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Dynamics in the lowest excited triplet state of Rh^{3+} -chelates

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Abstract

For a number of Rh^{3+} -chelates the spin dynamics in the ligand-localized lowest excited $^3\pi\pi^*$ state is studied by means of coherent ODMR spectroscopy. Irreversible triplet spin dephasing and non-stationary spin-diffusion in the photo-excited Rh^{3+} -chelates is attributed to hyperfine couplings with randomly fluctuating proton spins present in the ligand molecules having trapped the $^3\pi\pi^*$ excitations.

1. Introduction

The spectroscopic study of chelate complexes of d^6 transition metal ions and aromatic bidentate ligands has attracted considerable interest in recent years [1–5], partly because such complexes may be applicable in devices for the storage of solar energy. Recently, we have shown the feasibility of zero- and low-magnetic field optically detected magnetic resonance (ODMR) studies for a series of Rh^{3+} (d^6) trischelates in the lowest excited state [1–3]. The experiments provided definite proof of the ligand-localized $^3\pi\pi^*$ nature of the luminescent state in these compounds. In addition, the study of the spin population relaxation dynamics in the phosphorescent $^3\pi\pi^*$ state of the Rh^{3+} chelates was reported using optically detected microwave recovery techniques [3]. Typically, the lifetime of the individual triplet sublevels varies from 200 to 1500 μs . The lowering of the lifetime as compared to the free-ligand molecule values by two orders of magnitude has been discussed in terms of the heavy-atom effect, in which the spin-orbit coupling-induced

mixing with $^1d\pi^*$ states in which the metal d-orbital is involved in σ -bonding to the ligand is most important in enhancing the radiative decay [3].

In this paper, we report on optically detected electron spin echo and stimulated spin echo transient experiments performed for photo-excited $[\text{Rh}(\text{thpy})_2(\text{bpy})]^+$ and $[\text{Rh}(\text{thpy})(\text{phpy})(\text{bpy})]^+$, doped for 0.25% and 0.5%, respectively, in a single crystal of $[\text{Rh}(\text{phpy})_2(\text{bpy})]\text{PF}_6$. Here, $\text{thpy}^- = 2,2'$ -thienylpyridine, $\text{phpy}^- = 2$ -phenylpyridine and $\text{bpy} = 2,2'$ -bipyridine. In the crystal lattice, the dopant complex cations are substitutional for host complex cations in such a way that dopant-bpy always occupies a host-bpy site [4]. We use the notation TTB^+ for $[\text{Rh}(\text{thpy})_2(\text{bpy})]^+$; the two conformations for $[\text{Rh}(\text{thpy})(\text{phpy})(\text{bpy})]^+$ are abbreviated as TPB^+ and PTB^+ . The structures of the TPB^+ and PTB^+ cations differ in that the positions of the phpy^- and thpy^- ligands are interchanged. From low-field ODMR anisotropy measurements it was previously established that the lowest excited triplet state in the three dopant cations is localized only one thpy^- -ligand, which is sited at the same crystallographic site in

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TTB⁺ and TPB⁺, whereas in PTB⁺ the excited thpy⁻-ligand occupies the other non-bpy site in the complex [2].

2. Experimental

The crystals used in the experiment were prepared as described previously [4]. Optical excitation was achieved by means of a cw Ar⁺ laser at a wavelength of 488 nm for TTB⁺, 502 nm for TPB⁺, and 476 nm for PTB⁺. The emission was dispersed by a Monospek 1000 monochromator, having a 515 nm cut-off filter in front, and photo-detected by means of a GaAs photomultiplier tube. In all experiments, TTB⁺, TPB⁺ and PTB⁺ could be individually studied, using the zero-phonon line positions in the emission spectrum at 520.2, 519.3 and 517.1 nm [2,4], as the respective detection wavelengths in the double resonance experiments. The crystals were placed inside a slow-wave helix and immersed in a liquid helium bath. The ODMR spin echo spectrometer has been described elsewhere [6]. The spin coherent transients were measured at a temperature of 1.4 K.

3. Results and discussion

In zero magnetic field, ODMR resonances are observed for TTB⁺ (at 1730, 2580 and 4310 MHz), TPB⁺ (at 1675, 3970 and 5640 MHz), and PTB⁺ (at 1485 and 2875 MHz) in the photo-excited triplet state [2]. The ODMR lines are inhomogeneously broadened with line widths in the range 15–45 MHz. Using coherent ODMR techniques we obtain information concerning the dynamical processes underlying the homogeneous broadening of the ODMR transitions. Optically detected Hahn echo decays were measured by applying a $\pi/2 - \tau - \pi - \tau' - \pi/2$ pulse sequence at one of the spin resonance microwave frequencies, while optically exciting the Rh³⁺-complex. Spin coherence within the phosphorescent triplet state, created after the first pulse, is restored at a time $\tau' = \tau$ after the second pulse. The third $\pi/2$ pulse serves as the probe pulse to optically detect the spin coherence as an intensity change of the phosphorescence [6].

Fig. 1. Hahn echo decay curves for the $|D| - |E|$ zero-field ODMR transition of TTB⁺, with resonance frequency 2578 MHz, detected at the emission maximum of 520.2 nm, at $T = 1.4$ K, (a) magnetic field $H = 0$: $T_M = 3.14$ μ s, (b) magnetic field $H = 21$ G: $T_M = 0.33$ μ s.

As an example, in Fig. 1(a) the Hahn echo decay curve for the $|D| - |E|$ transition of TTB⁺ is shown. All measured Hahn echo decays could be fitted to a mono-exponential decay function. A summary of all measured phase memory times, T_m , and the corresponding homogeneous line widths, $(\pi T_m)^{-1}$, is given in Table 1. Compared to the inhomogeneous line widths of 15–45 MHz of the zero-field ODMR transitions, the homogeneous line widths are about two orders of magnitude smaller.

Irreversible dephasing is about two orders of magnitude faster than population relaxation of the individual triplet sublevels. This result implies that a pure dephasing mechanism is responsible for the irreversible loss of phase coherence. Most likely, this dephasing has its origin in hyperfine couplings to nuclear spins, probably proton spins in the ligand molecule. As in the photo-excited triplet state in the free ligand molecule [7], the random flipping of surrounding nuclear spins will cause a change in the local field felt by the triplet spins.

Table 1

Resonance frequencies and inhomogeneous line widths of the four ODMR transitions for which optically detected Hahn echo decays were measured. The resulting phase-memory times, T_M , and the corresponding homogeneous line widths (in brackets) are given in the last row

	TTB ⁺ 2 E	TTB ⁺ D – E	TPB ⁺ D – E	PTB ⁺ D – E
ν_{res} (MHz)	1726	2578	3972	1485
Γ_{inhom} (MHz)	15	28	30	25
T_M (μ s)	3.42 (93)	3.14 (101)	4.32 (74)	1.70 (187)
(Γ_{hom} (kHz))				

resulting in a variation of the precessional frequency and a loss of phase coherence. This spin dephasing mechanism is supported by the results in a small magnetic field. When magnetic fields (up to 21 G) are applied, the dephasing time shortens considerably, as can be seen in Fig. 1(b). (For magnetic field strengths higher than 30 G the S/N ratio of the echo decay becomes too small to reliably resolve the echo signal.) The origin of the magnetic-field induced enhanced dephasing is well known [7]: the magnetic field partially lifts the quenching of the (zero-field) triplet electron spin magnetic moment and, as a result, hyperfine couplings to fluctuating nuclear spins, that give rise to irreversible electron spin dephasing, now become first order. It is noted from Table 1 that the phase memory times for TTB⁺ and TPB⁺ are comparable in magnitude. However, the spin dephasing time for PTB⁺ differs appreciably from the values for TTB⁺ and TPB⁺. These findings are not unexpected since the triplet state excitation in TTB⁺ and TPB⁺ is trapped at a similar thpy[−] ligand site in both cations. The thpy[−] ligand in PTB⁺ is at a crystallographically different position within the Rh³⁺-chelate. An appreciable effect on the electronic charge distribution in the excited ligand molecule arising from the different crystal field is expected, this in turn leading to different hyperfine couplings between the triplet electron spin moment and the proton spins at thpy[−].

The effects of spectral diffusion were studied by means of stimulated spin echo decay experiments in which a repetitive $\pi/2-\tau-\pi/2-T-\pi/2-\tau-\pi/2$ pulse sequence is applied. The first two pulses produce a spin grating such that the population difference of the two resonantly pumped spin levels varies

sinusoidally, with a period $1/\tau$, across the inhomogeneously broadened line. As T is scanned, the grating pattern is erased due to spin diffusion and population relaxation processes. In case the relaxation of the stimulated spin echo amplitude is found to vary with the applied grating $1/\tau$ period this is taken as evidence for the presence of spin diffusion. Fig. 2 illustrates for TTB⁺ the variation of the observed stimulated echo decays with the grating period, $1/\tau$. The stimulated echo decay transients were fitted to a function of the form [6],

$$I_{\text{SE}} \propto [\exp(-k_1 T) + \exp(-k_2 T)] \times \exp(-k(\tau)RT). \quad (1)$$

In Eq. (1), the first factor is representative of the population relaxation of the spin levels probed in the SED experiment to the ground state (SLR is negligible in this system at liquid helium temperatures [3]). The second factor is the contribution to the SED arising from spin diffusion characterized by a diffusion kernel of the form,

$$D(\tau, T) \propto \exp\{-k(\tau)[1 - \exp(-RT)]\}, \quad (2)$$

where $k(\tau) = a\tau$ for a Lorentzian-type diffusion and $k(\tau) = b\tau^2$ for a Gaussian-type diffusion, a and b being the respective stationary widths of the diffusion kernel, $K(\omega_f - \omega_i, t = \infty)$. In Eq. (2), R is representative of the rate of change of the width of the frequency distribution of the microwave excitation in the non-stationary diffusion limit. In Fig. 2 we plot the best-fit values for $k(\tau)$ for the three observed zero-field spin transitions as a function of τ . As can be seen from Fig. 2, the stimulated echo decay rate constant increases with increasing time

Fig. 2. Stimulated echo decay function $k(\tau)$ (cf. Eq. (2) in text) as a function of time τ between the first and second pulse of the SED pulse sequence: (a) $2|E\rangle$, TTB^+ ; (b) $|D\rangle - |E\rangle$, TTB^+ ; (c) $|D\rangle - |E\rangle$, TPB^+ . Straight lines represent best linear fits to experimental data and are indicative of Lorentzian-type spin diffusion. Inset: stimulated echo decay curve for the $|D\rangle - |E\rangle$ transition of TTB^+ when $\tau = 400$ ns. The drawn line represents the best fit according to Eq. (1), with $R = 0.15 \text{ ms}^{-1}$ and $k(\tau) = 22$.

τ , or, equivalently, with decreasing grating period. Evidently, non-stationary spectral diffusion takes place and from the linear dependence of $k(\tau)$ on τ it is inferred that the spin diffusion is Lorentzian. Lorentzian diffusion is expected when the environment of the probed spins is non-uniform, and, as a result, the spins on the average undergo large frequency jumps, so the wings become more pronounced than expected for a Gaussian shape, which applies in the statistical limit. This result suggests that the non-stationary spin diffusion, like the irreversible dephasing, is caused by isotropic hyperfine couplings to fluctuating proton spins in the excited ligand.

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