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On the Zero-phonon Structure of Single-crystal $[Ru(bpy)_3](PF_6)_2$

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Abstract

Further evidence is presented that in single-crystal $[Ru(bpy)_3](PF_6)_2$ at low temperatures one observes two zero-phonon lines corresponding to the lowest excited states at 17 809 cm^{-1} (line I, $A'_1 \leftrightarrow 1E'$ in D'_3) and at 17 816 cm^{-1} (line II, $A'_1 \leftrightarrow 2E'$). It is shown that the observed electronic states can be adequately described in a model of isolated $[Ru(bpy)_3]^{2+}$ chromophores. The zero-phonon line II has been recorded in absorption, emission and excitation at exactly the same energy. Its molar extinction coefficient has a value of $\epsilon \approx 5$ l mol^{-1} cm^{-1}, while ϵ for line I is estimated to be about 0.03 l mol^{-1} cm^{-1}, and therefore line I could not be detected in absorption. An assignment of the zero-phonon structure to impurity centers – as has been speculated elsewhere – is definitely excluded.

Introduction

The electronic properties of $[Ru(bpy)_3]^{2+}$ (with bpy = 2,2'-bipyridine) have been discussed in many publications for more than a decade [1–6] but no agreement has been obtained about the symmetry of the excited complex and the number of the excited and emitting states as well as their group-theoretical representations. Especially the properties of the very lowest excited states, which determine the emission behavior, have been the subject of an extensive debate. Most investigations have been carried out with complexes dissolved in solutions or diluted into matrices of undefined site symmetries of the guest molecules. Therefore, we started to investigate single crystals of neat $[Ru(bpy)_3](PF_6)_2$ [7–8]. In this system the site symmetries of the two complexes in the unit cell are both fixed to D_3, and the C_3 axes of the complexes lie parallel to the crystallographic ***c*** axis [9]. This situation involves the advantage that polarized spectra can directly be assigned group-theoretically. Further, one expects to be able to record spectra of high resolution due to a reduction of inhomogeneous broadening effects. Indeed, very sharp spectra could be measured. The observed structures at the blue flank of the emission possess half-widths of about 3–4 cm^{-1} and they have been classified as zero-phonon transitions [10–14]. In a recent paper, Krausz and Nightingale [15] criticized this classification, basing their objections mainly on not finding the corresponding zero-phonon absorption. Moreover, they alleged that the occurrence of the sharp structure is coupled to a small amount of $[Os(bpy)_3]^{2+}$ impurities. It is the main subject of this paper to further confirm our assignments of zero-phonon transitions by presenting the highly resolved polarized absorption and the excitation spectrum in the relevant energy range. In addition, we want to discuss whether in neat crystals of $[Ru(bpy)_3](PF_6)_2$ excitonic interactions and energy transfer may lead to new spectral features in the zero-phonon range, which would not exhibit (as has been speculated, see refs. 15 and 16) the intrinsic properties of the $[Ru(bpy)_3]^{2+}$ complex itself.

Experimental

$[Ru(bpy)_3](PF_6)_2$ was prepared as described elsewhere [7]. Hexagonal needles of the neat material (needle axis parallel to the crystallographic ***c*** axis) were grown under normal conditions by slow evaporation of solutions in acetonitrile/ethanol, ethylene glycol/acetonitrile, or water/acetone. Transparent crystals with well-formed faces and no signs of crystal imperfections were selected under a low-power binocular microscope and additionally checked under a polarization microscope for their suitability for polarized emission measurements. The samples were stuck over a hole in a copper strip and placed in a He bath cryostat for temperatures $T \leqslant 4.2$ K or in a He boil-off cryostat for $T > 4.2$ K. Luminescence was excited either by the UV or visible lines from an Ar^+ laser (Spectra Physics, model 171), the 543.5 nm line of a He–Ne laser (PMS, model LHGR-0100), or by a dye laser (Lambda-Physik, model FL 2000, Coumarin 153) pumped by a N_2 laser. Incident power levels were held well below 1 mW (about 0.05 mW for the He–Ne laser) to avoid

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sample heating. Checks on the sample temperature below 4.2 K are easily performed with the help of the temperature-dependent intensity ratio of the zero-phonon emission lines of single-crystal $[Ru(bpy)_3](PF_6)_2$ (see ref. 11). The optical set-up of the microspectrometer for polarized absorption and emission measurements has already been described in detail [17]. Luminescence was dispersed by a Spex 1401 double monochromator (equipped with a 1200/mm grating blazed at 500 nm), detected by a cooled EMI 9659 QB photomultiplier tube with an extended-red S20 photocathode, and recorded using a PAR SSR 1105 photon counter and a chart recorder. Emission spectra were not corrected for the spectral response of the detection system, and excitation spectra were not corrected for the incident laser power due to the small energy range investigated. The monochromator read-out was calibrated to ±1 cm^{-1} using a low-pressure mercury lamp. For the highly resolved spectra, resolution was better than 1 cm^{-1}. The bandwidth of the dye laser was 0.5 cm^{-1}.

In the following, some experimental details are given which are crucial for successful measurements of the polarized emission on small single crystals of $[Ru(bpy)_3]^{2+}$ compounds. First, the laser beam has to be focused exactly to the crystal face under observation. This means that the laser spot must be smaller than the crystal face. Particular care has to be taken not to illuminate crystal edges, scratches, flaws or other imperfections. Secondly, a luminescing area smaller than the laser spot has to be selected carefully by a diaphragm and must be focused on the entrance slit of the monochromator, in order to avoid that light propagating through the sample and being re-emitted from the crystal surface is collected by the imaging system. (A simple lense focusing the emitted light on the entrance slit is not sufficient.) Taking care of the above-mentioned experimental requirements, polarization ratios as high as 40 can be measured. If one fails to do so, severe mixing of the polarized spectra will occur, in particular when one of the polarized emission components is much weaker than the other, as is the case for the low-temperature emission of single-crystal $[Ru(bpy)_3](PF_6)_2$. Another source of trouble is the problem of re-absorption due to an overlap of absorption and emission bands. Figure 1 shows (as an example) the $E{\perp}c$-polarized emission spectra (E = electric field vector) of a $[Ru(bpy)_3](PF_6)_2$ single crystal at room temperature, taken by following the experimental requirements described above (spectrum a) and taken by recording the light emitted from the crystal edge, respectively (spectrum b). It is seen that the two spectra are totally different. The maximum of the 'correct spectrum' (a) at 575 nm appears only as a shoulder in the 'bad spectrum', where the main band is shifted to the red, maximizing at about 620 nm. Thereby it is shown that the 'best spectrum' is the spectrum for which re-absorption effects are minimized, *i.e.* the spectrum which has its intensity distribution at highest energies (in contrast to ref. 15, but see refs 7 and 8). This example emphasizes once more that careful experiments are a must for successful measurements of polarized emission spectra.

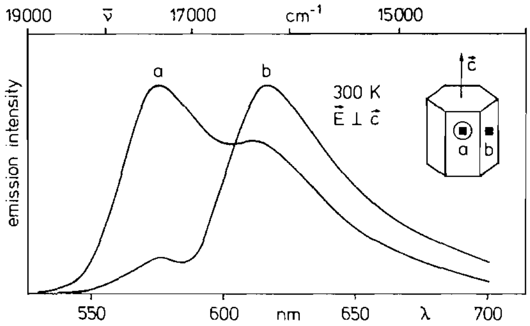

Fig. 1. $E{\perp}c$-polarized emission spectra of a $[Ru(bpy)_3](PF_6)_2$ single crystal at room temperature (E = electric field vector). At the right hand side a hexagonal needle of the compound is shown. The circle indicates the laser spot. The shaded rectangular area denotes the portion of the emitted light which is selected by a diaphragm and focused on the entrance slit of the monochromator. Spectra (a) and (b) were taken at area (a) and (b), respectively.

Results

Figure 2 shows polarized spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ at low temperatures. The emission is only reproduced in the blue flank and the absorption in the red flank of the corresponding total spectra, since this is the spectral range of the zero-phonon transitions. In the upper part of Fig. 2 we show the excitation spectrum which is recorded by measuring the (unpolarized) emission in the broad band maximum at 569 nm (≈17 570 cm^{-1}) and by tuning the wavelength of a dye laser (half-width ≈ 0.5 cm^{-1} ≈ 0.02 nm) over the spectral range displayed in Fig. 2. (The polarization of the exciting laser beam was approximately $E{\perp}c$.) Excitation into the maximum of peak II leads to the same broad-band emission spectra as are found for higher excitation energies. It is an important result that for peak II (at 561.3 nm ≅ 17 816 cm^{-1}) the $E{\perp}c$-polarized absorption, emission and excitation coincide within ±0.5 cm^{-1}, which is the (relative) error of our experimental set-up. Further, it is of importance that the $E{\perp}c$-polarized spectrum does not show any absorption (of ϵ being larger than 0.3 l mol^{-1} cm^{-1} = experimental uncertainty) down to 560.0 nm (17 860 cm^{-1}), while the molar extinction coefficient of peak II exhibits a value of ≈5 l mol^{-1} cm^{-1} in $E{\perp}c$. The intensity of the $E{\parallel}c$-polarized emission is at least by a factor of ≈20 weaker (= experimental uncertainty) than the

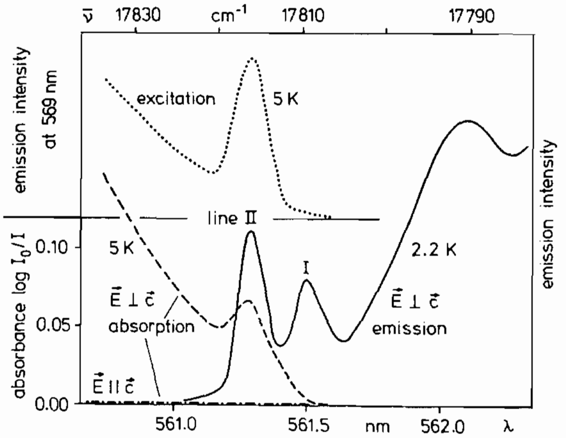

Fig. 2. Highly resolved polarized absorption, polarized emission and excitation spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ reproduced for the zero-phonon range. Crystal thickness for the absorption measurements: 80 ± 10 μm. The results do not depend on the solution in which the crystals were grown. However, the quality of the crystals has an influence on the polarization properties and on the half-widths of the observed peaks. The emission spectrum does not show any obvious dependence on the applied wavelengths of excitation. For $T \gtrsim 10$ K the structures vanish due to thermal broadening effects.

intensity in $E \perp c$. The half-widths of peak II are about 5, 3–4 and 4 cm^{-1} in absorption, emission and excitation, respectively. These values seem to be determined by the qualities of the crystals and therefore the lines are still inhomogeneously broadened.

Discussion

The classification of excited states observed in single-crystal compounds has in principle to be carried out within the symmetry of the space group of the crystal. However, such a classification is only useful if the interactions between the molecules lead to exciton bands and/or factor group splitting effects larger than the achievable resolution caused by inhomogeneous broadening effects. Until now, only very little information is available about the intermolecular interaction energies between transition metal complexes (except for square-planar complexes with relatively large intermolecular interactions [18]). Calculation of the exciton band widths for the lowest excited triplet states is extremely complicated since one should have knowledge of the tails of the molecular wave-functions outside the complexes, but this information is not available. Therefore, we try to give at least an upper limit of the discussed solid-state effects for the $[Ru(bpy)_3](PF_6)_2$ crystals. The intermolecular interaction between the $[Ru(bpy)_3]^{2+}$ complexes is certainly not determined by the well-shielded Ru center but by the bpy ligands. Thus, the excited-state interaction occurs between the bpy-π^* orbitals and one has to discuss the Frenkel-exciton case (see e.g. ref. 19).

Fortunately, one finds a great number of investigations on organic molecular crystals in which the solid-state interactions are also determined by the interactions between the π^*-orbitals. Especially, it is found that the triplet exciton band widths (and the Davydov splitting) arise mainly from the short-range exchange interactions between nearest neighbors (e.g. see refs. 20–23). For example, for 1,2,4,5-tetrachlorobenzene, which crystallizes in linear chains with a shortest separation of the in-chain molecules of 3.76 Å and a nearly plane-to-plane orientation within the stacks, one finds an exciton band width of only 1.3 cm^{-1} [21, 22]. Biphenyl represents another example; here, the shortest distance between nearest neighbors (C–C separation) is 3.72 Å [24]. For this system the exciton band widths are calculated to about 2–3 cm^{-1} and the estimated Davydov splitting is even smaller [20].

The crystallographic structure of $[Ru(bpy)_3](PF_6)_2$ shows that the shortest C–C separations between equivalent sites are larger than 3.83 Å and between the two non-equivalent sites larger than 4.02 Å. Further, an overlap of the π^*-orbitals of different complexes is reduced due to the special arrangement of the bpy wings of neighboring complexes [9, 25]. Consequently, we can safely assume (by comparing the structure of $[Ru(bpy)_3](PF_6)_2$ with those of the organic systems mentioned) that for $[Ru(bpy)_3](PF_6)_2$ the widths of the triplet exciton bands and the corresponding Davydov splitting are smaller than 1–2 cm^{-1}; that means smaller than the inhomogeneous broadening of the observed lines.

Moreover, in $[Ru(bpy)_3](PF_6)_2$ the two enantiomeric molecules in the unit cell are related to each other by an inversion center; consequently they see exactly the same second coordination and therefore exhibit the same electronic spectra under the action of linear polarized light. Thus, the arguments presented represent a justification for classifying the electronic states of $[Ru(bpy)_3](PF_6)_2$ in a model of identical isolated complexes [7, 8, 10–14].

Independently, the classification of the electronic states of $[Ru(bpy)_3](PF_6)_2$ in a model of isolated but oriented chromophores is substantiated by the fact that the lowest excited electronic states of the crystals and their emission properties are very closely related to the states deduced from measurements in diluted systems (see refs. 1 and 2 and the comparison given in refs. 11 and 8).

Extensive investigations [10–14] of the emission properties clearly show that in the recorded energy range (Fig. 2) one finds two zero-phonon lines (peak I at 17 809 cm^{-1} and peak II at 17 816 cm^{-1}). The ratio of the radiative rates of the corresponding transitions is as large as ≈ 200 [11, 14]. Both lines can be traced back to triplet components of MLCT-transitions of Ru4d → bpyπ^* character [1–8, 10–16]. As is expected and seen in Fig. 2, the zero-phonon line corresponding to peak II is clearly observed in absorption and lies within limits of experimental error of ± 0.5 cm^{-1} at the same energy as in emission. [Krausz and Nightingale [15] state that an absorption peak is not to be seen. However, they measured with a crystal which was too thick and thus they reached their limit of detection near 561.6 nm (17 806 cm^{-1}). It is worthwhile to mention that they based their 'arguments' on a non-finding by looking in the wrong energy range!].

As is further expected, the excitation spectrum exhibits also a distinct peak for transition II. Moreover, the fact that an excitation into this peak (17 816 cm^{-1}) leads to the same broad-band emission spectra (which are reproduced in refs. 8, 10 and 11) as are found for higher energy excitations, represents a further manifestation of the intrinsic nature of the zero-phonon transition.

Up to now we could not find the absorption peak corresponding to the low energy transition I which is clearly observed in emission at low temperatures (see Fig. 2 and refs. 10–13). This is not surprising since this transition is strongly forbidden. An estimate of the molar extinction coefficient gives a value of about 0.03 l mol^{-1} cm^{-1}. Detailed arguments that peak I represents also a zero-phonon transition are worked out in refs. 11, 13 and 14.

A group-theoretical classification of the two zero-phonon transitions is readily given: the [Ru(bpy)$_3$]$^{2+}$ chromophores lie at sites of D_3 symmetry in [Ru(bpy)$_3$](PF$_6$)$_2$. No indication is found that the symmetry of the complex in the two very lowest excited states might deviate from that of the ground state. Therefore, we assign the excited states within the D'_3 double group, to take also spin-orbit coupling into account. The representation of the electronic ground state is A$'_1$. Thus, the selection rules tell us that transitions, which are completely $E \perp c$- and $E \parallel c$-polarized, are connected to excited E$'$ and A$'_2$ states, respectively. Consequently, it follows from the experimental results that the two zero-phonon lines represent transitions being connected to excited E$'$ states [10, 11].

– In ref. 15 it was speculated that the sharp structure (see Fig. 2) may be due to [Os(bpy)$_3$]$^{2+}$ impurity centers. Such an interpretation is definitely excluded due to the following reasons:

– The temperature dependence of the emission intensities of the two zero-phonon lines I and II is clearly displayed by the broad emission bands of [Ru(bpy)$_3$](PF$_6$)$_2$ [11].

– Absorption, emission, and excitation spectra of transition II coincide within ± 0.5 cm^{-1}.

– Excitation into transition II gives the known broad emission spectra of [Ru(bpy)$_3$](PF$_6$)$_2$.

– Under application of high magnetic fields the broad-band emission spectra and the zero-phonon line structure exhibit drastic changes which are clearly correlated [13, 14].

– An impurity amount of [Os(bpy)$_3$]$^{2+}$ in [Ru(bpy)$_3$](PF$_6$)$_2$ of less than 10^{-4} mol/mol (as is assumed to be the natural trace in the starting Ru material [15]) with a molar extinction coefficient of the impurity of (less than) 10^3 l mol^{-1} cm^{-1} in the relevant energy range [3] would cause an absorbance of about two orders of magnitude lower than has been observed for peak II (Fig. 2).

– [Ru(bpy)$_3$](ClO$_4$)$_2$ exhibits also the zero-phonon structures [27] which show a similar trend in spectroscopic behavior under temperature variation as those of [Ru(bpy)$_3$](PF$_6$)$_2$. However, there are still obvious differences in the radiative rates, the electron-phonon coupling strengths and in the absolute energy positions of the zero-phonon lines.

Finally, we want to discuss whether processes of energy transfer between [Ru(bpy)$_3$]$^{2+}$ complexes or to [Os(bpy)$_3$]$^{2+}$ complexes may modify the interpretation which is presented in this paper. It is evident from a great number of investigations that a transport of excitation in the host material can be very efficient coherently or by hopping processes, even under conditions of extremely small intermolecular interactions or small excitonic band widths [19–23]. Consequently, very small [Os(bpy)$_3$]$^{2+}$ concentrations might efficiently quench the [Ru(bpy)$_3$]$^{2+}$ emission. However, preliminary results [26] show that (at low temperature) one needs several 10^{-3} mol/mol of the impurity centers for an obvious quenching of the [Ru(bpy)$_3$]$^{2+}$ emission. Thus, only relatively high concentrations lead to a strong emission from the [Os(bpy)$_3$]$^{2+}$ centers. This emission appears distinctly separated in its wavelength from the [Ru(bpy)$_3$]$^{2+}$ emission ($\bar{\nu}\{$[Os(bpy)$_3$]$^{2+}$ emission$\} \lesssim 14\,500$ cm^{-1}). The occurrence of an energy transfer impurities is further manifested by a reduction of the emission lifetime of the [Ru(bpy)$_3$]$^{2+}$ host. Therefore, the occurrence of energy transfer and the modification of the emission properties of the host material can clearly be observed and thus an erroneous classification is excluded.

Krausz and Nightingale [15] proposed that the process of energy transfer is governed by a dipole–dipole mechanism without presenting any justification for the validity of this process. Further, for estimating the transfer rate between [Ru(bpy)$_3$]$^{2+}$ centers they use values for the relevant oscillator strengths and for the spectral overlap which are too large by several orders of magnitude. Contrary to an application of the dipole–dipole approximation for explaining the occurrence of an energy transfer, it is much more reasonable to take into account the exchange interaction between adjacent complexes (see ref. 28 and also refs. 29 and 30), as has been shown in the beginning of the discussion.

Conclusions

Polarized absorption, polarized emission and excitation spectra in the energy range of purely electronic transitions of [Ru(bpy)$_3$](PF$_6$)$_2$ single crystals show that the corresponding sharp peaks (half-widths: 3–5 cm^{-1}) are found (within limits of experimental error of ±0.5 cm^{-1}) at the same energy. It is excluded that [Os(bpy)$_3$]$^{2+}$ impurities as well as the structure of exciton bands can lead to these sharp lines. Therefore, the classification of zero-phonon transitions is further evidenced.

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