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Magnetic Field Induced Absorption of Zero-Phonon Lines in $[Ru(bpy)_3](PF_6)_2$ and $[Ru(bpy)_3](ClO_4)_2$ Single Crystals

Sir:

In recent studies we have investigated the spectroscopic properties of $[Ru(bpy)_3]X_2$ single crystals (with X = PF_6 and ClO_4 and bpy = 2,2′-bipyridine).[1–4] In particular, it was possible to discover sharp, purely electronic (zero-phonon) transitions corresponding to the two lowest excited states in the emission spectra of $[Ru(bpy)_3](ClO_4)_2$[3] and $[Ru(bpy)_3](PF_6)_2$.[2,4] We communicate here the observation of the corresponding zero-phonon lines also in the absorption spectra and report on changes of the absorption under application of high magnetic fields.

The procedures for synthesizing neat material of $[Ru(bpy)_3](PF_6)_2$ and $[Ru(bpy)_3](ClO_4)_2$ and growing of single crystals of good quality are described in earlier publications.[1,3,4] For details concerning the spectrophotometer[5] equipped with a superconducting magnet,[6] see the cited references. The absolute error of the monochromator readout was $\lesssim 1$ cm^{-1}, and the spectral resolution was ≈ 1 cm^{-1}.

Figure 1 shows the highly resolved spectra of $[Ru(bpy)_3](PF_6)_2$ single crystals in the spectral range of the zero-phonon transitions. Line II (17 816 cm^{-1}, $H = 0$ T) coincides (within limits of experimental error of ± 0.5 cm^{-1}) in emission and absorption while in the range of line I (at 17 809 cm^{-1}) no absorption peak is detectable at zero magnetic fields. Both lines represent zero-phonon transitions[2–4,7,10] of triplet components of Ru(4d) → bpy(π^*) character,[8,9] as has been elaborated in detail in the cited references. The nonoccurrence of line I in absorption is not surprising since the corresponding radiative rate k_I is by a factor of about 200 smaller than the radiative rate k_{II} of transition II.[10] Further, due to the known crystal structure[11] of $[Ru(bpy)_3](PF_6)_2$ (the complexes lie at D_3 sites, C_3 axes parallel to the crystallographic $\vec{c}$ axis) and due to the experimental result that the spectra are completely $\vec{E} \perp \vec{c}$-polarized, it was possible to assign both states to group-theoretical E′ representations (in D'_3: ground state A'_1).[1–4]

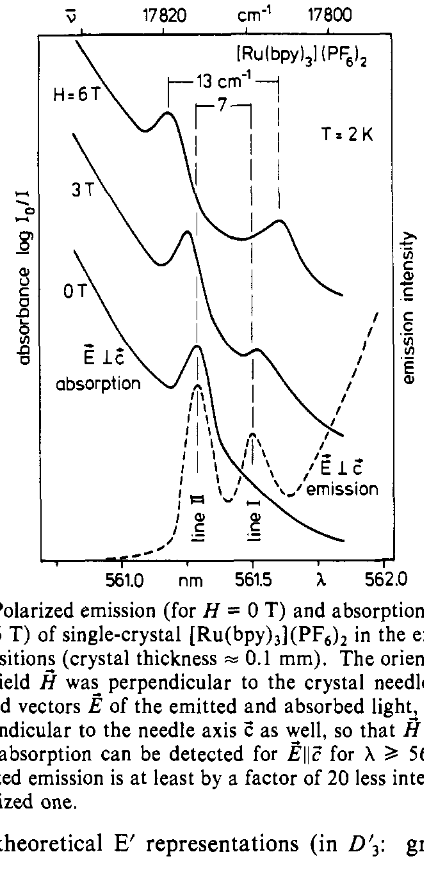

Figure 1. Polarized emission (for $H = 0$ T) and absorption spectra (for $H = 0, 3, 6$ T) of single-crystal $[Ru(bpy)_3](PF_6)_2$ in the energy region of 0–0 transitions (crystal thickness ≈ 0.1 mm). The orientation of the magnetic field $\vec{H}$ was perpendicular to the crystal needle axis $\vec{c}$, the electric field vectors $\vec{E}$ of the emitted and absorbed light, respectively, were perpendicular to the needle axis $\vec{c}$ as well, so that $\vec{H}$ was parallel to $\vec{E}$. No absorption can be detected for $\vec{E} \| \vec{c}$ for $\lambda \geq 560$ nm. The $\vec{E} \| \vec{c}$-polarized emission is at least by a factor of 20 less intense than the $\vec{E} \perp \vec{c}$-polarized one.

In absorption, line I appears with application of high magnetic fields. At $H = 6$ T the ratio of absorbances (=ratio of radiative rates) of the two zero-phonon lines is nearly one. Moreover, the energy separation of the two absorption lines increases from $\Delta E = 7$ cm^{-1} at low magnetic fields ($H \lesssim 1$ T) to 13 cm^{-1} at $H = 6$ T (Figure 1). Further, within limits of experimental error the $\vec{E} \| \vec{c}$ spectra do not show any new spectroscopic features. These properties are fully consistent with the emission behavior of the two transitions under high magnetic fields. We found the same changes in the radiative rates and the same increase of the energetical separation.[7,10]

The situation for $[Ru(bpy)_3](ClO_4)_2$ is very similar (Figure 2). On the blue side of the emission spectrum we find at $H = 0$ T the two zero-phonon lines, which occur at slightly lower energies than in $[Ru(bpy)_3](PF_6)_2$ (line I at 17 606 cm^{-1} and line II at 17 614 cm^{-1}).[3] Again, in absorption, line II is clearly resolved and coincides (within ± 0.5 cm^{-1}) with the corresponding emission peak. In contrary to $[Ru(bpy)_3](PF_6)_2$ one observes an absorption shoulder at the position of line I for $[Ru(bpy)_3](ClO_4)_2$. An estimate of the ratio of the radiative rates—with use of the tem-

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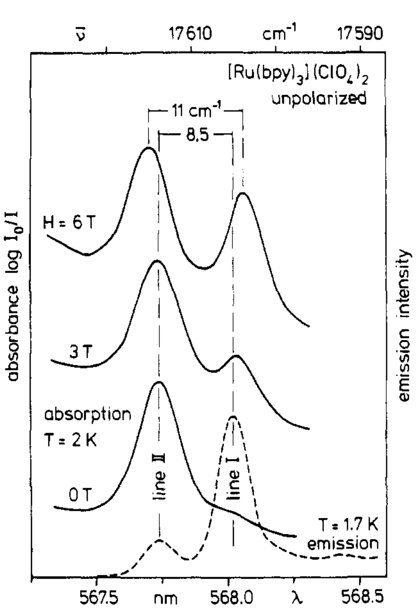

Figure 2. Unpolarized emission and absorption spectra of single-crystal $[Ru(bpy)_3](ClO_4)_2$ (crystal thickness ≈ 0.1 mm). A shoulder for line I can be detected in absorption even at $H = 0$ T. Note that at $T = 1.7$ K the emission from the lowest excited state (line I) is already dominant.

perature dependence of the emission intensities in the zero-phonon lines[3]—delivers a value of $k_{II}/k_I \approx 40$. Thus, the occurrence of this shoulder without magnetic fields is reasonable. (A group-theoretical classification for the transitions in $[Ru(bpy)_3](ClO_4)_2$ cannot yet be presented due to the lack of crystal structure data.) With application of magnetic fields the absorbance of line I at $H = 6$ T reaches approximately the same value as that of line II. Further, the energy separation between the lines increases from $\Delta E = 8.5$ cm^{-1} at $H = 0$ T to 11 cm^{-1} at $H = 6$ T.

The reported effects can be interpreted on the basis of a two-states model and a mixing of the corresponding wave functions under magnetic fields. The amount of mixing of wave function ψ_{II} into ψ_I is determined by the mixing coefficient β. In first-order perturbation theory the value of β is proportional to the magnetic field H (e.g. see ref 6)

$$\beta = \mu_B H \frac{\langle \psi_I | \vec{L} + 2\vec{S} | \psi_{II} \rangle}{\Delta E} \sim H \qquad (1)$$

with $\mu_B H(\vec{L} + 2\vec{S})$ being the Hamiltonian of the magnetic-field induced perturbation.

From perturbation theory it follows[6,7]

$$\frac{k_I(H)}{k_{II}(H)} \approx \frac{\beta^2}{1 - \beta^2} \qquad (2)$$

For $[Ru(bpy)_3](PF_6)_2$, for example, the measurements of the magnetic field dependence of the emission intensities of line I and line II deliver at $H = 6$ T a value of about 0.45 for the ratio of the radiative rates.[10] Thus, β^2 is determined to be ≈ 0.3 (see eq 2). As $\beta^2 = {}^1/_2$ means complete mixing of the two wave functions, we can conclude that the two lowest excited states of the compound and therefore the properties coupled to these states become very similar due to the magnetic field. Further, it is expected that the magnetic field induced interaction leads to a Zeeman effect. Indeed, this effect is also clearly observed in the H dependence of ΔE.

In conclusion, it must be emphasized that the observed lines, which are found exactly at the same energies in emission and absorption and which exhibit the described magnetic field effects, represent zero-phonon lines. An assignment to impurity centers—as is speculated in the ref 12—is excluded. This is further substantiated by the fact that the two salts investigated in this paper exhibit very similar spectroscopic properties, which, however, are displayed in slightly different energetical regions.

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Institut für Physikalische und Theoretische Chemie
Universität Regensburg
D-8400 Regensburg, FRG

G. Hensler
E. Gallhuber
H. Yersin*

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Effect of Particle Size on the High-Spin ($^5T_2$) ⇌ Low-Spin ($^1A_1$) Equilibrium in Supported Spin-Crossover Complexes

Sir:

In a recent series of publications under the above (or similar) titles, Wei and Jean[1-3] have discussed an interesting observation related to the relative fraction of a given transition-metal compound present in the high-spin (HS) or low-spin (LS) form, depending on the adsorption and loading of the complex on a (presumed) inert support. Using ^{57}Fe Mössbauer-effect spectroscopy, these authors have cited[2] evidence that a typical complex, for example $Fe(ppi)_2(NCS)_2$ (where ppi = *N*-phenyl-2-pyridinecarboxaldimine), which exists at room temperature only in the HS form, on adsorption on carbon or MgO, gives rise to Mössbauer spectra which suggest that a significant fraction of the adsorbed material converts to the LS form at 298 K. This unexpected result has been ascribed to the state of subdivision of the complex on the support, with smaller sample size favoring the predominance of the LS fraction at a given temperature. In their experiments, at levels of less than 2–4% loading (defined as wt % Fe/wt % C or MgO), the samples showed evidence only for the LS form at 298 K. At higher loading levels, the spectra were interpreted in terms of an increasing fraction of the iron complex present in the (normal) HS form at room temperature, with spectral parameters corresponding to those of the neat (unsupported) sample at 298 K.

A great deal of data have been reported in the spin-crossover literature concerning the effects of stress and the concentration of deliberately introduced defects on the crossover temperature,[4,5] the effect of fine subdivision[6] and grinding[7] on both the transition temperature and its hysteresis, the influence of small crystallite size on the residual paramagnetism observed at low temperatures,[8a] and a number of related phenomena.[8b] A review of some of these effects has been published by Gütlich.[9] From these studies it is clear that the very sharp temperature dependence of the crossover phenomenon, which is observed in a number of systems, can be broadened by several of the above effects. At the same time, the crossover temperature, which can be defined as that temperature at which the HS and LS populations are equal, is

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