

# Zero-Field Splitting of the Lowest Excited State of $[\text{Os}(\text{bpy})_3]^{2+}$ Doped into $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$

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A zero-field optically detected magnetic resonance (ODMR) signal has been observed at  $T = 1.5$  K for  $[\text{Os}(\text{bpy})_3]^{2+}$  doped into a matrix of single-crystal  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ . In the investigated microwave frequency range of  $2 \text{ GHz} \leq \nu \leq 6 \text{ GHz}$ , a resonance is seen at  $4.56 \text{ GHz}$  ( $\approx 0.152 \text{ cm}^{-1}$ ) corresponding to the lowest excited state of the dopant. Thus, it is shown that this state is split into sublevels. From the occurrence of the ODMR signal, it follows that the relaxation rates between the sublevels are smaller than other deactivation rates.

## Introduction

In older investigations  $[\text{Os}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine) was discussed mainly on the basis of unresolved broad-band spectra.<sup>1-6</sup> Recently, the complex became more attractive through the observation of highly resolved emission spectra that occur if  $[\text{Os}(\text{bpy})_3]^{2+}$  is doped into  $[\text{Ru}(\text{bpy})_3]\text{X}_2$  matrices with  $\text{X}^- = \text{ClO}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ , or  $\text{SbF}_6^-$ .<sup>7-12</sup> The spectroscopic features can be ruled back to several closely lying excited (and emitting) states which result from  $\text{Os } 5d \rightarrow \text{bpy } \pi^*$  charge-transfer transitions.<sup>1-12</sup> The lowest excited states are mainly of triplet character (with a singlet ground state), and they differ substantially in their physical properties, e.g., in their radiative rates,<sup>7,11,12</sup> their vibronic coupling,<sup>7,10</sup> their electron-phonon coupling,<sup>12</sup> and their spin-orbit coupling.<sup>5,6</sup> Crosby's group<sup>3,4</sup> assigned the very lowest excited state of  $[\text{Os}(\text{bpy})_3]^{2+}$  (assuming a  $D_3$  symmetry) to a nondegenerate  $A_1$  state (from which the transition to the  $A_1$  ground state is symmetry forbidden). On the other hand, the linearly polarized emission at  $T = 2$  K led to a classification to a doubly degenerate E state,<sup>11</sup> based on group-theoretical selection rules. Although symmetry-allowed ( $E \rightarrow A_1$ ), this transition is extremely weak due to its quantum-mechanical forbiddenness.<sup>10,11</sup>

In doped single-crystal  $[\text{Ru}_{1-x}\text{Os}_x(\text{bpy})_3](\text{PF}_6)_2$  a high-symmetry environment surrounds the  $[\text{Os}(\text{bpy})_3]^{2+}$  complex. However, small distortions may slightly reduce the idealized  $D_3$  symmetry, giving rise to small zero-field splittings of the degenerate parent E term. In the limit of resolution of our present emission spectra of about  $0.5 \text{ cm}^{-1}$ , no splittings of lines could be observed. Therefore, we applied the ODMR (optical detection of magnetic resonance) technique. This method represents a phosphorescence microwave double resonance and expands the resolution to much smaller energy separations.<sup>13-16</sup> The ODMR technique was very successful in determining the zero-field splittings in  $[\text{Ru}(\text{bpy})_3]\text{X}_2$  ( $\text{X}^- = \text{PF}_6^-$ ,  $\text{ClO}_4^-$ ) crystals<sup>17</sup> (see also ref 18 for further ODMR data on  $[\text{Ru}(\text{bpy})_3]^{2+}$ ). The purpose of this contribution is to investigate the lowest excited state of  $[\text{Os}(\text{bpy})_3]^{2+}$  by this high-resolution method in order to prove that this state is nearly degenerate.

## Results and Discussion

The emission of the  $[\text{Os}(\text{bpy})_3]^{2+}$  guest molecules in  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  is clearly identified since it is distinctly separated from that of the host material and thus can be analyzed without interferences from  $[\text{Ru}(\text{bpy})_3]^{2+}$ . The emission spectra at low temperature ( $T \leq 2$  K) originating from the lowest excited state of the dopant are characterized by a very weak electronic origin and intense vibronic satellites. Further, the emission occurs as a superposition of the spectra of three different sites, A, B, and C, which can be distinguished by site-selective spectroscopy.<sup>10-12</sup>

ODMR signals may be detected if one monitors the emission (excited by a CW laser) at a fixed wavelength and registers intensity changes of the emission under microwave irradiation. In the case of resonance between closely spaced sublevels, which in general are not thermally equilibrated at low temperatures, an ODMR signal can be observed if the population and/or decay rates of the sublevels differ from each other.

ODMR spectra of  $[\text{Os}(\text{bpy})_3]^{2+}$  doped into  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  (concentration 0.01 mol/mol, see ref 11) were recorded at  $T = 1.5$  K in the microwave frequency range  $2.0 \text{ GHz} \leq \nu \leq 6.0 \text{ GHz}$  ( $30 \text{ GHz} \approx 1 \text{ cm}^{-1}$ ), detecting the emission (spectral resolution  $2 \text{ cm}^{-1}$ ) separately for the three sites at the energy positions of the vibronic satellites. (Excitation wavelength was 514.5 nm and the microwave power  $\approx 8$  W. The spectra were recorded with a sweep time of 1.5 s and accumulated over several hundred scans.) A detection of the emission at  $\lambda_{\text{det}} = 715.3 \text{ nm}$  ( $479\text{-cm}^{-1}$  vibronic satellite corresponding to site B<sup>11</sup>) yields a weak negative resonance at  $\nu = 4.56 \text{ GHz}$  ( $\approx 0.152 \text{ cm}^{-1}$ ) (which means that the emission becomes weaker in the case of resonance). The occurrence of the ODMR signal shows that the lowest excited electronic state of  $[\text{Os}(\text{bpy})_3]^{2+}$  is split into sublevels; i.e., the parent term represents a doubly degenerate E state, which is in accordance with the result obtained from polarized emission measurements.

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For the other two sites A and C ( $\lambda_{\text{det}} = 717.2$  and  $713.4$  nm for the corresponding  $479\text{-cm}^{-1}$  satellite<sup>11</sup>), no resonances could be found in the investigated frequency range. This result is not surprising, since different sites usually exhibit different zero-field splittings representing different resonance frequencies.<sup>16,17,19</sup> Presumably, the resonances of the sites A and C lie outside the investigated frequency range.

An interesting correspondence can be seen comparing the signal found for the lowest excited state of  $[\text{Os}(\text{bpy})_3]^{2+}$  to the ones found for the lowest excited state of neat  $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$  which is also assigned to be doubly degenerate. In both compounds the

signals are negative (the second excited state of  $[\text{Ru}(\text{bpy})_3]^{2+}$  exhibits positive resonances).<sup>17</sup> This points to similarities in the behavior of the two different complex ions.

#### Conclusion

The assignment of the lowest excited state of the title compound to a nearly degenerate state is substantiated by the observation of a microwave resonance between the sublevels of this state detected as an ODMR signal. From the frequency of the signal the zero-field splitting can be evaluated to be in the order of tenths of a wavenumber. Hence, the lowest excited state of  $[\text{Os}(\text{bpy})_3]^{2+}$  can be considered to be nearly degenerate in the scope of the resolution of usual optical absorption and emission spectroscopy.

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