

ZERO-FIELD SPLITTINGS OF THE TWO LOWEST EXCITED ELECTRONIC STATES IN CRYSTALLINE $[\text{Ru}(\text{bpy})_3]\text{X}_2$ WITH $\text{X}=\text{PF}_6, \text{ClO}_4$

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Received 1 June 1989; in final form 11 July 1989

For the title compounds zero-magnetic field ODMR signals have been observed on the zero-phonon lines which correspond to the two lowest excited states and which result from $\text{Ru}4d \rightarrow \text{bpy}\pi^*$ charge-transfer transitions. The splitting into sublevels are of the order of 0.1 cm^{-1} and the corresponding electronic states may be classified as doubly degenerate on the basis of the usual resolution of the optical emission spectra. Several microwave resonances are detected and assigned to different sites of the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophores. Small relaxation rates between the sublevels (compared to other excited-state deactivation rates) are found to be important for a description of the spectroscopic properties at low temperatures.

1. Introduction

$[\text{Ru}(\text{bpy})_3]^{2+}$ (with $\text{bpy}=2,2'$ -bipyridine) has been studied extensively during the last fifteen years mainly because of its outstanding electron-transfer properties involving the complex in the ground and/or excited states (for reviews see refs. [1–5]). These have been discussed in a large number of investigations [1–21] which, for example, showed that there are several close lying long-lived excited (and emitting) states. It is largely agreed throughout the literature that these states result from $\text{Ru}4d \rightarrow \text{bpy}\pi^*$ CT transitions and are mainly of triplet character. (The ground state is a singlet.) Several of these states exhibit very different physical properties, e.g. with respect to their radiative rates [6–9, 18–21], vibronic spectra [9, 21–24], coupling strengths to the surroundings [21] and shifts along specific normal co-

ordinates [21, 24, 25]. However, several questions are still open or under debate, especially concerning detailed properties of the two lowest excited states which lie only several wavenumbers apart and which determine the low-temperature emission behavior. These two states have been classified on the basis of D_3 site symmetry of the chromophores in $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ to doubly degenerate E representations by measuring the polarization properties (with respect to linearly polarized light) of the corresponding electronic zero-phonon lines and by applying group-theoretical selection rules [19–21, 24, 26]. However, for a real system one expects that at least small distortions of the idealized D_3 symmetry of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes may occur (e.g. in traps). This should lead to small zero-field splittings of the two parent E states into sublevels. In optical spectra with the highest obtained resolution of about 0.5 cm^{-1} , splittings in the zero-phonon lines were not observed. Consequently, we have decided to investigate the excited states of this class of compounds using zero-magnetic field ODMR spectroscopy (optically detected magnetic resonance) which

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is also reported in the literature as "phosphorescence microwave double resonance" [27-30]^{#1}. In this method one monitors the luminescence (excited as usual) at a fixed wavelength and tunes (repetitively) the microwave frequency. This allows the detection of splittings in the energy range of several GHz ($30 \text{ GHz} \approx 1 \text{ cm}^{-1}$). In the case of microwave resonance between the sublevels one may register intensity changes in the emission, representing the ODMR signal. Thus, if these signals are found, one has (beside further information) direct proof of the existence of two sublevels. In this work we investigate the two lowest excited electronic (parent) states of the title compounds with this high-resolution method, mainly focusing on the properties of the zero-phonon lines.

2. Experimental

The compounds were prepared, purified, and crystallized as described previously. (See ref. [31] for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and ref. [22] for $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$.) The samples were placed in a quartz tube and then positioned in a broad-band microwave resonator (slow wave helix), which was placed in a boil-off He cryostat. As microwave sources Hewlett-Packard oscillators (types 8350 and 8620 A) were used with different plug-in units to cover the desired microwave ranges. The samples were excited with the 514.5 nm line of an argon ion cw laser at very low power and the emission was focused onto the entrance slit of a double monochromator (Spex 1402). The light was detected with a cooled photomultiplier (RCA 31034 A 02) using a photon-counting technique. To record the ODMR spectra the emission intensity was observed at a fixed wavelength while slowly sweeping ($\approx 600 \text{ ms}$) the microwave frequency (power used: several watts). Changes in the

emission intensity at resonance (ODMR signal) were recorded in a repetitive way several 100 times and averaged to enhance the signal/noise ratio. For further instrumental details see refs. [29,32].

3. Results and discussion

The occurrence of an ODMR signal does not depend just on the resonance of the microwave frequency between the sublevels of an individual chromophore but also on differences of the populating rates and the radiative decay constants of the respective sublevels. A further very important property is the relaxation rate between the sublevels (usually the spin-lattice relaxation), which is strongly temperature dependent and often becomes very small for $T \leq 2 \text{ K}$ compared with the decay rate to the ground state. In this case the sublevels are not thermally equilibrated and emit independently. By using microwave resonance with the appropriate frequency the population of the corresponding sublevels is saturated and one may observe an intensity change in emission as a positive or negative ODMR signal (see e.g. refs. [28,29]).

The low-temperature emission spectra of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ result from two different electronic (parent) states for which the electronic zero-phonon lines have been detected at 17809 cm^{-1} (line I) and 17816 cm^{-1} (line II). These are accompanied by multi-phonon sidebands as well as a large number of vibronic components. A superposition gives the known broad band spectra [21,26]. For $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ the corresponding electronic zero-phonon lines are slightly red-shifted to 17605 cm^{-1} (line I) and 17613 cm^{-1} (line II) [21-23]. Due to the differences in the electronic properties of the corresponding two states we expect to find different ODMR signals by detecting the emission on line I and line II, respectively. In addition the two salts should give different ODMR signals since the site symmetries and the nearest neighbors of the chromophores are not the same.

ODMR spectra of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ single crystals were recorded at $T = 1.5 \text{ K}$ in the microwave frequency range from $0.2 \leq \nu \leq 6.0 \text{ GHz}$. A typical result is shown in fig. 1. Detection on zero-phonon line II (at 17816 cm^{-1}) gives several ODMR signals at

^{#1} In the nomenclature of triplet state ODMR a transition between the corresponding sublevels is characterized by the $2E$ transition. The $D+E$ and the $D-E$ transitions, respectively, determine the energy of the third component of the triplet. Here, E and D are the triplet zero-field splitting parameters where the splitting is due to magnetic dipole-dipole interactions. For the Ru complex, representing a compound with relatively strong spin-orbit coupling and several strongly mixing triplet sublevels [18] we cannot use this nomenclature.

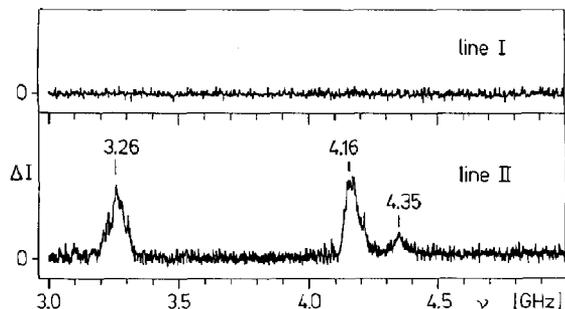


Fig. 1. ODMR spectra of a $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$ single crystal at $T=1.5$ K. ΔI gives the change of the emission intensity under microwave resonance. The signal was averaged 400 times to enhance the signal/noise ratio. The emission was detected on zero-phonon line I (at 17809 cm^{-1}) and on line II (at 17816 cm^{-1}), respectively. The spectral resolution was better than 4 cm^{-1} .

1.89, 2.81, 3.26, 4.16 and 4.35 GHz (not all are reproduced in fig. 1). These signals are partly structured probably due to second-order hyperfine interaction and/or Ru-isotope effects which, however, are not further discussed in this paper. One obtains the same results when the emission is detected on the corresponding broad multi-phonon sideband at $\approx 17600\text{ cm}^{-1}$. All ODMR signals are *positive*, i.e. the emission intensity increases at resonance. The frequencies of the microwave resonances as well as the spectral shapes of the ODMR signals exhibit a slight dependence on the investigated samples. On the other hand, if detection of the emission is fixed at zero-phonon line I (at 17809 cm^{-1}) or to the corresponding multi-phonon sideband (representing the emission maximum at $\approx 17200\text{ cm}^{-1}$ at this temperature [19–21]) no ODMR signal is observed in the investigated microwave frequency range.

It is interesting to compare these results with those obtained for $[\text{Ru}(\text{bpy})_3]^{2+}(\text{ClO}_4^-)_2$. We investigated (at $T=1.5$ K) the same frequency range from 0.2 to 6 GHz and a typical result is shown in fig. 2. (The observed resonance frequencies are indicated.) An important difference from the PF_6^- salt is found for the ClO_4^- compound. Detection of the emission on zero-phonon line I (and on the corresponding multi-phonon sideband) results in relatively strong but *negative* ODMR signals. On the other hand, the detection on the line II leads to a positive signal near 3.41 GHz, which, however, is extremely weak. This weakness may be explained by the fact that the emis-

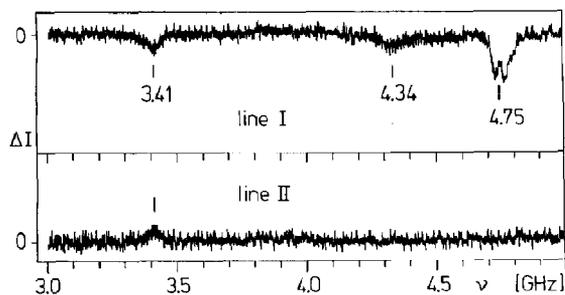


Fig. 2. ODMR spectra of $[\text{Ru}(\text{bpy})_3]^{2+}(\text{ClO}_4^-)_2$ crystalline powder at $T=1.5$ K. The emission was detected on zero-phonon line I (at 17605 cm^{-1}) and on line II (at 17613 cm^{-1}), respectively. (Spectral resolution better than 8 cm^{-1} ; repetitive sweeping of the microwave frequency: 800 times.)

sion intensity from this second excited state is nearly frozen out at 1.5 K [21,22].

These results are consistent with the model of two nearly degenerate doublets (parents of E representations in D_3) which are split by about 0.1 cm^{-1} . The microwave resonances occur between these doublet sublevels. Further evidence for the existence of two nearly degenerate parent terms was found recently by the observation of a magnetic-field-induced (Zeeman) splitting for each of the two states. Both parent terms exhibit a field-dependent splitting, which extends to $3.5 \pm 0.5\text{ cm}^{-1}$ at $B=6$ T. The two Zeeman components of each term are distinguished – according to the group-theoretical selection rules – by their polarization relative to the magnetic field direction [33].

The appearance of several resonance frequencies for the same emission line is not unusual [30] and is ascribed to different trap sites for the chromophores emitting in the relatively small energy range of the width of the zero-phonon lines ($\approx 2\text{ cm}^{-1}$). Especially with respect to the established occurrence of different $[\text{Os}(\text{bpy})_3]^{2+}$ sites in the $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$ lattice [34] and the observed dependence of the shapes and frequencies of ODMR signals on the different investigated samples, this assignment is reasonable. The fact that we could only find resonances (positive signals) for the second excited state of the PF_6^- compound and not for the very lowest one seems – at first sight – to be puzzling. But the close analogy of the properties of the PF_6^- salt compared to the ClO_4^- compound [21,35] and the

finding of negative ODMR signals for the very lowest excited state as well as a positive although very weak signal for the second excited state in $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ strongly indicates the existence of two sublevels for the lowest excited electronic state of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the PF_6^- salt as well. There are several reasons why the splitting could not be observed for the zero-phonon line of state I. First, the corresponding splitting might be outside the investigated microwave frequency range. Alternatively, the conditions for the occurrence of ODMR signals could be less favourable for this parent due to the fact that the steady-state population differences might be small.

A further interesting aspect should be reported. The ODMR signal of single-crystal $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ at 3.26 GHz, which is relatively strong at $T=1.5$ K, could not be detected after the temperature was increased to $T \gtrsim 3.7$ K, while for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ dissolved in ethanol a signal found at 3.27 GHz persisted up to $T \approx 5$ K. This behavior can be ascribed to the temperature dependence of the relaxation rates between the corresponding sublevels. Further, the results show that these rates depend on the chromophore environment. The importance of spin-lattice relaxation processes for this class of compounds has already been emphasized by DeArmond and coworkers [10] (although the model presented in ref. [10] must be criticized, see below).

Relaxation processes between sublevels are shown by several other spectroscopic properties of single-crystal $[\text{Ru}(\text{pby})_3](\text{PF}_6)_2$: For example, changes of the polarization ratios observed in the emission spectra as the temperature increases from 1.5 to 4.2 K or with magnetic fields may be understood in this way. Further, the emission decay measured on the zero-phonon lines and on several vibronic satellites exhibits at $T \leq 2$ K in addition to the main long-lived component of about $2 \times 10^2 \mu\text{s}$ a faster one, which disappears with the magnetic field and/or with increasing temperature (to ≈ 10 K). This behavior also seems to be connected to these relaxation properties. Corresponding effects are known for organic molecules and a comprehensive discussion is found in refs. [28,36].

The described properties of the title compounds provide – due to the occurrence of two nearly degenerate sublevels split by $\approx 0.1 \text{ cm}^{-1}$ – clear evi-

dence that a recent model from Riesen and Krausz [37] is incorrect. This model proposes non-degenerate parent terms from an interpretation of measurements of the temperature dependence of magnetic circularly polarized luminescence (MCPL).

ODMR signals have also been found for the broadband emission of neat and dissolved $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ [38]. In this reference it is reported that five microwave resonances occur in the energy range from 0.5 to 4.5 GHz but no other ODMR signals were observed in the region up to 12.4 GHz. The microwave resonances lie at somewhat different frequencies than for the PF_6^- and ClO_4^- salts as is expected due to the changed environment. Three of the microwave transitions were not very convincingly interpreted – by analogy to the situation found in organic molecules [27–30] – as being due to $2E$, $D-E$ and $D+E$ transitions of a normal T_1 triplet, while the other transitions were also ascribed to different sites. Nevertheless, the investigation of Hirota and coworkers [38] represents an interesting experimental work. Following this T_1 model DeArmond and coworkers [10] tried to explain the optical properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ on the basis of a single orbitally non-degenerate spin triplet. This model, however, ignores the well-established $d\pi^*$ -CT character of the many-electron excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ which exhibit relatively large spin-orbit couplings. It further disregards the extensive investigations on zero-field splittings in compounds like the metalloporphyrins [39,40] and the metallophthalocyanines [41]. In these compounds even the $^3\pi\pi^*$ states with a much smaller d-admixture than in the $d\pi^*$ states exhibit relatively large zero-field splittings through the enhanced spin-orbit coupling from the heavy metal ion. Thus, one finds T_1 splittings of several cm^{-1} , e.g. 2 cm^{-1} and 26 cm^{-1} for Pd(II)- and Pt(II)-phthalocyanines, respectively [41]. Consequently, we do not believe that transitions corresponding to $D+E$ and $D-E$ can be observed in ODMR experiments for the compounds investigated here. Thus, we suggest that the interpretations given in refs. [10,38] are incorrect.

4. Conclusions

Further evidence for the doublet character of the

two lowest excited electronic E states of the title compounds – originally assigned for $[\text{Ru}(\text{bpy})_3]-(\text{PF}_6)_2$ single crystals on the basis of the linear polarization of the emission spectra [19–21,26] – is provided by the observation of microwave resonances between the two sublevels of both electronic states. The splittings – detected as ODMR signals on the corresponding zero-phonon lines – are of the order of 0.1 cm^{-1} . Thus, the energy states may be considered as degenerate with respect to the spectral resolution of the emission spectra. The occurrence of these resonances points to interesting phenomena, governed by small relaxation rates at low temperatures between the sublevels of the parent E terms compared to the radiative rates. Therefore, we believe that research on $[\text{Ru}(\text{bpy})_3]^{2+}$ compounds should proceed further into the interesting and sophisticated field of microwave resonance spectroscopy, especially to learn more about the detailed properties of the individual sublevels such as their populations and deactivation rates.

Acknowledgement

The authors thank the Stiftung Volkswagenwerk for financial support.

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