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High-Resolution Spectroscopy of Cyclometalated Rh(III) Complexes

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Abstract

Optical spectroscopic properties of Rh(III) complexes with the cyclometalating ligands 2-phenylpyridine and 2-thienylpyridine are discussed. Using mixed crystals high-resolution spectra are obtained. They allow us to determine the vibrational structure in both the lowest excited states and the ground state. Zeeman spectra of the origin lines reveal that i) the field dependent splitting is isotropic and has a g-value of 2.0 + 0.1 and ii) the zero field splitting is smaller than 0.4 cm^{-1}. The spin-lattice relaxation rate constant depends quadratically on the applied field strength and equals the luminescence decay rate constant at 4.2 K in a field of 2.5 T.

1. Introduction

In this brief review we focus on the cyclometalated Rh(III) complexes [Rh(phpy)$_2$(bpy)]$^+$ and [Rh(thpy)$_2$(bpy)]$^+$, where phpyH and thpyH stand for 2-phenylpyridine and 2-thienylpyridine, respectively and bpy for 2,2'-bipyridine. They will be abbreviated [PhpyBpy] and [ThpyBpy] in the following. The three ligands have isoelectronic π-systems and exert a strong ligand field on Rh(III), which is in the (4d)^6 configuration. In this type of complexes the lowest spin allowed excitation is a ^{1}MLCT (metal-to-ligand charge transfer, dπ*) transition and the next band higher in energy belongs to a ^{1}LC (ligand centered, $\pi\pi$*) configuration [1]. This is in good agreement with the ordering of the molecular orbitals as obtained from an 'Extended Hückel' calculation [2]. The corresponding triplet states form the lowest excited states and we are interested in a detailed description of their photophysical properties. For this purpose highly resolved spectra are needed, which we can obtain using various techniques.

At temperatures below 20 K [PhpyBpy]PF$_6$ exhibits a very sharp-lined single crystal absorption spectrum in the triplet region, which is approximately four orders of magnitude weaker than the ^{1}MLCT transition [3]. Using polarised absorption spectra and the recently determined X-ray crystal structure, the triplet absorptions are found to be ligand localised and essentially in-plane polarised [4]. For [ThpyBpy]PF$_6$ the lattice is not nearly as perfect and the linewidth in the absorption spectra is more than 10 times larger than in [PhpyBpy]PF$_6$ [5].

From the above mentioned neat crystals we obtained sharp-lined luminescence spectra at cryogenic temperatures. Yet the spectra are not intrinsic, i.e. they do not stem from the complexes that absorbed the light, and we attribute the luminescence to excitation traps. Excitation energy migration is very important in our concentrated systems: we found that at 5 K in a neat crystal of [PhpyBpy]PF_6 the hopping rate constant between nearest neighbours is approximately five orders of magnitude faster than the decay rate constant of an isolated [PhpyBpy] complex [5]. The energy transfer rate depends strongly on the separation of the complexes and the rate can therefore be reduced by diluting the luminophore.

We obtained diluted samples by doping the complexes into glassy matrices such as poly-(methylmethacrylate) (PMMA). In these disordered systems many different sites are available to the complexes. Hence many different species with slightly different physical properties are present in the sample, even if a chemically pure complex is introduced into the matrix. This leads to considerable inhomogeneous broadening and concomitant loss of information. The resolution can be improved again using laser techniques such as luminescence line narrowing (LLN) and excitation line narrowing (ELN). Here the laser excites only a subset of all species. At sufficiently low temperatures the vibrational finestructure of both luminescence and excitation spectra can be fully resolved [6-8]. In our experiments, the linewidth of 1 cm^{-1} is instrumentally limited. Application of hole burning techniques on the luminescent origin yields ultra-high resolution spectra with linewidths of the order of 0.003 cm^{-1} [9].

2. Mixed crystals

We also used mixed crystals in order to obtain high-resolution spectra of the cyclometalated complexes. As in the doped glassy matrices the guest complexes are well separated from each other because of the low concentration (0.01% - 1%). For the study of [ThpyBpy] guest complexes, a [PhpyBpy]PF_6 host crystal is a good choice, since the host crystal forms a perfectly ordered lattice and the guest nicely substitutes for host complexes. In addition, the luminescent state of the guest complexes is redshifted compared to the host states.

Guest luminescence can be excited either by way of excitation of the host followed by host to guest energy transfer or by direct excitation below the host absorption. Upon excitation in the UV the mixed crystals show luminescence both of the [PhpyBpy]PF_6 host and of [ThpyBpy] guest complexes, which have a concentration of 1%. The two luminescences have comparable intensities at 5K. Above 22000 cm^{-1} the host absorbs 100 times stronger than the guest in this diluted crystal; part of the host excitation is thus efficiently transferred to the [ThpyBpy] complexes [5].

The luminescence linewidth of the guest in the doped crystal is more than an order of magnitude narrower (5 cm^{-1}) than in the neat crystal (100 cm^{-1}). Hence the quality of the host crystal is not seriously disturbed by introducing our guest complexes. The luminescence and excitation origins of the guest complexes fully coincide, as expected. The guest luminescence (shown in Fig 1) is indeed coming from [ThpyBpy] complexes as is verified by the perfect match of the vibrational sidebands with Raman lines obtained from a [ThpyBpy]PF_6 single crystal. The luminescence is dominated by a strong origin and 5 fundamental vibrational sidebands, which form combinations and progressions. The same 5 modes are found in the excitation spectrum, see Fig 1. Their energies change only slightly (-8...+6%) compared to the ground state vibrations. A similar behavior was found for $Ru(bpy)_3^{2+}$ [10]. Using either the vibrational frequencies or the sideband intensities, the geometry change upon excitation can be estimated to be of the order of 0.05Å for each of the 5 normal coordinates [11].

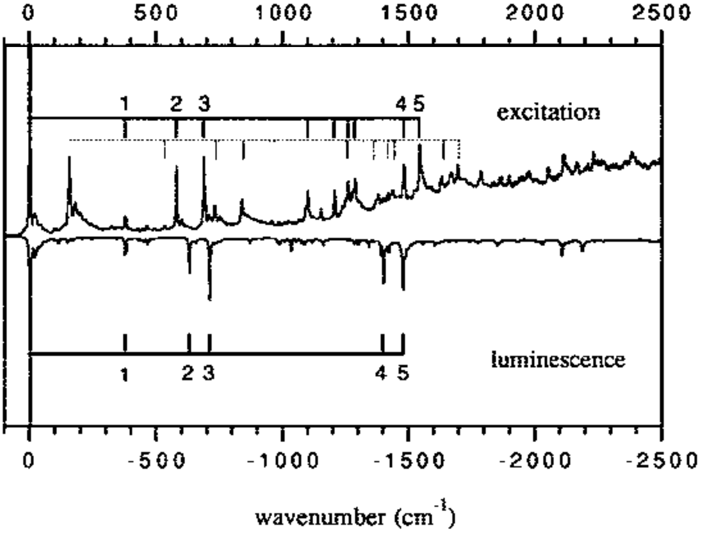

Figure 1. Excitation and luminescence spectra at 5 K of the [ThpyBpy] doped mixed crystal. The spectra are drawn so that the common origins coincide and the vibrational sideband structure can be compared.

Some of the additional lines in the excitation spectrum are attributed to a second excited state, separated from the first triplet state by 156 cm^{-1}. These two lowest triplet states are best considered as localised on the two cyclometalating ligands, which were found to be crystallographically non-equivalent in this lattice [4].

3. Zeeman spectra

Zeeman spectra are a powerful tool to characterise triplet states of aromatic molecules [12] and of metal complexes [13, 14]. In the limit of pure $^3\pi\pi^*$ states the zero field splitting is of the order of 0.1 cm^{-1}. The energy splitting will depend linearly on the applied field strength with a g-value of 2.0, independent of its orientation. In our Rh(III) complexes we estimate a contribution to the zero-field splitting from spin-orbit coupling of approximately 0.3 cm^{-1}. Figure 2 shows the results of two Zeeman experiments on [ThpyBpy] doped into [PhpyBpy]PF$_6$. The linewidth of our mixed crystal luminescence and excitation spectra is just sufficiently narrow that the Zeeman splitting of the electronic origin is resolved at 4 Tesla, see Fig 2a. The experiment was run on a polycrystalline sample, hence the splitting is isotropic.

Using LLN and ELN techniques, the linewidth was reduced to 1 cm^{-1}, see Fig 2b. From this we estimate that the zero field splitting is ≤ 0.4 cm^{-1}. From the field dependence we determine a g-value of 2.0 ±0.1 [15]. In all these properties the emitting state of [ThpyBpy] strongly resembles a purely organic $^3\pi\pi^*$ state. Or in other words, the mixing in of $^1d\pi^*$ or $^1n\pi^*$ character by spin-orbit coupling is of the order of one percent and thus has only a very small effect on the energy splittings. In contrast, it has a very pronounced effect on the luminescence lifetime, which is reduced in [ThpyBpy] by about two orders of magnitude from the free ligand.

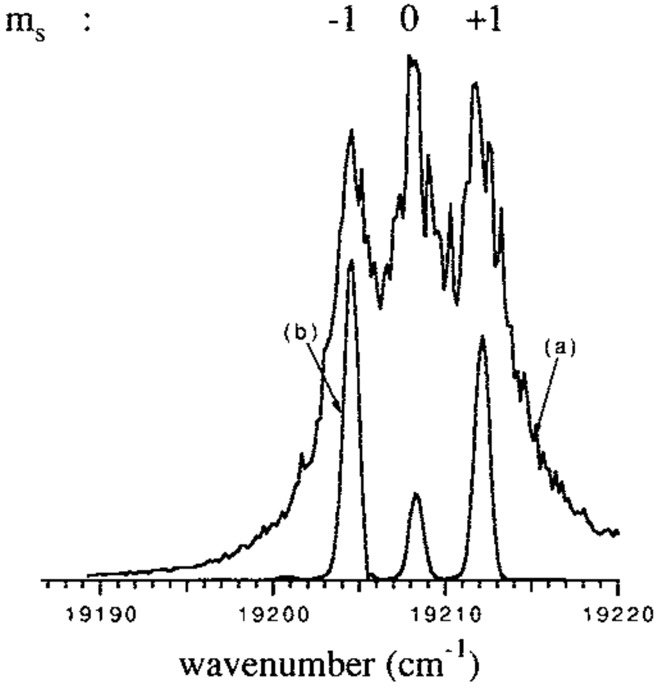

Figure 2. Zeeman excitation spectra of [ThpyBpy] doped into [PhpyBpy]PF_6 at 4 T and 4.2 K. a) monitored with a resolution of 30 cm^{-1}; b) narrowed spectrum with a resolution of 1 cm^{-1}.

The narrowing techniques were also applied to [ThpyBpy] doped PMMA, where the inhomogeneous linewidth of the origin is of the order of 300 cm^{-1}. Here we excite three sets of triplets with equal probabilities, which have either their m_s = -1, 0 or +1 level in resonance with the laser. This leads to the formation of a five-line pattern with a peculiar intensity distribution [16]. The intensities of the five lines depend mainly on the temperature, field strength and spin-lattice relaxation rate constant k_{SLR}, which connects the Zeeman levels nonradiatively. The intensity distribution can be used to estimate k_{SLR}.

In Figure 3 the k_{SLR} values are plotted as a function of the Zeeman splitting, which was varied by the magnetic field. The dependence is nearly quadratic, as expected theoretically [17, 15].

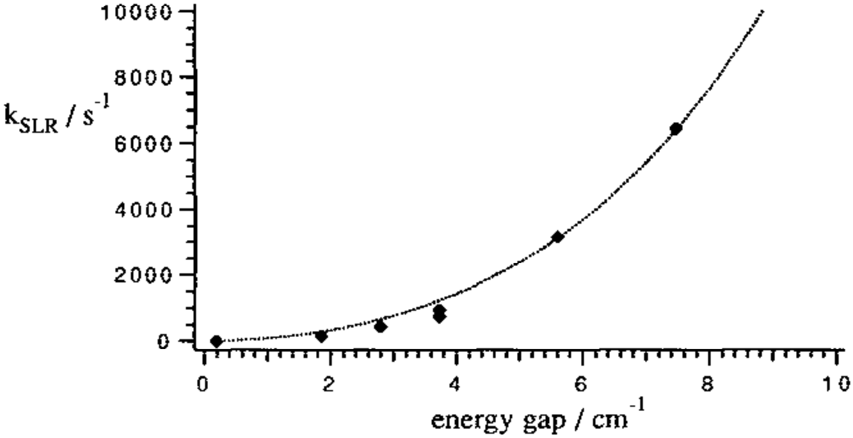

Figure 3. Estimated values for k_{SLR} as a function of the bridged energy gap for a [ThpyBpy] doped mixed crystal at 4.2 K. The luminescence decay rate is 2000 s^{-1}.

Acknowledgements

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