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Spin–lattice relaxation and intersystem crossing in single molecules of terrylene embedded in a *p*-terphenyl crystal

M. Białkowska, A. Makarewicz, M. Banasiewicz, B. Kozankiewicz *

Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

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ABSTRACT

Thermal evolution of fluorescence intensity correlation functions of single molecules of terrylene in a *p*-terphenyl crystal was studied and double-exponential decay at 5 K was found to change to a mono-exponential decay above 17.5 K. Such behavior was attributed to spin–lattice relaxation (SLR), which couples the long-lived zero-field triplet spin sublevel T_Z with the short-lived and experimentally unresolved T_X and T_Y sublevels. For two of the studied molecules, which were probably deformed from planar symmetry, we observed overpopulation of the spin sublevel T_Z and activation of the SLR at temperatures above 20 K. The SLR rate constant exhibited Raman relaxation.

1. Introduction

Spin–lattice relaxation (SLR) in phosphorescent triplet states of aromatic molecules has already been intensively studied as long as 30–40 years ago (see cross-references in Ref. [1]). The possible mechanisms of this process were recognized by the study of temperature dependence of the relative populations of the triplet spin sublevel. The systems studied so far dealt with huge ensembles of molecules with the photo-physical properties which are not appropriate for single-molecule detection, mainly because of their excessively high triplet population yields.

The signal detected in a typical single-molecule experiment consists of fluorescence photons emitted as a result of excitation of this molecule. Every spin-forbidden act of the intersystem crossing (ISC) from the excited singlet state S_1 to the lower energy triplet state T_1 makes this molecule dark during its residence time in the triplet state, thus reducing the total number of emitted photons. Therefore, molecules with a very low ISC yield ($\leqslant 10^{-5}$, which do not emit measurable phosphorescence) are favored in a typical single-molecule experiment [2].

Information about population and depopulation rates of the triplet state T_1 of a single molecule can be obtained either by analyzing the distributions of lengths of the bright and dark periods (called on- and off-times), that reflect the presence of molecule in its singlet and triplet state, respectively, or by recording the fluorescence intensity correlation function, which measures the temporal distribution of the probability of detecting the second photon after monitoring the first one [2–4]. Single molecule correlation experiments carried out at the temperature $\leqslant$1.8 K on pentacene [5], terrylene [6] and dibenzanthanthrene [7,8] showed two distinct exponential components. Such a result is consistent with the fact that two of the zero-field triplet spin sublevels, T_X and T_Y, of the above mentioned planar hydrocarbons usually have similar and short lifetimes (indistinguishable within the experimental noise), whereas the slowly decaying component is weak and assigned to the T_Z sublevel with the spin polarized perpendicular to the molecular plane. Later experiments, in which the population rates of the zero-field triplet sublevels were changed by using resonant microwaves, allowed separation of kinetic parameters and proved that the two short lifetimes are indeed similar [9]. The above mentioned result clearly indicated that the short- and the long-lived triplet spin sublevels of the investigated single molecules are isolated at ~1.8 K. When temperature increases the SLR between different spin sublevels of the lowest triplet state can be activated and at sufficiently high temperature this relaxation process becomes faster than the electronic decay into the ground state. Consequently, the fluorescence intensity correlation function decays mono-exponentially [10]. To our best knowledge, the SLR process has never been studied before at the single molecule level.

In this Letter we present the first experimental results on SLR between the zero-field spin sublevels of the excited triplet state T_1 of single molecules as a function of temperature. We studied single molecules of terrylene (Tr) embedded in a *p*-terphenyl (*p*T) crystal. The triplet state kinetics of this system has already been investigated at 1.8 K [6,9], at room temperature [11] and over the temperature range between 5 and 300 K [10].

2. Experimental

Single crystals of zone-refined *p*T slightly doped with Tr (purchased from Dr. W. Schmidt, Greifenberg, Germany) were obtained

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* Corresponding author. Fax: +48 22 843 09 26.
E-mail address: kozank@ifpan.edu.pl (B. Kozankiewicz).

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by cosublimation of both components under ~150 mbar argon (N5.0) atmosphere. The crystal ‘flakes’ were inserted into a low temperature optical cryostat in which the sample chamber was filled with helium gas at atmospheric pressure. Temperature of the sample was stabilized at between 5 and 40 K with temperature control of better than 0.2 K. The optical experiment was performed with the aid of a home-made confocal microscope. The excitation source was a Coherent 700 dye laser (operating with Rh6G) pumped by a Verdi18 Nd:YAG laser. The spot position on a sample was scanned by the system composed of a galvo scanner (Cambridge Tech. 6230) and telecentric arrangement of two lenses located outside the cryostat. The excitation beam was focused on the sample with the aid of a high aperture microscope objective (Bernhard Halle Nachfl. GmbH, Berlin, Germany) specially designed to operate over a broad temperature range (laser light spot diameter <500 nm). Fluorescence photons were separated from the scattered excitation light by a dichroic beam-splitter (Chroma Tech. Q585LP) and two band pass filters (Chroma Tech. HQ645/75 M and HQ625/60 M). Spatial filtering was guaranteed by a small pinhole (30 μm diameter). Fluorescence photons were detected with a photon counting module (Perkin Elmer SPCM-AQRH-14) and acquired with a multi-channel scaler card (LightScan) inserted into a PC.

3. Results and discussion

The fluorescence intensity correlation function at low temperatures (when the SLR does not operate) is given by the sum of two exponents with the decay rates λ_1, λ_2 and contrasts C_1, C_2:

$$g^{(2)}(\tau) = 1 + C_1 \cdot \exp(-\lambda_1 \cdot \tau) + C_2 \cdot \exp(-\lambda_2 \cdot \tau).$$

The experimentally accessible decay rates and contrasts are complicated functions of the population and depopulation rates of the triplet spin sublevel [7]. It was experimentally determined that the correlation decay rates are very sensitive to the depopulation rates of the triplet spin sublevels and have negligible dependence on the exciting light intensity, whereas the contrasts, which are mostly determined by the ISC yields, increase with the excitation light intensity and finally saturate [7]. In the present work we are mainly interested in the temperature evolution of the lifetimes of the triplet spin sublevels and thus, we concentrated on the correlation decay (depopulation) rates. Such approach allowed us to avoid prolonged acquisition of the intensity dependence on the correlation function at each of the studied temperatures.

By using the excitation wavelength of ~570.4 nm we excited single Tr molecules to the vibronic lines (attributed to the site X_2 in the *p*T crystal [12]) separated from the electronic origin by ~250 cm^{-1} [13]. At each of the studied temperatures we tried to keep the same excitation intensity, ~10 kW/cm^2 (or the same number of fluorescence photons, 10–15 kcps), which in our setup corresponds to about 1/2 of the saturation intensity [13].

A typical set of fluorescence intensity correlation functions collected for the same Tr molecule at 5 different temperatures is shown in Figure 1. At 5 K the correlation decay composes of two, well resolved components. The short-lived component, with the decay time 490 ± 10 μs and contrast ~0.1, is attributed to unresolved combination of the spin sublevels T_X and T_Y, whereas the long-lived component, decay time 3075 ± 50 μs and contrast ~0.05, to the spin sublevel T_Z. Such a result is in very good agreement with the kinetic parameters reported in Ref. [9] for the single Tr molecule in a *p*T crystal at 1.8 K. When temperature increased from 5 to 13 K we observed only a small change in the decay characteristics. At 15 K the correlation decay was still double-exponential. The short-lived components had the decay time of 335 ± 12 μs, contrast ~0.04, the long-lived component had the decay time 1920 ± 70 μs, contrast ~0.02. At temperatures above 15 K, within the narrow temperature range of up to 17.5 K, the correlation decay evolved to the mono-exponential dependence. For the considered molecule (Figure 1) the mono-exponential decay time becomes 335 ± 10 μs at 17.5 K, and 295 ± 12 μs at 20 K. Further increase of temperature, up to 30 K had practically no influence on the correlation decay time. We studied the correlation function as a function of temperature for 12 other single Tr molecules in a *p*T crystal and for all of them we observed similar decay rates and that the double-exponential decay dependence evolved to the mono-exponential within the narrow temperature range between 15 and 17.5 K. This allows us to concluded that within this temperature range the SLR couples the long-lived spin sublevel T_Z with one or both of its fast-lived spin sublevels T_X and T_Y. Very weak contrast of the long-lived decay component makes quantitative analysis of the SLR mechanism difficult.

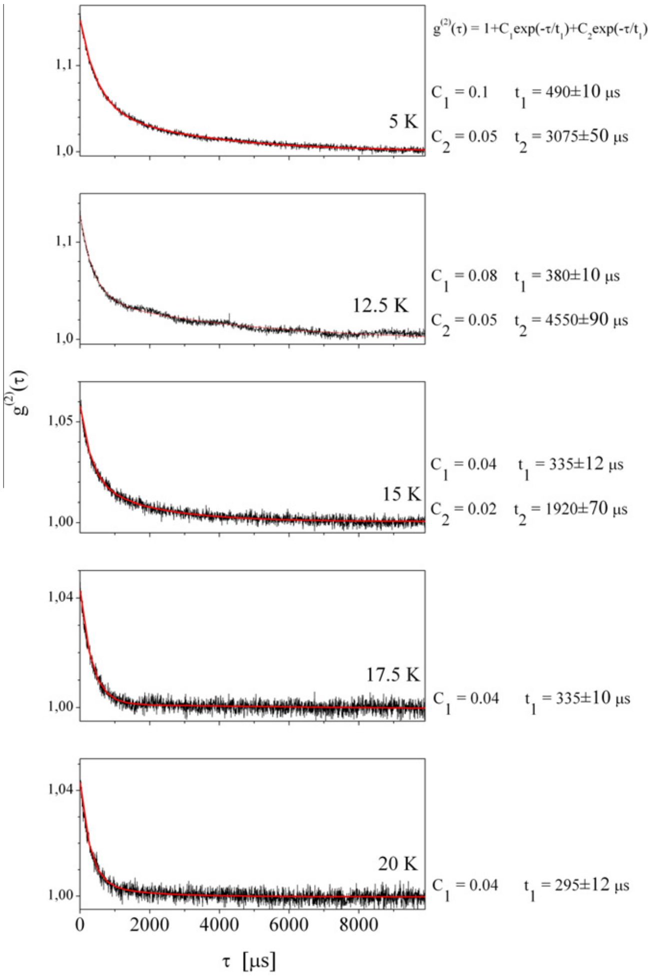

Figure 1. Fluorescence intensity correlation function of a typical Tr molecule in a *p*T crystal at five different temperatures. Decay parameters (contrasts and decay times) obtained from fits to the double- and mono-exponential dependences are given on the right side of the corresponding curve.

Besides those molecules, which showed the temperature behavior similar to that described above, we also found two other (‘anomalous’) single Tr molecules which behaved differently. Fluorescence intensity correlation functions of one of these molecules at the selected temperatures are presented in Figure 2. The decay parameters, obtained by fitting to the double- or mono-exponential dependence, are given on the right hand side of the corresponding correlation curve. At 5 K, the correlation function decays similarly