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THE QUANTUM EFFICIENCY OF THE PHOTO-EXCITATION IN A Fe (II) SPIN-CROSSOVER COMPOUND

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In this paper we discuss on the quantum efficiency in spin crossover compounds. Spin crossover solids are text-book examples of photo switchable materials that present a thermal spin transition from the diamagnetic low-spin state, thermodynamically stable at low temperatures, to the paramagnetic high-spin state becoming the thermodynamically stable state at elevated temperature. By irradiating them with an appropriate wavelength, they can pass from the stable low spin state to the metastable high spin state at temperatures below the thermal transition temperature. For the compound $[Fe(pic)_3]Cl_2{\cdot}EtOH$, the question regarding the quantum efficiency of the photo-conversion process that is the number of molecules converted by one single photon and its possible dependency on irradiation intensity gave rise to a controversy. The experimental results presented in this paper demonstrate that the quantum efficiency of the photo-conversion at 11 K is on the order of unity, with no noticeable dependency of the quantum efficiency on light intensity. It does, however, depend to a small extent on the fraction of complexes already converted to the high-spin state.

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1. Introduction

$[Fe(pic)_3]Cl_2{\cdot}EtOH$ (pic = 2-picolylamine) is a spin-crossover compound that presents a very abrupt thermal spin transition due to the large cooperative effects of elastic origin [1]. For this compound, the spin transition temperature, defined as the temperature at which half the complexes are in the high-spin state, is 118 K.

The two states in question have not only distinct magnetic properties, they also have quite different optical and geometrical properties. In the high-spin state, $[Fe(pic)_3]Cl_2{\cdot}EtOH$ is yellow, with a comparatively weak absorption band centred at 830 nm corresponding to the spin-allowed ligand field transition ${}^5T_2 \rightarrow {}^5E$ (see Fig. 1). In the low-spin state, it is red due an intense metal-to-ligand-charge-transfer (MLCT) band, which dominates the spectrum in the visible [2]. Furthermore, the metal-ligand bond length as well as the volume of the molecules is greater in high-spin state than in the low-spin state

In spin-crossover compounds, the high-spin state can be populated as metastable state below the thermal transition temperature by irradiating into ligand-field or into metal-to-ligand-charge-transfer (MLCT) bands, the so-called LIESST (light induced excited spin state trapping) effect, presented schematically in the inset of Fig. 1 [2, 3]. At sufficiently low temperatures the complex is trapped in the high-spin state as a result of the energy barrier due to the large bond length difference between the two states. For $[Fe(pic)_3]Cl_2{\cdot}EtOH$ at temperatures below 10 K, the lifetime of the metastable state is longer than 20'000 s. It decreases to several hundreds of seconds at 50K.

There are only a few studies concerning the problem of quantum efficiency in spin crossover solids. For a typical spin-crossover compound, $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole) [4], which

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shows a relaxation behaviour quit similar to the one of the title compound, a quantum efficiency value around unity was reported by Hauser et al [4]. This value was considered valid for all spin transition compounds, until very recently when Ogawa et al. [5] studied the photo-conversion in the title compound. They suggest that at temperatures of 10 K or below, the quantum efficiency of the photo-conversion from the low-spin to the high-spin state depends on the excitation light intensity, and they report values for the quantum efficiency of this process, that is, the number of iron complexes converted per absorbed photon, of up to 34. Our independent determination of the quantum efficiency [6] and its dependency on temperature as well as on light intensity does not confirm this astonishing value and are presented in the following.

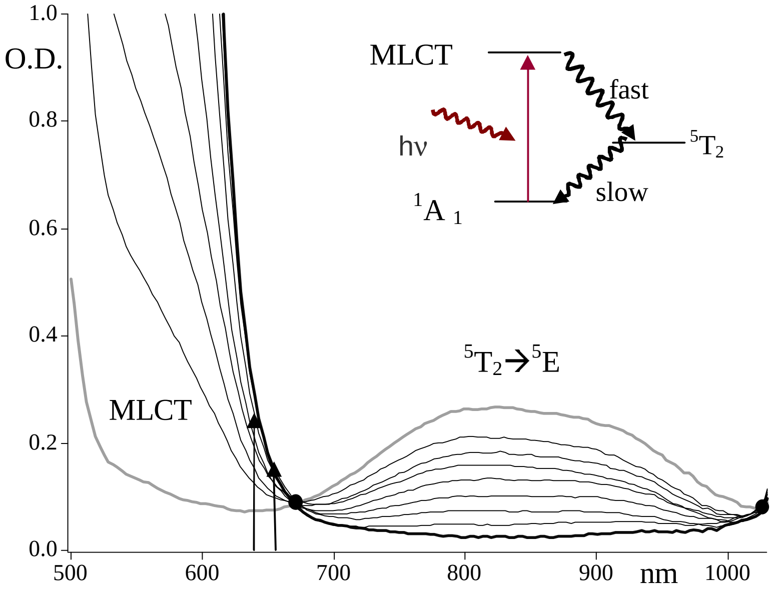

Fig. 1 Time evolution of the single crystal absorption spectrum of Fe-pic during the excitation process at T = 11 K. The thick curves correspond to the initial low spin state and to the final high spin state. In the inset: schematically LIESST effect.

2. Experimental method

In our experiments we used single crystals of $[Fe(pic)_3]Cl_2{\cdot}EtOH$ with a thickness of around 60 μm and a diameter of ~300 μm was mounted to entirely cover a small aperture the copper sample holder, inserted into a closed cycle cryostat capable of achieving sample temperatures down to 11 K. This thickness ensures that the variation of the intensity inside the sample is minimal. The sample was sitting in 1 bar of He exchange gas for efficient cooling. To irradiate it, we used the 647 nm and 676 nm lines of a Kr^+-laser with intensities I ranging from 0.02 to 7.2 mW/mm^2, corresponding to a photon flux at the sample Φ of 6.5×10^{15} to 2.5×10^{18} $s^{-1}cm^{-2}$. These lines are in the tail of the MLCT band of the low-spin species, where the high-spin species do not absorb. The absorbance at this wavelength of the crystal in the low-spin state was ~0.12 (ε_{647} = 12 l mol^{-1} cm^{-1}, $\sigma = 4.6 \times 10^{-20}$ cm^2). This value of the absorbance ensures that concentration gradients inside the crystal during photo-conversion are minimal, and that the crystal survives the process without fracturing [7]. The fraction of complexes in the high-spin state, γ_{HS}, as a function of irradiation time was determined from the intensity of the high-spin band as obtained from full absorption spectra recorded between 500 and 1000 nm at appropriate time intervals. Using this method, we obtained reproducible photoconversion curves.

3. Results and discussion

Fig. 2 shows the excitation curves of $[Fe(pic)_3]Cl_2 \cdot EtOH$ at 11 K for irradiation at 647 nm and intensities between 0.02 and 7.2 mW/mm^2 as obtained by the above procedure. For the highest irradiation intensity of 7.2 mW/mm^2, the photo-conversion was complete within less than 30 s, that is, within the same total time as observed by Ogawa et al. [5] at their highest irradiation intensity.

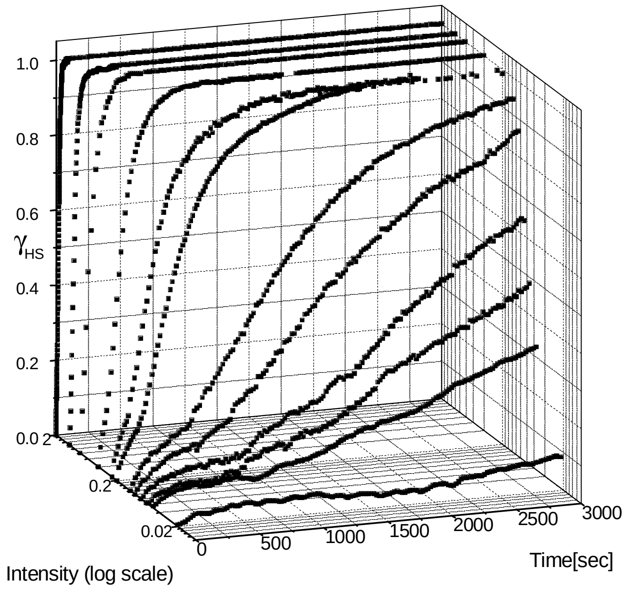

Fig. 2. Excitation curves for $[Fe(pic)_3]Cl_2 \cdot EtOH$ at 11 K. Irradiation at 647 nm with intensities varying from 0.02 to 7.2 mW/mm^2.

For a quantitative evaluation of this data, it is preferable to plot the high-spin fraction, γ_{HS}, as a function of the product of irradiation time and intensity, I•t [mJ//mm^2], as shown in figure 3. It's easy to prove that in this representation, all curves with irradiation intensities $I > 0.24$ mW/mm^2 are superimposable within experimental accuracy. For such intensities, the quantitative excitation to $\gamma_{HS} = 1$ is achieved in less than 10^3 s, that is, much faster than the high-spin→low-spin relaxation at 11 K. For $I > 0.24$ mW/mm^2 the latter is thus negligible. Thus, it can be concluded that the quantum efficiency, η, for the photo-conversion does not depend upon irradiation intensity. In fact, it is straight forward to extract η from these curves using the differential equation for the build-up of the high-spin state in the case of negligible relaxation

$$\frac{d\gamma_{HS}}{dt} = \eta k_{ex}(1 - \gamma_{HS}) \tag{1}$$

where

$$k_{ex} = \sigma\Phi = 1.5 \times 10^{-2} \cdot I \ [s^{-1}] \tag{2}$$

is the rate constant for the primary excitation, σ and Φ are the absorption cross section at the irradiation wavelength and the photon flux, respectively, and I is the irradiation intensity in mW/mm^2. The factor of 1.5×10^{-2} corresponds to an irradiation wavelength of 647 nm and an absorption cross section $\sigma = 4.6 \times 10^{-20}$ cm^2 ($\varepsilon_{647} = 12$ l mol^{-1} cm^{-1}). With a value for $I \cdot t \approx 80$ mJ/mm^2 at $\gamma_{HS} = 0.64$, η must be around unity. However, inspection of the excitation curves of Fig. 3 shows that the photo-conversion is not exactly single exponential, and that therefore η depends to some extent on the actual high-spin fraction γ_{HS}. This is not surprising, as intersystem crossing rate constants are known to be influenced by cooperative effects in spin-crossover systems [7, 8]. Indeed, a similar behaviour has previously been observed for other spin crossover compounds [9]. η as a function of γ_{HS} can be extracted from the experimental curves by numerical differentiation according to equation (1). Fig. 4 shows η as function of γ_{HS} obtained from the ensemble of curves with $I > 0.24$ mW/mm^2. η starts of at a value of around 0.5 at the beginning of the irradiation and increases somewhat with increasing values of γ_{HS}. Within experimental accuracy it does not significantly exceed the value of unity, that is, per absorbed photon only one complex is converted to the metastable high-spin state.

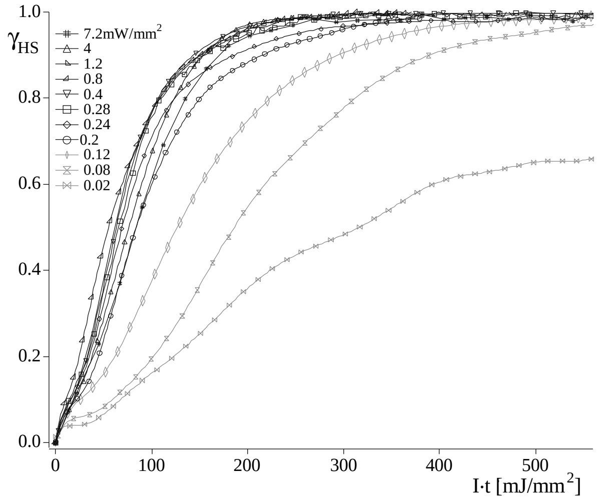

Fig. 3. The excitation curves $[Fe(pic)_3]Cl_2\cdot EtOH$ at 11 K for irradiation at 647 nm from Fig. 2a plotted against the irradiation energy I·t [mJ/mm^2].

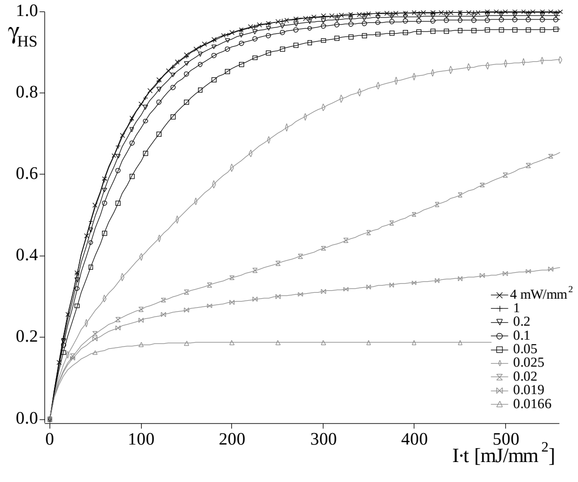

Fig. 4. Simulated excitation curves plotted against the irradiation energy I·t [mJ/mm^2].

For values of $I < 0.24$ mW/mm^2, the excitation is not sufficiently fast to overcome the non-zero high-spin→low-spin relaxation due to low-temperature tunnelling. Thus, for $I = 0.02$ mW/mm^2 the photo-conversion curve levels off at a steady state value of γ_{HS} well below unity. At still lower values of I, the steady state high-spin fraction obtained after very long irradiation times becomes smaller and smaller. The increasingly sigmoidal shape of the curves as the irradiation intensity is lowered can be understood on the basis of the self-accelerating character of the high-spin→low-spin relaxation due to the above mentioned cooperative effects [7, 8]. It can be modelled on the basis of the differential equation (master equation) [9] which takes into account the competition between the photo-conversion and the relaxation according to (3).

$$\frac{d\gamma_{HS}}{dt} = \eta k_{ex}(1-\gamma_{HS}) - k_{HL}\gamma_{HS}, \tag{3}$$

where k_{HL} is a function of the high-spin fraction, γ_{HS}. In mean-field approximation, this function takes the form of an exponential dependence according to Ref. [10]

$$k_{HL} = k_{HL}(\gamma_{HS} = 1)\exp[\alpha(1-\gamma_{HS})]. \tag{4}$$

Despite the fact that this form of $k_{HL}(\gamma_{HS})$ only describes the relaxation curves for $\gamma_{HS} > 0.5$ [7], it is the correct form to take for the present case of a continuous irradiation. As Romstedt et al. [7] have shown, under irradiation the title compound behaves as predicted by the mean-field approach for all values of γ_{HS}, because the irradiation actually destroys correlations. For the title compound at 11 K, the exponential self-acceleration factor $\alpha \approx 4.5$, and the initial rate constant $k_{HL}(\gamma_{HS} = 1) \approx 2 \times 10^{-5}$ s^{-1}. With these values the numerical solution of the above differential equation gives the theoretical excitation curves shown in Fig. 4. The key features of the observed curves, namely a threshold value for the irradiation intensity above which full photo-conversion occurs, and an incubation period for lower values of the intensity [11] with a plateau before the curve reaches its final steady state value of γ_{HS}, are nicely reproduced by the simulations. In particular for the second case a very good agreement between the sigmoidal shape of the experimental curves and the simulated curves is obtained.

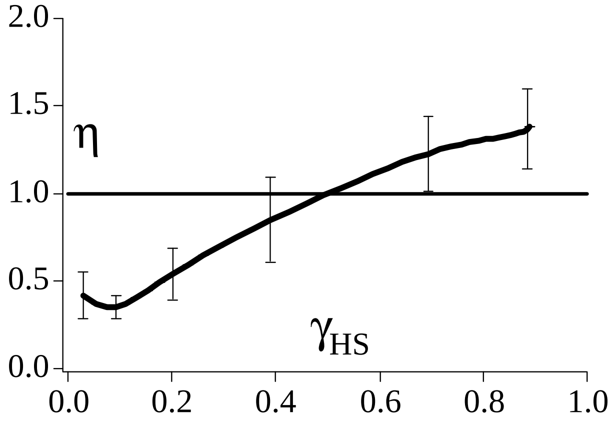

Fig. 5. The quantum efficiency η of LIESST for $[Fe(pic)_3]Cl_2\cdot EtOH$ at 11 K and irradiation at 647 nm.

Fig. 6 compares the excitation curves at 11 and at 22.3 K for irradiation at 647 nm and a light intensities of 0.4 mW/mm^2. The difference between excitation curves recorded at 11 and at 22.3 K, could, in principle, be due to either a faster relaxation or to a smaller quantum efficiency for LIESST at 22.3 K. It is comparatively straight forward to show that it is basically due to the former: From the relaxation curves at 11 and 22.3 K shown in the insert of Fig. 1a, both the above mentioned values of 2×10^{-5} s^{-1} for $k_{HL}(\gamma_{HS} = 1)$ and 4.5 for α at 11 K, as well as values of 1×10^{-4} s^{-1} and close to 4.5 for 22.3 K can be extracted.

In Fig. 6 the excitation curves calculated by numerical integration of the differential equation (3) and using the dependence of $k_{HL}(\gamma_{HS})$ according to equation (4) with the above sets of parameters for the curves and a temperature independent quantum efficiency according to Fig. 5 are included. The good agreement between experimental and calculated curves allows the conclusion that the quantum efficiency of LIESST is indeed temperature independent.

Fig. 6 also includes the excitation curve at 11 K, obtained for irradiation at 676 nm and the same light intensity as for the irradiation at 647 nm. Of course, irradiation at 676 nm results in a slower population of the high-spin state than irradiation at 647 nm. But this is simply due to the fact that at 676 nm the absorption cross section is roughly half as large than at 647 nm. The effective quantum efficiency, that is the number of high-spin complexes created per absorbed photon, is the same for the two irradiation wavelengths.

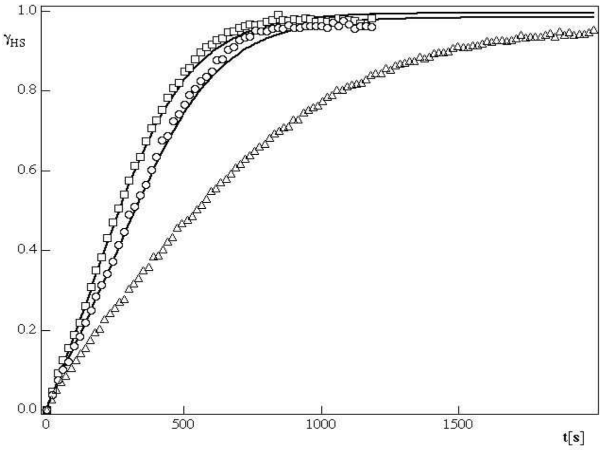

Fig. 6. Excitation curves for $[Fe(pic)_3]Cl_2\cdot EtOH$ at 11 K (squares) and at 22.3 K (circles) for irradiation at 647 nm and at 11 K for irradiation at 676 nm (triangles). lines: calculated curves using the parameters as described in the text. Irradiation intensity at both wavelengths: 0.4 mW/mm^2.

4. Conclusions

We have demonstrated that the quantum efficiency of the photo-conversion at 11 K is of the order of unity, with no noticeable dependency of the quantum efficiency on light intensity. It shows a slight dependence on the fraction of complexes already converted to the high-spin state but we did not observe dependencies of the quantum efficiency on the temperature or wavelength.

The results presented in this manuscript lead to a quantitative, comprehensive and consistent understanding of the various aspects of light-induced excited spin state trapping in this compound.

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