

FLUORESCENCE EXCITATION SPECTRA OF SINGLE IMPURITY MOLECULES OF TERRYLENE IN *n*-DECANE

Olavi OLLIKAINEN^a, Viktor PALM^a, and Karl REBANE^b

^a Institute of Physics, Riia 142, EE-2400 Tartu, Estonia; e-mail: viktor@fi.tartu.ee

^b Estonian Academy of Sciences, Riia 142, EE-2400 Tartu, Estonia; e-mail: rebane@fi.tartu.ee

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Abstract. High spectral resolution and good quality (signal-to-noise ratio up to 15) spectra of single impurity molecules are reported for terrylene in a new Shpol'skii matrix *n*-decane at 1.7 K. Main attention is paid to the differences in measured single molecule linewidths. They differ not only for different impurity molecules, but also for the same molecule in different measurements. Linewidths smaller than the natural linewidth known for terrylene in a bulk polyethylene sample are also reported.

Key words: single molecule spectroscopy, terrylene, Shpol'skii matrix, *n*-decane, linewidth.

1. INTRODUCTION

Single impurity molecule spectroscopy (SMS) is a novel promising field of laser spectroscopy of molecules embedded in solid matrices (see [1] and review articles [2–5], and references therein). The foundation stone of SMS (as well as of the high resolution spectral hole burning) is the purely electronic zero-phonon line (ZPL) – the optical analogue of the Mössbauer γ -resonance ZPL [6–8]. For quite a number of molecules at low temperatures (about 4 K and below) the peak absorption cross section of ZPL reaches 10^{-10} – 10^{-11} cm², i.e., exceeds the geometrical size of the molecule by a factor of up to 10^5 [9].

Until now SMS for about 20 host-guest systems has been performed and every new system in the SMS club is welcome. We report on high resolution spectra of a single impurity molecule for terrylene in a new Shpol'skii matrix [10–12] *n*-decane (Tr-C₁₀). Shpol'skii matrixes already successfully used in SMS experiments are *n*-hexadecane, *n*-dodecane, and *n*-nonane [13–17]. Single molecule

spectra of terrylene were studied in *n*-hexadecane [^{13,14}], lately they were also reported in *n*-dodecane [¹⁷]. In [¹⁸], *n*-decane is found to form an optimal *n*-alkane matrix for terrylene.

High quality single molecule spectra for Tr-C₁₀ have been recorded, for the best ZPLs the signal-to-noise ratio (SNR) is up to 15 (see Fig. 1). The main attention is paid to the differences in measured linewidths. They differ not only for molecules in different impurity sites, but also for the same molecule in different measurements (separated by time intervals of about 1000 s).

2. EXPERIMENTAL

An optical assembly for fluorescence excitation SMS experiments was designed to fit the chamber of our optical immersion helium cryostat. Main parts of the assembly are the small 12.7 mm focal length lens for focusing the excitation laser beam on the sample and the parabolic mirror for collection of the fluorescence. The design is in principle similar to that described in [¹⁹] with some minor differences. In more detail it will be described elsewhere.

The Tr-C₁₀ solution (concentration about 10⁻⁷ mol·l⁻¹ as calculated from the optical density [¹³]) was prepared by dissolving a very small amount of solid terrylene in liquid *n*-decane (Fluka) at room temperature. Terrylene was kindly provided by Prof. U. P. Wild, ETH Zürich. A small drop of the solution was placed between two 0.3 mm thick fused silica plates. It formed a thin film due to the capillary forces. In some cases a spacer ring was used to get a thicker sample. The thickness of the sample was estimated to be between 1 and 25 μm in our series of experiments. The plates with the Tr-C₁₀ solution were mounted into the optical assembly at the joint focus of the focusing lens and the collection paraboloid. In case of 1 μm thick sample, about 1000 terrylene molecules are expected to reside in the excited volume (estimated laser beam diameter in the focus is about 5 μm). The whole assembly was inserted into the cryostat, the sample was quenched to liquid helium temperature in about 3 min. The frozen solution mostly formed an invisible transparent film, probably a single crystal. All the experiments were performed in pumped superfluid helium at 1.7 K.

A single frequency ring laser CR-699-29 Autoscan with Rh6G dye was used as a source of excitation light with frequency jitter of about 1 MHz. The amplitude of the laser output was stabilized and controlled by an electrooptical modulator CA307 (Coherent) in the range of sample illumination (P) 0.1–4 W/cm². Linearly polarized light with controllable orientation of the E-vector (prismatic polarization rotator SP-310-21 used) was applied for the excitation. Only one laser frequency scan was used when recording every single fluorescence excitation spectrum to avoid broadening of spectral features due to the limited accuracy in the positioning of the absolute laser frequency by the laser spectrometer before starting every successive scan. The accuracy of the

frequency scale during a single scan was provided by the CR-699-29 Autoscan construction and was defined by the long-term drift of the laser frequency (about 100 MHz per hour). Signals of the two laser wavemeter etalons were simultaneously monitored to reveal possible laser mode-hops during the scans.

An optical setup applied for the collection and registration of the fluorescence signal was very similar to that described in [20]. A red-pass filter used was a combination of two dielectric coating filters and an absorption filter OS-14 in between. Sandwich design allowed us to minimize the fluorescence of the filter; transmission was over 15% for λ over 605 nm.

3. RESULTS

Low resolution fluorescence excitation spectra were measured for thick Tr-C₁₀ samples; these spectra revealed the site structure similar to that reported in [18]. Two stronger Shpol'skii sites, B site, centred at 17 361 cm⁻¹ ($\lambda \approx 576$ nm), and A site with the maximum at 17 602 cm⁻¹ ($\lambda \approx 568$ nm), as well as a weak C site at 17 409 cm⁻¹ ($\lambda \approx 574.4$ nm), were observed. Site B has a symmetric band shape with full width at half maximum (FWHM) about 14 cm⁻¹. Band at 568 nm is broader (FWHM ≈ 25 cm⁻¹) and has a strong asymmetry, apparently due to the spectral overlap of the A site with the 245 cm⁻¹ terrylene vibration band corresponding to the B site [18]. Site C is very weak and could only be observed for a ~ 25 μ m thick sample (FWHM about 14 cm⁻¹). Even in spectra with the resolution of only 1 GHz considerable statistical fine structure was observed.

Fluorescence excitation spectra with the resolution of 10 MHz were recorded for different wavelengths, common excitation intensity (P) was about 1 W/cm². Narrow lines are present in the spectra, they are mostly concentrated at wavelengths in the proximity of A and B Shpol'skii sites, but can be found everywhere in the spectral interval between 566 and 578 nm. A broad distribution of linewidths is observed, with the most common values between 40 and 50 MHz FWHM, in a good agreement with the lifetime-limited linewidth of 42 MHz determined for a bulk sample of terrylene-doped polyethylene [13]. We attribute the narrow lines observed to ZPLs of single terrylene molecules. An excitation spectrum with good SNR of single molecule lines, recorded for a thin Tr-C₁₀ sample near the centre of the B site, is shown in Fig. 1.

To determine single molecule homogeneous linewidths (Γ_h) more precisely, fluorescence excitation spectra with the resolution of 1 or 2 MHz were recorded. In repeated scans over the same spectral region, spectral jumps of single molecule lines were often observed; the behaviour seems to be similar to that reported for terrylene in *n*-hexadecane [13]. Stable lines were selected to enable recording of their contours during several laser scans. We report here on the results of monitoring a single molecule line with a rather stable spectral position during about 2.5 h.

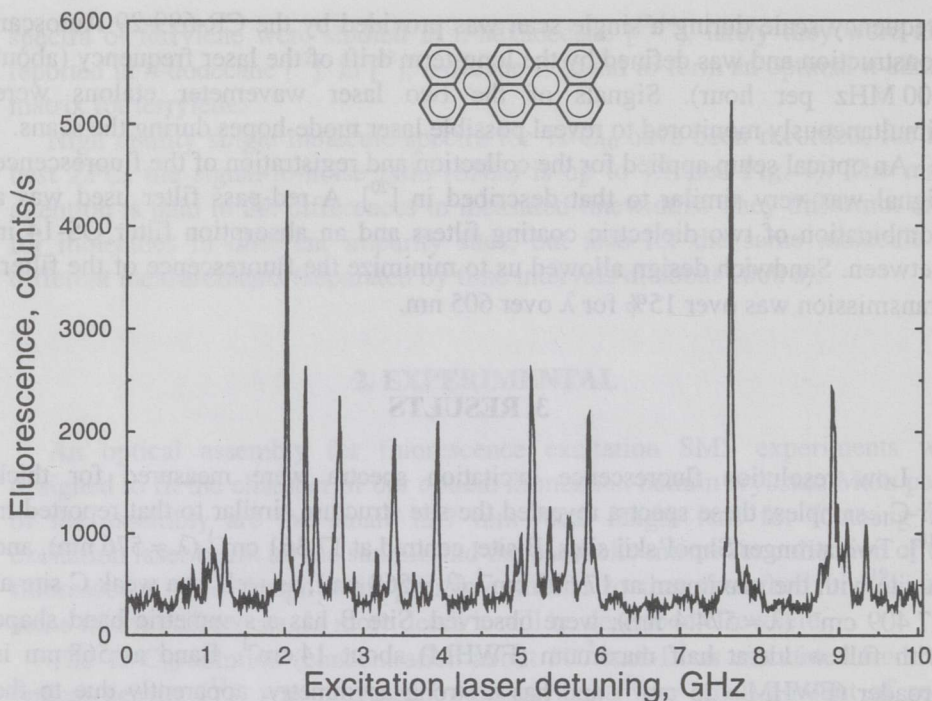


Fig. 1. The fluorescence excitation spectrum of terrylene (molecular structure presented in the insert) in *n*-decane at 1.7 K. Sample was about 3 μm thick, excitation intensity 0.1 W/cm^2 . Zero laser detuning corresponds to $\lambda = 576.0 \text{ nm}$ ($\nu = 17\,361.11 \text{ cm}^{-1}$). Laser scanning rate 10 MHz/s; signal collection 1 s per point. Spectral resolution is 10 MHz. Sharp peaks correspond to ZPLs of the $S_1 \leftarrow S_0$ transition of individual terrylene molecules.

Measurements were performed near the centre of the B site where we expected to find more stable single molecule lines. Only about 10 clear peaks were observed in a 10 GHz scan – we estimate the thickness of our sample to be between 1 and 3 μm . Sixteen spectra were recorded with time intervals of about 10 min between the scans. Intensity and polarization of the exciting light were changed from scan to scan to optimize these parameters for the selected terrylene molecule. Spectra No. 11 and 12 are presented in Fig. 2. The spectra were fitted with the Lorentzian curve superimposed on a constant background; in further discussion we will mean the respective parameters of this curve when talking about amplitude, linewidth (FWHM), or central frequency of the spectral line.

We found that the amplitude of the line changes nearly linearly with P in the range between 0.1 and 1 W/cm^2 with noticeable saturation at higher P . Still, we found that the linewidth Γ_h changes between 24 and 42 MHz in the same range of P without any remarkable correlation with the actual P value. In fact, Γ_h is in several cases considerably smaller than the lifetime-limited linewidth of 42 MHz as determined for

a bulk sample of terrylene-doped polyethylene [13]. Figure 2 shows an example of two spectra recorded for the same P and yielding remarkably different Γ_h .

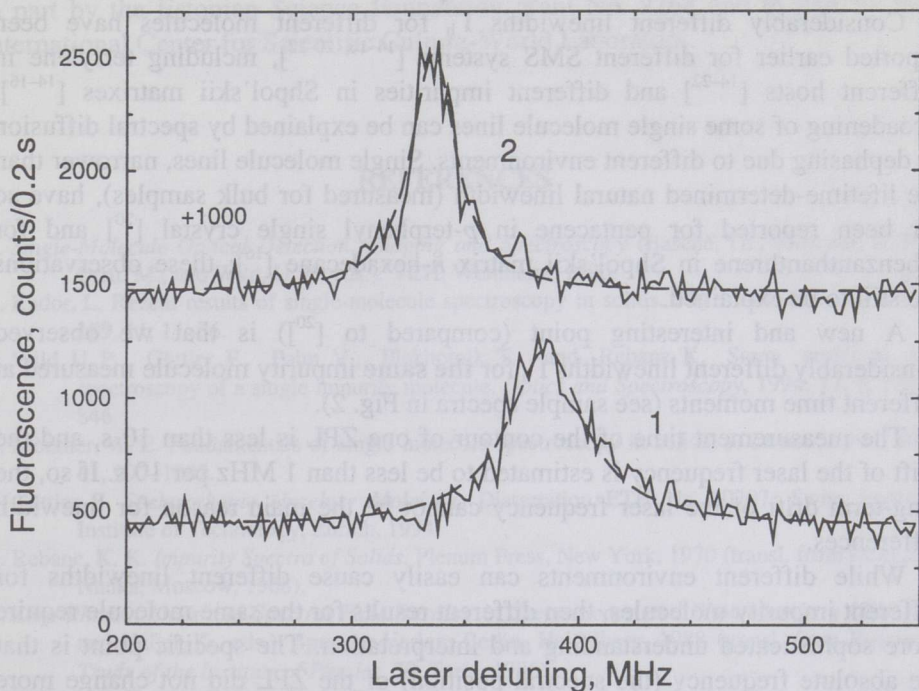


Fig. 2. Fluorescence excitation spectra for a thin ($\sim 1 \mu\text{m}$) sample of Tr-C₁₀ at 1.7 K. Solid lines represent two successive scans of the same spectral interval with a delay of about 10 min; spectral resolution is 2 MHz. Zero laser detuning corresponds to $17\,361.34 \text{ cm}^{-1}$ ($\lambda \approx 575.992 \text{ nm}$). Excitation intensity was 1 W/cm^2 ; laser scanning rate 10 MHz/s; signal collection 0.2 s per point. The spectrum of scan 2 is shifted in vertical direction for 1000 units. A single zero-phonon line (ZPL) of a stable terrylene molecule is present in both scans. Dashed lines represent the Lorentzian least-squares fits for both spectra with FWHM of 40 and 24 MHz for scans 1 and 2, respectively. Shift of the central frequency of the spectral line is 50 MHz and does not exceed the specified maximum error (60 MHz) of the laser spectrometer in fixing the preset absolute laser frequency before starting a scan. ZPL in scan 2 has a larger amplitude due to a change in the polarization of the excitation: E-vector of the linearly polarized laser light was turned for 45° to optimize the excitation conditions for the molecule under study.

4. DISCUSSION

The fluorescence excitation spectrum (Fig. 1) looks like a typical SMS one. Quite a good SNR is achieved – 15:1 for the most intense peak. Great differences in the peak and integrated intensities of the ZPLs of different molecules are to be understood as the result of different excitation intensities at

different sites of the spot illuminated by the laser and also by different angles between the electric vector of the exciting light and the dipole moment of the transition. We will further discuss the appearance of different single molecule linewidths in our fluorescence excitation spectra.

Considerably different linewidths Γ_h for different molecules have been reported earlier for different SMS systems [^{14-16, 20-22}], including terrylene in different hosts [¹⁴⁻²²] and different impurities in Shpol'skii matrixes [¹⁴⁻¹⁶]. Broadening of some single molecule lines can be explained by spectral diffusion or dephasing due to different environments. Single molecule lines, narrower than the lifetime-determined natural linewidth (measured for bulk samples), have so far been reported for pentacene in *p*-terphenyl single crystal [²⁰] and for dibenzanthanthrene in Shpol'skii matrix *n*-hexadecane [¹⁶]; these observations are still to be explained.

A new and interesting point (compared to [²⁰]) is that we observed considerably different linewidths Γ_h for **the same** impurity molecule measured at different time moments (see sample spectra in Fig. 2).

The measurement time of the contour of one ZPL is less than 10 s, and the drift of the laser frequency is estimated to be less than 1 MHz per 10 s. If so, the long-term drift of the laser frequency cannot be the main reason for linewidth differences.

While different environments can easily cause different linewidths for different impurity molecules, then different results for the same molecule require more sophisticated understanding and interpretation. The specific point is that the absolute frequency (the spectral position) of the ZPL did not change more than 60 MHz (the precision of our laser wavemeter) in the course of measurements. (Recall that the transition frequency of ZPL is usually much more sensitive than Γ_h – this is in fact the source of inhomogeneous broadening.)

One possible way to understand the situation is to take the structure of the electromagnetic field at the site of the impurity into account. Because of the matrix, the density of electromagnetic modes differs from that for the free electromagnetic field. For an optically inhomogeneous solid the differences can be drastic, especially if the inhomogeneities are of the size of the wavelength. To some extent this is the case for quite a number of SMS systems, including the Shpol'skii systems.

Changes in the matrix far away from the molecule during the time between measurements (e.g., caused by a two-level system) can easily shift the transition frequency of the molecule for some tens of MHz. We cannot measure such small shifts reliably due to limited precision of the laser wavemeter. But these shifts can still be large enough to change the number of electromagnetic modes in resonance with the frequency of the electronic transition and, consequently (if the density is far from being constant), the spontaneous emission lifetime and its contribution to Γ_h . The latter can both increase or decrease. More detailed discussion of linewidth will be published elsewhere.

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TERRÜLEENI ÜHE LISANDIMOLEKULI FLUORESTSENTSI ERGASTUSSPEKTRID *n*-DEKAANIS

Olavi OLLIKAINEN, Viktor PALM ja Karl REBANE

Terrüleeni ühe lisandimolekuli kõrge lahutusega spektrid on registreeritud Špolski maatriksis (*n*-dekaanis) temperatuuril 1,7 K. Parimate joonte puhul on signaali ja müra suhe kuni 15:1. Põhitähelepanu all on lisandi foononvabade joonte laiuse erinevus. Lisandimolekuli joone laius ei tule erinev mitte üksnes erinevate molekulide korral, vaid ka ühesama molekuli korduval mõõtmisel. On leitud joonelaiusi, mis on väiksemad terrüleeni lisanditehulga ergastatud elua mõõtmistel määratutest.