Terrylene-doped biphenyl monocrystals for optical single-molecule spectroscopy

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ABSTRACT

Biphenyl forms at normal pressure and temperatures below 40 K incommensurate crystalline structures with physical properties varying in space on a scale of nanometers. As biphenyl crystals are optically transparent, there is a possibility to study these natural nanostructures optically, by doping the host crystal with nanoscopic probes with optical properties depending on their local environment. It has already been demonstrated that terrylene impurity molecules in polycrystalline biphenyl sample can successfully play the role of such kind of sensitive nanoprobe when studied by the methods of high-resolution laser spectroscopy. We report growing of thin biphenyl monocrystals doped with terrylene molecules at very low concentrations. These sublimation-grown flakes can be studied at liquid helium temperatures using the technique of single-molecule spectroscopy. Compared to polycrystalline biphenyl samples, much higher signals and better signal-to-noise ratio can be achieved in single-molecule spectra. This allows to perform much faster spectral scans to find intensive single-molecule lines even in very dilute samples in spite of a very broad inhomogeneous absorption band of terrylene in biphenyl. Fast scanning also allows observation of single-molecule lines with much better temporal resolution, revealing processes of spectral diffusion occurring at different time scales. This can be helpful in our attempts to learn about the role of the matrix incommensurability in spectral features observed. Extremely high variability of temporal and spectral behaviour of terrylene single-molecule lines is reported, which is unusual for crystalline hosts.

Keywords: biphenyl monocrystal, incommensurability, single molecule spectroscopy, sublimation, terrylene, spectral diffusion.

1. INTRODUCTION

Biphenyl molecule (C12H10) consists of two phenyl rings, connected to each other with a flexible single carbon bond. At normal pressure biphenyl crystals can exist in two different incommensurate phases, one in temperature interval between 17 K and 40 K (IC II) and another at temperatures below 17 K (IC III). In these phases the torsion angle between the two phenyl rings of a biphenyl molecule varies in space and is modulated with a period incommensurable with that of the crystalline lattice, causing the lack of translation symmetry. These variations can be studied spectroscopically by doping biphenyl with impurity molecules with spectral behaviour depending on their local environment.

Terrylene (C30H16) is a polycyclic aromatic hydrocarbon molecule that, due to its favorable spectroscopic properties, became very popular as an impurity used with several types of host materials for single-molecule spectroscopy (SMS). Terrylene molecules have already been used to dope polycrystalline biphenyl samples and studied by high-resolution techniques of non-photochemical spectral hole burning and SMS, demonstrating remarkable sensitivity to their local environment: a very large variety of probabilities of photoinduced spectral transitions for light-sensitive molecules as well as broad distribution of single-molecule (SM) linewidths for stable ones has been observed. Still there were certain concerns that many of the terrylene impurity molecules could be located near the structural defects of polycrystalline biphenyl matrix like borders of the microcrystals and that for these molecules there could be stronger disturbing factors than the incommensurate modulation of biphenyl crystals. It has also been shown in a relevant publication that in the
case of perylene impurity the quality of SM spectra strongly depends on the structure and quality of biphenyl host crystals. Mentioned factors influenced us to attempt the preparation of monocrystalline terrylene-doped biphenyl samples and the performing of SMS measurements with an intention to compare the results with those obtained earlier for polycrystalline samples.

In section 2 of this paper the preparation of terrylene-doped biphenyl single crystals using the sublimation technique is described. Some of the SMS experiments performed on these samples together with brief discussion and preliminary interpretation of the results are presented in subsequent sections. It appears that extremely low impurity concentration of our crystals and dramatically improved signal-to-noise ratio of SM spectra allows us to obtain qualitatively new information on temporal and spectral behaviour of terrylene SM lines, which are the clue to understanding the dynamics of biphenyl matrix.

2. EXPERIMENTAL

The procedure of growing biphenyl single crystals doped with terrylene molecules is similar to that described for naphthalene crystals in ref. 6. Biphenyl has been previously purified by sublimation at the same conditions as described below. 0.5 g of biphenyl and some tiny specks of terrylene were melted together yielding a purple melt that was used as the starting material for sublimation. The melt was placed into a glass tube, which was sealed with a cold finger and for half an hour flushed with dry argon gas (dried over ascarite). After that the glass tube was immersed into an oil bath heated to 170°C, so that the cold finger was about 1 cm above the level of the oil surface. During the sublimation the tube was constantly flushed with dry argon gas and the cold finger cooled with running water at 20°C; the bath temperature was kept at 170-180°C. After 60 minutes the heating was switched off and the system was allowed to cool down.

During the process of sublimation, smaller biphenyl single crystal platelets (mostly with surface smaller than 4 mm²) were quickly formed at the lower part of the cold finger; larger platelets with surface over 5 mm² were slowly grown at the upper part. Crystal flakes were carefully collected from the finger, separately the lower and the upper fractions. According to our estimation, the thickness of sublimation-grown single crystal flakes varies between 1 and 5 microns, which makes them ideal samples for SMS. In spite of higher average quality of the upper-fraction sublimation flakes, we avoided using them as SMS samples due to their lower terrylene concentration. Thin biphenyl monocrystals can be stored for several weeks in a hermetically sealed flask.

To prepare an SMS sample the selected flake of terrylene-doped biphenyl was placed between two thin fused silica plates, which were then installed into a home-built optical cell for SMS, placed in an optical immersion helium cryostat. The experimental setup is in detail described elsewhere. All the measurements referred in this paper were performed at T = 1.8 K.

A single-frequency ring laser CR-699-29 Autoscan with rhodamine-6G dye (jitter-determined linewidth about 2 MHz) was used for selective excitation of the samples; scan rates of up to 2 GHz/s were applied in our fast scans. Up to 7 cm⁻¹ automatic laser frequency scans were stacked up to look for SM lines across the inhomogeneously broadened absorption band of the impurity.

3. RESULTS

Due to the very different molecular weights, the co-sublimation of biphenyl and terrylene yields biphenyl single crystals doped with terrylene impurity molecules at extremely low concentrations. Therefore we were not able to perform any spectral hole burning experiments on these crystals for comparison with the earlier hole-burning results on polycrystalline samples with higher terrylene concentration. Our first impression was that the concentration is too low even for SMS experiments, because (also due to the large inhomogeneous broadening, see Fig. 1) finding any terrylene SM line by our standard SMS procedure (scan rates of 20 MHz/s) appeared to be a difficult and time-consuming task. But soon we realized that intensity of these lines is at least an order of magnitude higher in biphenyl single crystals than it was earlier observed for polycrystalline samples (see Fig. 2). This allowed us to perform much faster excitation laser frequency scans in broader spectral intervals to find the few intensive SM lines even in very dilute crystals. In Fig. 1 the result of laser scanning over virtually the entire inhomogeneously broadened 0-0 absorption band of terrylene in biphenyl is shown for a fixed spot on one of our sample crystals where about 50 intensive SM lines could be observed. Assuming that the excitation volume was about 100 μm³, one can estimate the terrylene concentration in this sample as
Part of our sublimation-grown crystals seem to have even significantly lower concentrations of terrylene molecules. Of course, a single scan over the contour of an SM line does not necessarily give us reliable information about the stability of this line. However, asymmetry of many lines registered during such a scan presents evidence that significant amount of these lines are unstable even on a timescale of tens of ms. But more valuable information can be obtained by performing repeatable fast scans over a spectral region where SM line was detected. In this way we are able to get much deeper insight into the temporal and spectral behaviour of terrylene SM-s than it was possible with polycrystalline biphenyl samples.

Fig. 1. Spectral positions and intensities of about 50 terrylene SM lines observed at T=1.8 K for a fixed spot on a biphenyl single crystal as a result of 301 sequential laser scans of 1 cm² (scan rate 2 GHz/s) in spectral interval from 580 nm to 570 nm. Starting at 574.7 nm the spot position could be slightly different. Only lines with intensity higher than 2000 counts/s were registered. Solid line designates the broadband excitation spectrum of terrylene impurity obtained at T=1.8 K for polycrystalline sample4. Molecular structures of terrylene and biphenyl are shown in the inset. Arrows designate spectral positions where the following spectra have been recorded: a) - Fig. 2a and Fig. 4; b) - Fig. 3a; c) - Fig. 3b; d) - Fig. 5 and Fig. 6; e) - Fig. 7.

Fig. 2. Comparison of intensities of the most intensive terrylene SM lines registered in monocrystalline (a) and polycrystalline (b) biphenyl matrices. In both cases a very stable doublet structure has been observed, which can be very well fitted with a sum of two Lorentzians with virtually equal halfwidths (FWHM) δ. a) - λ ~ 576 nm, δ ~ 78 MHz (see also Fig. 4); b) - λ ~ 578 nm, δ ~ 185 MHz².
Consistently with earlier results on polycrystalline biphenyl, we can observe terrylene SM lines with variety of different individual patterns of dynamical behaviour. Below we will make an attempt to classify these patterns, starting with the most stable molecules observed.

1. Molecules that we call **stable** because their SM line contour can be repeatedly measured on timescales from tens of ms to hours and retains its spectral position with precision of at least tens of MHz (absolute precision of the wavemeter of our Autoscan laser is limited to 60 MHz, but within a single scan the spectral precision is limited only by slow drift of the laser frequency, which normally does not exceed 100 MHz per hour). These molecules yield stable contour with nearly perfect Lorentzian shape, thus the linewidth can be determined to a high precision. The narrowest lines we observed had a linewidth (FWHM) of about 70 MHz (which is still nearly twice as much as the known value of the lifetime-limited width for terrylene^4), and this seems to be the lower limit in biphenyl, at least at T=1.8 K. Stable SM linewidths of up to 600 MHz have been observed, but this value does not seem to be the upper limit. In Fig. 3 examples of two stable SM lines with linewidths of 82 and 420 MHz are shown. Even in spite of their short-term stability, virtually all the SM lines we observed in monocrystalline biphenyl performed single spectral jumps on a timescale of some minutes or hours, probably leaving to some distant spectral positions. Still, the stable lines returned shortly to their stable positions, although irreversible “burn-outs” after some hours of observation were not uncommon either.

2. Molecules that we call **stable doublets** because of the shape of their SM line. Such a molecule has as stable SM line as other stable molecules, but the line shape cannot be described as a single Lorentzian (see Fig. 2,a). It can instead be very well fitted with a sum of two Lorentzians with virtually equal widths (see Fig. 4,a). Of course, the first obvious assumption is that we have actually two terrylene molecules with their SM lines positioned nearby. Such a coincidence seems very improbable, especially in our single crystals where distances between nearby SM lines are measured in tens of cm, and especially taking into account the equal width of the two spectral components. But to virtually completely rule out such a possibility, we collected spectra of our stable doublet, where a larger spectral jump occurs during the laser scan through the region, where the line contour has significant contributions from the both Lorentzian components. Example of such spectrum is shown in Fig. 4,b. It appears that in all cases contributions of the both components vanish simultaneously, within a 100 ms time bin. Our conclusion is that the both spectral components represent the same SM line, which changes its spectral position on a time scale significantly shorter than 5 ms, jumping between two nearby positions. Intensity ratio of the two spectral components refers to the probability of finding the molecule in one of the two states correspondingly. Similar structure was also observed in polycrystalline biphenyl sample^4 (see Fig. 2,b), where the two spectral components were significantly broader. But in that case, in spite of a strong feeling that both components represent the same SM line, it turned out to be impossible to correctly prove this assumption because of higher terrylene concentration and larger distance between the components. It should also be mentioned that in both cases the stronger component of the doublet is among the most intensive SM lines observed for the given type of host matrix, exceeding in intensity many of the “stable singlet” SM lines.
3. SM lines of multistate molecules are jumping between several well-defined nearby spectral positions on a timescale of seconds or minutes, resembling very much similar phenomena described e.g. for terylene in a Shpol’skii matrix hexadecane\(^8\). This behaviour is quite usual for crystalline hosts and we did not pay to such kind of SM lines much attention.

4. Spectrally confined unstable molecules have SM lines which are seemingly chaotically jumping around within a kind of “spectral envelope” as shown in Fig. 5. To analyze the character of these spectral jumps the laser frequency can be fixed in different spectral positions inside the envelope and fluorescence signal monitored, as shown in Fig. 6.
5. **Wandering** molecules have SM lines that behave similarly to that of spectrally confined unstable molecules, but the span of their chaotic spectral jumping is much larger and in some cases it is probably larger than can be reliably determined due to the limits of the laser scanning technique or due to possible presence of other wandering molecules within the inhomogeneously broadened band of terylene. Spectral signature of such kind of molecule can be recognized by presence of intensive sharp peaks in spectra obtained by fast laser scanning over the inhomogeneous band in search for SM lines. These peaks are completely irreproducible and never appear in the same spectral position again, but it is possible to approximately localize the frequency region in which certain “wandering” SM line is jumping, by monitoring the frequency of appearance of the mentioned peaks in different spectral regions. A short fragment of spectral signature of a “wandering” molecule, for which the jumping span of at least 17 cm\(^{-1}\) has been estimated, is presented in Fig. 7.

![Fig. 6. A short fragment of the time dependence of the fluorescence signal, monitored with time resolution of 5.1 ms under fixed-frequency laser excitation, corresponding to 1.2 GHz on the “spectral envelope” in Fig. 5 (λ ~ 578.89 nm). Statistical analysis of the spectral jumps of corresponding SM line lies outside the scope of this paper and will be presented elsewhere.](image6.png)

![Fig. 7. An example of spectral signature of a “wandering” molecule, for which the jumping span of at least 17 cm\(^{-1}\) has been estimated, in a fragment of a long fast scan. The spectrum is in principal similar to what is seen in Fig. 5, but the “spectral envelope” is much broader and much longer signal accumulation would be needed to obtain its spectral shape. In fast scans made with scan rate of 2 GHz/s and time bin of 10 ms, the spectral width of the peaks representing the “wandering” SM line is about 100 MHz, in which contributions of both spectral and temporal behaviour of the line are present; peaks usually have random asymmetrical shape.](image7.png)
4. DISCUSSION

Our new results confirm earlier observations of a broad distribution of terrylene SM linewidths in polycrystalline biphenyl. While such a large variance of SM linewidth is characteristic for glassy solids, it is quite uncommon for crystals. It is reasonable to assume that the overwhelming contribution to the observed linewidths comes from processes of fast spectral diffusion ("dynamical inhomogeneity"), originating from specific for incommensurate systems dynamics (thermal depinning-repinning of the spatial modulation wave). Experiments with single crystals give further support to such view, reducing probability that the observed spectral "jumping" is characteristic of probe molecules located in some non-regular less stable regions of matrix (close to grain boundaries, e.g.). Still there is a large difference between the inhomogeneous (static) spectral span of probes (hundreds of wavenumbers) and the extent of spectral diffusion (observed up to several tens of wavenumbers), showing different origin of these processes. Fig. 5 demonstrates that quite a large number of different spectral positions can be visited in the course of spectral diffusion. This rules out the possibility that the phenomenon is of local origin (e.g., introduced by doping local instability) as far as it is impossible to accommodate locally the needed degrees of freedom. On the other hand, of course, the observed large variety of SM spectral-temporal patterns shows a non-ergodic dynamical behaviour of the system – no complete averaging occurs.

5. CONCLUSION

Further experiments and statistical analyses of the lineshape statistics could yield interesting comparison with the SM data for glasses. Extension of SMS experiments into high-pressure domain to study the pressure-induced phase transition from incommensurate to commensurate phase at 180 MPa is another goal of these studies. This could shed light on the broadening of probe spectra and governing it by host dynamics in an interesting region of physical conditions, where formation of a spatial nanometer-scale structure (incommensurate modulation) occurs at very low temperatures.

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