very lowest excited states.

Furthermore, there has arisen debate over whether the promoted electron of the excited state is delocalized over the ligand framework (the excited state thus preserving the D_3 ground-state symmetry) or whether it is localized on one bpy ligand (the symmetry of the excited state thus being reduced to C_2). The conception of a single-ring-localized excited state resulted from excited-state resonance Raman investigations,[9] excitation polarization measurements,[10] ESR data,[11] and excited-state absorption investigations.[12] It is important to mention that all these investigations were carried out with dissolved $[Ru(bpy)_3]^{2+}$ complexes.

In order to contribute to the current discussion we report in this paper on polarized emission measurements of *single-crystal* $[Ru(bpy)_3](PF_6)_2$ under temperature variation. In two recent publications[13,14] we demonstrated that investigations on pure single crystals deliver substantial and additional information on the excited-state properties of these compounds, for single-crystal spectra generally show more details than solution spectra and differently polarized transitions can in many cases be separated and assigned group-theoretically.[15] The method of varying the crystal temperature starting from very low temperature often reveals the existence of energetically close-lying excited states by the temperature-dependent appearance of transitions in the emission spectra. Especially in the case of close-lying excited states with small transition moments, a situation often found with the lowest excited states of transition-metal complexes, absorption spectroscopy is unable to resolve the states since bands overlap and are weak. But by carrying out emission measurements—if possible—the various excited states may be picked out successively from the manifold by temperature-dependent thermal population from the very lowest excited state. Thus, under these circumstances, resolution is greatly enhanced. This method is called REESTA spectroscopy (resolution enhancement of excited states by thermal activation).

In this paper we mainly concentrate on characterizing the manifold of the emitting states of $[Ru(bpy)_3](PF_6)_2$ single crystals with respect to the following questions:

(a) How many emitting states can be detected?

(b) What are the proper symmetry representations of the emitting states?

(c) Do the single-crystal emission spectra reveal a reduced symmetry of the excited compared to the nonexcited complex?

Experimental Section

$[Ru(bpy)_3](PF_6)_2$ was synthesized as described previously.[13] Single crystals were grown by slow evaporation of 1:1 ethanol–acetonitrile solutions at room temperature. $[Ru(bpy)_3](PF_6)_2$ crystallizes as hexagonal needles with the C_3 axis of the complex ion parallel to the needle axis

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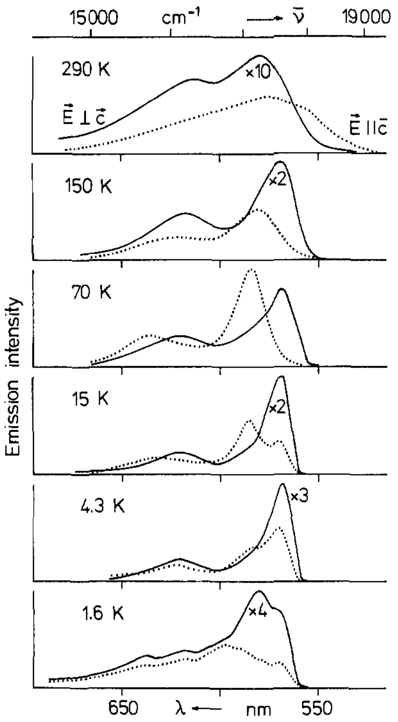

Figure 1. Polarized emission spectra of single-crystal [Ru(bpy)$_3$](PF$_6$)$_2$ at various temperatures. The spectra are recorded with the electric field vector **E** polarized either parallel ($\mathbf{E}\parallel\mathbf{c}$) or perpendicular ($\mathbf{E}\perp\mathbf{c}$) with respect to the crystallographic **c** axis. The intensities of the differently polarized spectra are comparable after multiplication with the indicated factors. For different temperatures the intensities of the spectra are not comparable. The excitation wavelength (and polarization) was 364 nm ($\mathbf{E}\parallel\mathbf{c}$).

(=crystallographic **c** axis).[16] Crystals of good quality were selected under a polarization microscope. The typical sample size was 0.4 × 0.1 × 0.1 mm^3. The crystals were mounted on a copper block and placed in a liquid-helium dewar which could be cooled to 1.6 K by pumping on the sample chamber. Luminescence measurements were carried out with a spectrophotometer, especially constructed for investigations of the polarized emission of microcrystals.[17] The crystals were excited with the 364-nm line of an argon ion laser with the exciting electric field vector parallel to the crystal needle axis. The laser beam was attenuated, so as not to heat up the sample, and was focused on the crystal surface. Only light emitted from a small area of high optical quality was selected by a diaphragm and used for recording. The spectra were not corrected for the spectral response of the detection system.

Results

Figure 1 shows the polarized emission spectra of single-crystal [Ru(bpy)$_3$](PF$_6$)$_2$ at various temperatures with the electric field vector **E** lying parallel or perpendicularly to the crystallographic **c** axis. Figure 2 reproduces the intensity ratio $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\parallel\mathbf{c})$ for the temperature range from 1.6 to 300 K.

At $T = 1.6$ K the $\mathbf{E}\perp\mathbf{c}$-polarized spectrum has its maximum at 581 nm with a shoulder at about 570 nm. The $\mathbf{E}\parallel\mathbf{c}$-polarized spectrum shows a peak at 570 nm. Shoulders at 581 and 590 nm and the maximum at 599 nm indicate a vibrational progression of 260 ± 30 cm^{-1}. At 620 and 635 nm further vibronic peaks can be detected in both the $\mathbf{E}\perp\mathbf{c}$-polarized and the $\mathbf{E}\parallel\mathbf{c}$-polarized spectra. It is important that the $\mathbf{E}\perp\mathbf{c}$-polarized emission intensity is a factor of about 10 stronger than the $\mathbf{E}\parallel\mathbf{c}$-polarized one.

When the temperature is increased up to about 4 K, the band shape changes drastically and the total emission intensity increases by a factor of 3–5. Within experimental error (±1 nm), the maxima of the differently polarized spectra are found at the same wavelengths (569 nm). Thus, the $\mathbf{E}\perp\mathbf{c}$-polarized maximum has been blue shifted by 350 ± 30 cm^{-1}. The differently polarized spectra have nearly the same shape beside an additional shoulder at 584 nm in the $\mathbf{E}\parallel\mathbf{c}$-polarized component. A pronounced vibronic peak is found at 620 nm that is 1450 ± 30 cm^{-1} below the main peak.

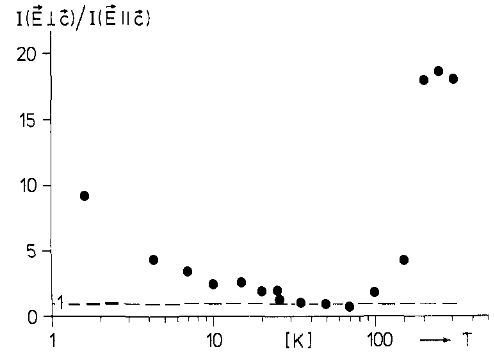

Figure 2. Intensity ratio $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\parallel\mathbf{c})$ for the differently polarized emission of single-crystal [Ru(bpy)$_3$](PF$_6$)$_2$ from 1.6 to 300 K. Note that the intensity of the $\mathbf{E}\perp\mathbf{c}$-polarized component is distinctly higher than the intensity of the $\mathbf{E}\parallel\mathbf{c}$-polarized one, except for the temperature range 40 K $\lesssim T \lesssim$ 80 K.

On further temperature increase the above-mentioned shoulder at 584 nm in the $\mathbf{E}\parallel\mathbf{c}$-polarized spectrum grows out, which leads to a red shift of the maximum, getting to 584 nm above 12 K and staying constant up to about 100 K. The relative intensity of the corresponding polarization increases considerably, and in the temperature range 40 K $\lesssim T \lesssim$ 80 K it carries half (or even more) of the total emission intensity (Figure 2). The $\mathbf{E}\perp\mathbf{c}$-polarized spectrum remains nearly unchanged from 5 to 100 K. For this temperature range the total emission intensity is constant (experimental error 25%). From a ln $[I(\mathbf{E}\parallel\mathbf{c})(584\text{ nm})/(I(\mathbf{E}\perp\mathbf{c})(569\text{ nm}) + I(\mathbf{E}\parallel\mathbf{c})(569\text{ nm}))]$ vs. $1/T$ plot we estimated an activation energy for the 584-nm transition in the $\mathbf{E}\parallel\mathbf{c}$-polarized spectrum of 20–30 cm^{-1} relative to the excited state being mainly responsible for the emission at about 4 K.

For $T \gtrsim 100$ K a strong increase in the intensity ratio $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\parallel\mathbf{c})$ is observed (Figure 2), the $\mathbf{E}\perp\mathbf{c}$-polarized spectrum broadens, involving mainly the red side of the main peak, and furthermore a slight red shift of the emission maximum is registered. The $\mathbf{E}\parallel\mathbf{c}$-polarized spectrum broadens, too, but a blue shift of the maximum occurs. For $T \gtrsim 250$ K a shoulder grows out on the blue side of the spectrum at about 555 nm. Furthermore, for $T \gtrsim 250$ K the intensity ratio $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\parallel\mathbf{c})$ begins to decrease again. The total emission intensity at room temperature is only about a third of the intensity at $T \simeq 100$ K.

Discussion

When the temperature (starting from 1.6 K) is increased, the polarized emission spectra of single-crystal [Ru(bpy)$_3$](PF$_6$)$_2$ exhibit considerable changes with respect to (a) the energetic positions of emission bands, (b) the intensities of the transitions, and (c) the shapes and half-widths of the emission spectra. These changes are explained by the successive appearance of new transitions by thermal activation of excited states, which is the essence of REESTA spectroscopy. To facilitate the interpretation and discussion of the results we first present the deduced energy-level diagram (Figure 3) and then discuss in detail how it is concluded from our measurements also taking into account already published results from other investigators.

As has been pointed out earlier,[14] the emission spectrum of [Ru(bpy)$_3$](PF$_6$)$_2$ single crystals is determined by the [Ru(bpy)$_3$]$^{2+}$ complex and, thus, can be assigned within the symmetry group of the complex ion. In the (PF$_6$)$^-$ salt, the [Ru(bpy)$_3$]$^{2+}$ molecule lies at a special position, having a D_3 point symmetry with the molecular $\mathbf{C}_3$ axis in the direction of the crystallographic **c** axis.[16] From our spectroscopic investigations we find no compelling reason which demands a reduced symmetry of the excited states compared to the ground-state symmetry. This point will be the subject of further discussion below. Thus, the emitting states of single-crystal [Ru(bpy)$_3$](PF$_6$)$_2$ are classified in the $D_3{}'$ double group, which is the appropriate symmetry group to take into account spin–orbit

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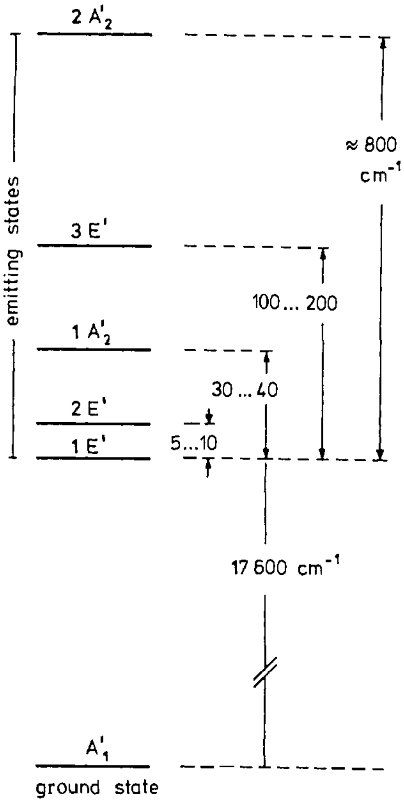

Figure 3. Energy-level diagram for the emitting states of single-crystal $[Ru(bpy)_3](PF_6)_2$. The assignment of the excited states is accomplished in the D_3' symmetry group. The given energetic separations (not to scale) are deduced from the temperature-dependent development of the polarized emission spectra.

coupling. As the ground state—being mainly of singlet character—has the symmetry representation A_1' (in D_3'),[6] the selection rules for electric dipole transitions are as follows: $E' \rightleftarrows A_1'$ allowed for $\mathbf{E}\perp\mathbf{c}$, $A_2' \rightleftarrows A_1'$ allowed for $\mathbf{E}\|\mathbf{c}$, $A_1' \rightleftarrows A_1'$ forbidden. Thus, transitions which are clearly polarized with the electric field vector **E** perpendicularly to the **c** axis have to be assigned to emerge from E′ states, whereas transitions from A_2' states are to be detected in the $\mathbf{E}\|\mathbf{c}$-polarized spectra. We now turn to the characterization of the various emitting states of $[Ru(bpy)_3](PF_6)_2$.

Emission from the 1E′ State. As can be seen from Figure 1, a distinct red shift and a change in band shape of both the $\mathbf{E}\perp\mathbf{c}$- and $\mathbf{E}\|\mathbf{c}$-polarized spectra are obtained on cooling to 1.6 K. Furthermore, the total emission intensity decreases by a factor of about 3–5. This behavior indicates a different emission mechanism for $T \lesssim 2$ K compared to $T \gtrsim 2$ K. From the high intensity ratio $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\|\mathbf{c}) \approx 10$ we conclude—using the selection rules—that at 1.6 K an excited E′ state (1E′ in Figure 3) is responsible for the emission spectrum. Although the transition $1E' \rightarrow A_1'$ is group-theoretically allowed, it must be fairly forbidden. This can be deduced from the emission intensity decrease and the relatively high emission lifetime, $\tau \gtrsim 100$ μs, at $T = 1.6$ K.[5] We therefore conclude that the difference in the emission mechanism arises from a spin-forbiddenness of this transition. Consequently, we assign the very lowest excited state of $[Ru(bpy)_3](PF_6)_2$ to E′ with only a very small amount of singlet character mixed in.

Support for our assignment of the very lowest excited state as degenerate E′ state comes from MCPL (*m*agnetic *c*ircular-*p*olarized *l*uminescence) measurements of $[Ru(bpy)_3]^{2+}$ doped in $[Zn(bpy)_3](BF_4)_2$.[18] According to ref 18 this host delivers a D_3 site symmetry for the $[Ru(bpy)_3]^{2+}$ complex. These measurements and the characteristic change of the MCPL signal on a magnetic field increase from 1 to 5 T demand a degenerate excited state to be responsible for the emission at 2 K.

Application of magnetic fields to $[Ru(bpy)_3]^{2+}$ at 1.65 K delivers a distinct blue shift, a decrease in lifetime, and an increase in emission intensity.[19] Within our assignment of the very lowest excited state, this result can be explained by magnetic-field-induced mixing of singlet character into the 1E′ state, thus supplying more oscillator strength to the corresponding transition. Magnetic fields lead also to a reduction of the orbital symmetry with a subsequent mixing of states. This explanation was given in ref 19, where, however, a different representation of the very lowest excited state (A_1') was assumed. But this latter effect seems to be of less importance, because Ru complexes with mixed ligands (for example, $[Ru(bpy)_2(CN)_2]$) exhibit a very close similarity in their emission behavior at low temperatures. These compounds also show the red shift and the emission intensity decrease on cooling to 2 K[5a,d] as well as the above-mentioned magnetic-field effects.[19] Since these compounds have a lower symmetry than D_3 (for example C_2), which necessarily leads to a splitting of in D_3' degenerate E′ states and a subsequent mixing of states, one would not expect a quantitative similarity to the behavior of $[Ru(bpy)_3]^{2+}$ complexes. Therefore, we conclude that in the case of $[Ru(bpy)_2L_2]$, too, the very lowest excited state is mainly of triplet character. Thus, the emission behavior of these Ru complexes at $T \lesssim 2$ K is also dominated by spin restrictions rather than by orbital restrictions. It is worthwhile mentioning that the very lowest excited state of $[Ru(bpy)_2L_2]$ complexes was calculated to be (within the simplifications of the calculations) a pure triplet state.[6b]

Further support for our model of spin restrictions for the transition $1E' \rightarrow A_1'$ comes from theoretical results which predict an (almost) pure triplet E state to lie among the lowest excited states of $[Ru(bpy)_3]^{2+}$.[6,7] With respect to the approximations and simplifications necessarily introduced in the calculations, the exact energetic position of this state cannot be deduced from these investigations, however. But the pure triplet E′ state was found to be the very lowest one.

The question arises through which mechanism a transition from 1E′ could get a nonzero oscillator strength. Possibly a vibronic coupling provides the required mixing mechanism.[20] As mixing with higher lying singlet states through vibronic coupling is a second-order effect, the low intensity for the transition from 1E′ is explained. The red shift of the polarized spectra on cooling is also rationalized; it corresponds to the vibrational quantum[21] of the enabling mode. From the $\mathbf{E}\perp\mathbf{c}$-polarized spectra the value 350 ± 30 cm^{-1} is obtained for the energy difference between the peak maxima. Since the exact position of the 0–0-transition is not known, the frequency of the enabling mode cannot be determined. The occurrence of the $\mathbf{E}\|\mathbf{c}$-polarized spectrum can be explained by an equivalent mechanism as proposed above. However, besides the required singlet character a further mechanism must supply the correct orbital symmetry to make the $1E' \rightarrow A_1'$ transition allowed for the parallel polarization. Consequently, only a very small intensity is expected for this polarization. This is stated by the experiment with the $\mathbf{E}\|\mathbf{c}$-polarized intensity being by a factor of about 10 weaker than the $\mathbf{E}\perp\mathbf{c}$-polarized one at 1.6 K. Through this additional mechanism, the $\mathbf{E}\|\mathbf{c}$-polarized spectrum gets a different band shape than the $\mathbf{E}\perp\mathbf{c}$-polarized one; a vibrational progression of about 260 cm^{-1}, maximizing at longer wavelengths (599 nm), is characteristic for the $\mathbf{E}\|\mathbf{c}$-polarized spectrum at 1.6 K.

At $T \lesssim 2$ K, one observes on the blue side of the maximum a shoulder ($\mathbf{E}\perp\mathbf{c}$) and a peak ($\mathbf{E}\|\mathbf{c}$), lying at 570 nm. This transition may result, on the one hand, from a thermal population of the close-lying second-lowest excited state (2E′ in Figure 3) even at these low temperatures. On the other hand, it may also

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come from the transition from 1E′ to the ground state, caused by a different enabling mechanism. Furthermore, it is also possible that these high-energy features in the spectra come from a prompt emission from higher lying emitting states (perhaps 2E′). At present, a decision whether the three proposed explanations are valid simultaneously or whether one of them dominates cannot be given.

Emission from the 2E′ State. With a temperature increase from $T \lesssim 2$ K to $T \approx 4$ K a distinct change in band shape, a blue shift of the emission maximum, and an increase in emission intensity by a factor of 3–5 are observed. This behavior results from an emission band (near 570 nm) growing out on the blue side of both the $\mathbf{E}\perp\mathbf{c}$- and $\mathbf{E}\|\mathbf{c}$-polarized emission spectra. Thus, another excited state lying a few wavenumbers above the very lowest excited one (1E′) is responsible for the emission at $T \approx 4$ K. From the intensity ratio $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\|\mathbf{c}) \simeq 5$ we assign that state to E′ (2E′ in Figure 3).

As the transition from 2E′ carries considerably more intensity than that from 1E′, 2E′ seems to have some more singlet character mixed in. This rationalizes also that the transition from 2E′ to the ground state results in a blue shifted emission maximum on temperature increase. The allowedness of this transition has already been discussed by Crosby and co-workers,[5] who observed a substantial increase in quantum efficiency accompanied by a decrease in emission lifetime, when the emission from this state becomes dominant. Theoretical investigations give no information about states lying only some wavenumbers apart. The very lowest excited state is assigned in this paper to be mainly of triplet character. Kober and Meyer[6] calculate that only one state among the lowest excited ones of $[Ru(bpy)_6]^{2+}$ is a "pure" triplet, while the others have more or less singlet character mixed in. This result would qualitatively fit with our experimental data.

The energetic separation of 2E′ from the very lowest excited state is determined from the temperature-dependent development of the spectra, and a value of 5–10 cm^{-1} is estimated. This is in accordance with the value determined in the references.[5] According to this small energetic separation there may be some thermal population of 2E′ even at temperatures $T < 2$ K, which could result in the 570-nm features at 1.6 K, as discussed above.

The relatively large amount of $I(\mathbf{E}\|\mathbf{c})$ at $T \approx 4$ K is somewhat puzzling if one realizes the selection rules. This might be explained by a slight splitting of the 2E′ state due to a small perturbation, which group-theoretically would lead also to a $E\|\mathbf{c}$-polarized component. But such a splitting, if present, is obviously smaller than about 2 cm^{-1}—being the experimental error in the REESTA spectroscopy—since no differences in the temperature-dependent development of the differently polarized spectra could be detected. This situation of being unable to detect a splitting of the degenerate 2E′ state holds also true for 1E′. Therefore, we see no need to assign the emitting states of $[Ru(bpy)_3](PF_6)_2$ in a symmetry group lower than that of the ground state.

Emission from the $1A_2'$ State. For $T \gtrsim 4$ K a further transition can be registered steadily growing out on the red side of the main peak in the $\mathbf{E}\|\mathbf{c}$-polarized spectrum. As this transition is observed on the *red side* of the main peak it cannot be a hot vibronic emission band but must result from a further electronic state. Since the emission occurs only in the $\mathbf{E}\|\mathbf{c}$-polarized spectra, it is assigned to $A_2' \rightarrow A_1'$. From Figure 2 it can be seen that in the temperature interval 40 K $\lesssim T \lesssim$ 80 K this transition carries half (or even more) of the total emission intensity. Since the $1A_2'$ state is by about 20–30 cm^{-1} higher in energy relative to 2E′ (as reported in the Results section), the unfavorable Boltzmann factor can only be compensated if the transition $1A_2' \rightarrow A_1'$ carries more oscillator strength than the $2E' \rightarrow A_1'$ transition. Presumably, this results from a higher amount of singlet character mixed into $1A_2'$. Although the $1A_2'$ state is higher in energy than the 2E′ state, the transition $1A_2' \rightarrow A_1'$ occurs at longer wavelengths. This behavior is rationalized by the assumption of a displacement of the energy surface of $1A_2'$ compared to that of 2E′ with respect to the appropriate configurational coordinate.[22]

Emission from the 3E′ and $2A_2'$ States. From Figure 2 it can be seen that for $T \gtrsim 80$ K the intensity of the $\mathbf{E}\perp\mathbf{c}$-polarized spectrum increases drastically compared to the $\mathbf{E}\|\mathbf{c}$-polarized one. This behavior can be explained by the thermal depopulation of the $1A_2'$ state (and the other lower lying states) and the simultaneous population of a still higher lying *E*′ state. Although the transition from 3E′ is not resolved as an energetically separated peak, its appearance is clearly demonstrated by the increase of the $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\|\mathbf{c})$ ratio and furthermore by the distinct broadening of the main peak, involving mainly its red side. Thus, with increasing temperature (for $T \gtrsim 150$ K) a continuous red shift occurs of the $\mathbf{E}\perp\mathbf{c}$-polarized emission maximum. Finally, at room temperature the emission from 3E′ carries about 95% of the total intensity.[13,14] For the state 3E′ an energetic separation of 100–200 cm^{-1} from the lowest excited states is estimated from the temperature-dependent emission behavior.

The transition from the still higher lying $2A_2'$ state detectable on the blue side of the $\mathbf{E}\|\mathbf{c}$-polarized emission spectrum near room temperature has already been described and assigned elsewhere.[13] The appearance of this transition is manifested by the blue-side shoulder of the $\mathbf{E}\|\mathbf{c}$ spectrum, the drastic broadening of the $\mathbf{E}\|\mathbf{c}$-polarized emission band, the blue shift of the $\mathbf{E}\|\mathbf{c}$-polarized emission maximum, and the again beginning decrease of $I(\mathbf{E}\perp\mathbf{c})/I(\mathbf{E}\|\mathbf{c})$ for $T \gtrsim 250$ K (Figure 2). The energetic position of $2A_2'$ relative to 3E′ has been determined in ref 13 to about 650 cm^{-1}. Thus, $2A_2'$ lies about 800 cm^{-1} above the very lowest excited state.

Although the states 3E′ and $2A_2'$ lie high above the lowest emitting states 1E′, 2E′, and $1A_2'$, they are easily detected from the temperature-dependent development of the polarized spectra. When the unfavorable Boltzmann factors which govern the thermal population of these higher lying excited states are realized, the relatively high intensities of the transitions corresponding to 3E′ and $2A_2'$ must be accounted for by higher oscillator strengths presumably through substantial amounts of singlet character mixed in.

We now want to point out some further aspects concerning our investigations:

Further transitions with relatively small oscillator strengths, such as Laporte-forbidden ligand-field transitions and symmetry-forbidden ($A_1' \rightarrow A_1'$) or spin-forbidden charge-transfer transitions (e.g., from further A_2' or E′ states with very small amounts of singlet character mixed in) may be present but actually have not been detected by our investigations on the polarized emission of single-crystal $[Ru(bpy)_3](PF_6)_2$.

The data presented in this paper do not give sufficient information as to whether the various excited states are in thermal equilibrium or whether there exist energy barriers between the emitting states. There are indications from time-resolved emission measurements that for $T \lesssim 10$ K thermal equilibrium among the lowest excited states is partly lost.[18,22] The existence of energy barriers, however, would not alter the presented energy-level diagram with respect to the number and the symmetry representations of the emitting states.

With respect to the experimental results of other investigators[9-12] which indicate a reduced symmetry of the excited states (C_2 symmetry) of $[Ru(bpy)_3]^{2+}$ compared to the ground-state D_3 symmetry, it could be argued that our assignments of the emitting states of $[Ru(bpy)_3](PF_6)_2$ single crystals are not appropriate. But on the one hand, a splitting of the in D_3' degenerate E′ states into A′ and B′ resulting from a symmetry reduction to C_2' should be detectable from our REESTA spectroscopy investigations. Our spectroscopic data, however, can be rationalized quite well in the D_3' symmetry group, and we find no compelling reason to assume a reduced symmetry as an intrinsic property of the excited complex. On the other hand, it should be realized that all experiments indicating the reduced excited-state symmetry were carried out in polar solvents. But it is well-known that the spectroscopic properties of $[Ru(bpy)_3]^{2+}$ are strongly dependent on the solvent.[23]

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(22) In a very recent investigation it could further be shown by time-resolved and polarized emission measurements on single-crystal $[Ru(bpy)_3](PF_6)_2$ that $1A_2'$ is not in thermal equilibrium with 1E′ and 2E′. See: Yersin, H.; Hensler, G.; Gallhuber, E. Sixth International Symposium on the Photochemistry and Photophysics of Coordination Compounds, London, 1984.

Therefore, it is concluded that the symmetry reduction of the excited complex is a matrix effect. According to this view, the symmetry reduction is induced by the interaction of the excited complex with the surrounding solvent sphere. Support for this argument comes from the observation that the electrons of the doubly reduced complex in solution can be described as being localized in bpy π^* orbitals, whereas in the corresponding solid this interpretation fails.[11]

Conclusion

This paper reports on the polarized emission of single-crystal $[Ru(bpy)_3](PF_6)_2$ at various temperatures in the range from 1.6 K to room temperature and presents a detailed energy-level diagram for the emitting states, which are assigned in the D_3' symmetry group. At $T \lesssim 2$ K an E′ state being mainly of triplet character is responsible for the emission. It gains its intensity through vibronic coupling. With a temperature increase to about 4 K the blue shift and the intensity increase of the emission spectra indicate that a second E′ state becomes dominant which has some more singlet character mixed in. According to the assignments of the two lowest excited states to E′, the low-temperature emission is characterized by dominating $\mathbf{E}\perp\mathbf{c}$-polarized components. For $T \gtrsim 4$ K the $\mathbf{E}\|\mathbf{c}$-polarized transition resulting from a A_2' state appears. At about 70 K this transition carries more than half of the total emission intensity. In the temperature range from 100 to 300 K an emission from a third E′ state (or states) leads to the dominance of the $\mathbf{E}\perp\mathbf{c}$-polarized component which takes about 95% of the total emission intensity near room temperature. A second A_2' state, gaining influence above 250 K and giving a blue shift of the $\mathbf{E}\|\mathbf{c}$-polarized component, is of minor importance for the emission spectrum at room temperature.

It is found that a description of the emitting states of single-crystal $[Ru(bpy)_3](PF_6)_2$ within the D_3' double group accounts very well for the symmetry properties of the excited states detected in the temperature-dependent polarized emission spectra. It is argued that there is no indication of a substantial symmetry reduction in the excited states for the $[Ru(bpy)_3](PF_6)_2$ single crystals compared to the ground-state symmetry. Therefore, it is concluded that the symmetry reduction as was determined in ref 9–12 cannot be accounted for as an intrinsic property of the excited complex. In contrast, the observed symmetry reduction might originate from the use of polar solvents in these investigations. It is proposed that the interaction of the excited complex with the surrounding solvent (respectively matrix) molecules induces the distortion of the excited complex.

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The Behavior of Pyridine, Pyridinium Ion, and Pyridinium Halide on a Ag Electrode and Their SERS Spectra

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Abstract: A newly developed electrochemically plated Ag electrode was used to study the surface-enhanced Raman scattering from pyridine adsorbed on the electrode. It was found that in basic and neutral solution, the adsorbed species on the electrode is pyridine. In acidic solution without chloride ion, the pyridinium ion turns to pyridine on the electrode. However, in an acidic solution with chloride ion both pyridinium and chloride ions are adsorbed together on the Ag electrode and pyridinium chloride forms, then the 1026-cm^{-1} Raman band appears for the ν_8 mode. At a potential of −0.45 V (SCE), chloride ion is driven away from the electrode and pyridinium ion decomposes immediately into pyridine. This potential is called the "driving-off potential". The effects of bromide and iodide ions were also studied. A model is proposed for the behavior of pyridine, pyridinium ion, and pyridinium chloride on the Ag electrode with and without applied potential.

The Raman spectra of pyridine (Py, hereafter) adsorbed on the silver electrode at different potentials were observed first by Fleischmann, Hendra, and McQuillan[1] in 1974. Three years later, Jeanmaire and Van Duyne[2] studied this new Raman scattering in great detail and found many fascinating phenomena, such as the enhancement in Raman signal, the effect of reduction and oxidation cycles, the effect of potential, the effect of metal and the condition of the metal surface, etc. The name surface-enhanced Raman scattering or SERS was given to this Raman scattering. Since then, many physicists and chemists devoted themselves to this field. Many reviews have appeared recently.[3,4] However, many phenomena are not fully understood yet.

One of the big problems is the metals properties and surface conditions. Silver is always used because it gives the best signals compared to the other metals, such as Au, Cu, etc. SERS has been observed on various metal surfaces prepared by various methods. These methods are oxidation- and reduction-cycled Ag electrodes.[5-12] (ORC Ag electrode, hereafter), metallic films,[13,14]

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