

Aperture scanning near-field optical microscopy and spectroscopy of single terrylene molecules at 1.8 K

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Abstract

Single-molecule imaging and spectroscopy using an aperture scanning near-field optical microscope operating at 1.8 K in a helium bath cryostat is demonstrated. From near-field images at constant excitation frequency, the orientation of single molecules can be deduced. Spectral information is obtained using both near-field and confocal excitation schemes by scanning the excitation frequency at a fixed sample position. Differences between near-field and confocal spectra are discussed in terms of the position with respect to the aperture and the molecular orientation.

1. Introduction

Aperture scanning near-field optical microscopy was proposed in 1928 [1] to overcome the classical diffraction limit as formulated by Abbe in 1873 [2]. Its first experimental realization was achieved in 1984 by Pohl and co-workers [3]. Aperture scanning near-field optical microscopy of single molecules has proven to be a powerful technique, as it can show not only the position but also the three-dimensional orientation of the transition dipole moments of single molecules [4, 5], while the resolution is determined by the size of the aperture [6]. So far, much work has been performed at room temperature [7, 8] and at temperatures down to 5 K. For the latter case, research has focused mainly on quantum wires [9–11] and quantum dots [12, 13].

For single-molecule spectroscopy, the interesting temperature range is even lower than 5 K, as the line width of the zero-phonon lines gets close to the lifetime-limited value only at temperatures below 2 K [14]. So far at these temperatures, quantum wire [15] and single-molecule near-field optical spectroscopy have been demonstrated [16]. However, no direct comparison of near-field and confocal spectra was shown and no single-molecule near-field imaging was possible.

In this study, we show scanning near-field optical microscopy of single molecules and a direct comparison between near-field and confocal single-molecule fluorescence excitation spectra at 1.8 K in a helium bath cryostat.

2. Experimental details

The experiment was performed using the single-molecule model system terrylene in *p*-terphenyl [17]. Crystalline samples of *p*-terphenyl doped with a small amount of terrylene were prepared in a co-sublimation process [18]. A mixture of *p*-terphenyl and a small amount of terrylene was melted at about 220 °C under nitrogen atmosphere, to get a homogeneous base crystal. After pulverization of the doped base crystal, slow sublimation was started under a low pressure nitrogen atmosphere at a temperature of about 180 °C. During the sublimation, crystals were growing on a ‘cold finger’ which was kept at a temperature of 110 °C by a circulating liquid. The co-sublimation was terminated when the doped crystal flakes reached lateral sizes up to several millimetres and thicknesses of about 10 μm. The crystal flakes were carefully picked from the cold finger and transferred to clean glass cover-slips. Only crystal flakes that adhered to the glass cover-slips by van der Waals forces were used in the experiments.

Measurements were performed on the zero-phonon lines of the lowest singlet–singlet transition of single molecules in the red wing of the O₂ site of terrylene in *p*-terphenyl [18] at about 578 nm. Molecules in this site were found to be stable, well-suited for single-molecule spectroscopy and to be oriented almost perpendicular to the glass surface [18, 19].

The experimental set-up consisted of a home-built confocal microscope with a scanning near-field optical

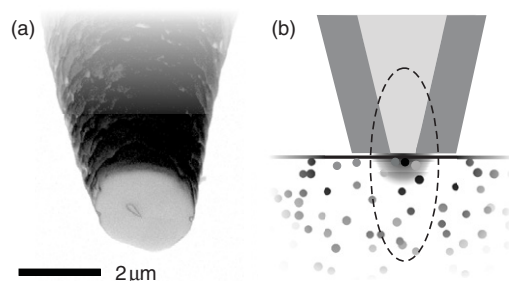


Figure 1. (a) SEM image of the tip that was used for the experiment. (b) The illuminated areas in confocal (dashed line) and near-field excitation. After careful alignment, the volume that is excited in the near-field configuration is a fraction of the volume excited in the confocal configuration.

microscope on top of it, designed for operation under both ambient conditions and down to 1.8 K in a helium bath cryostat. Details have been described elsewhere [20]. Briefly, the excitation light was provided by a single-mode ring-dye laser (Coherent 699-21, Rhodamine 6G) pumped by an argon-ion laser. After power stabilization (CRI LS100), light could either be directed into the confocal set-up or into an optical fibre with an aperture tip at its far end for near-field excitation. Switching between both light paths was possible using a flipable mirror. For light detection the same path was used for both near-field and confocal excitation. For alignment purposes, light could be directed to a CCD camera. A holographic notch filter was used to block the reflected and scattered laser light. The Stokes-shifted fluorescence from single molecules was transmitted by the notch filter and detected by a single-photon counting avalanche photodiode (SPAD) (SPCM-AQR13).

Aperture tips were fabricated by tube etching of single-mode optical fibres (3M, FS-SN-3224) for about 2 h at room temperature [21]. After that, a layer of about 500 nm aluminium was thermally evaporated onto the tips. The resulting tips were fully coated and no light emission could be detected from the tips when light was coupled into the far end. Apertures were produced by cutting thin slices from the end face with a focused ion beam (at EMPA Dübendorf, Switzerland). The tip used for this experiment had an elliptical aperture with dimensions of about 300 nm in the long and 100 nm in the short direction (figure 1(a)).

For rectangular slit-like apertures, the transmitted light was found to be mainly polarized along the short direction of the aperture [22], in agreement with theoretical predictions [23]. From this finding, we suppose that the light coming through the tip is strongly elliptically polarized with a main component along the short axis of the aperture. The field distribution at the aperture is expected to show strong field components along the fibre axis perpendicular to the sample surface at the rims on both sides of the aperture and field components parallel to the sample in the centre of the aperture. Molecules with transition dipole moments perpendicular to the sample surface are therefore expected to be imaged as two lobes situated beneath the rims of the aperture [4].

A critical part for the comparison of confocal and near-field images/spectra is the overlap of the volumes under study (figure 1(b)). For the confocal studies, light was focused on the upper side of the *p*-terphenyl crystal, which is the surface that is also accessible to the near-field probe. First, by confocal scanning, an area on the crystal was searched in which a number of molecules could be seen in excitation-frequency scans as well as in sample scan images at constant frequency. After that, the objective was moved 3 μm up such that the focus was positioned above the sample by the same amount. The excitation light was then sent into the fibre for near-field excitation, and with the help of the light coming through the aperture, the tip was positioned above the confocal excitation spot using the CCD camera. Finally, the tip was approached to the sample using a slip-stick drive, until the tip appeared to be in focus by minimizing the emission spot on the CCD ($\approx 3 \mu\text{m}$ above the sample surface). At this point, the objective was moved back such that the crystal surface was in focus again. For the remaining part of the tip approach, fluorescence excitation spectra were taken in order to make use of the change in the fluorescence background [16] as a measure for the tip-sample distance. At small gap-widths, when single-molecule peaks already appeared in the spectra, a tuning fork detected shear-force signal was monitored and the gap width was adjusted to a value just before shear-force contact occurred.

3. Results and discussion

Figure 2 shows an example of a 20 μm sample scan under near-field excitation at constant frequency. Signals from single molecules appear either as a single spot or as a closely spaced two-lobe pattern, often with unequal intensities of the lobes. Similar patterns have been observed in single-molecule scanning near-field optical microscopy at room temperature [4, 5] and were attributed to the orientation of the transition dipole moments of single molecules. As the terylene molecules in the O_2 site of a *p*-terphenyl crystal are expected to be oriented almost perpendicular to the substrate [18, 19], mainly two-lobe patterns with nearly equal intensities in the lobes are expected. Even for larger distances between the tip and the molecule, these two-lobe patterns are conserved [4]. This is indeed the pattern found for most molecules in the image. However, also single spots, indicating a parallel orientation, and two-lobe patterns with clearly unequal intensities, indicating an intermediate orientation, are found. The finding of the distinct patterns is already proof for the fact that a well-defined absorption dipole moment is involved. A second check is that, on changing the excitation frequency in steps of 20 MHz, the patterns change in intensity, as the molecules go in or out of resonance, but the relative intensities in the lobes of each pattern stay the same. This clearly indicates that single molecules with narrow zero-phonon lines are observed. The patterns that indicate an orientation of single molecules different from (almost) perpendicular to the substrate are attributed to molecules sitting at imperfections in the crystal.

Figure 3 shows two examples of typical 20 GHz fluorescence excitation spectra in both confocal and near-field excitation. Zero detuning was at about 578 nm and all spectra

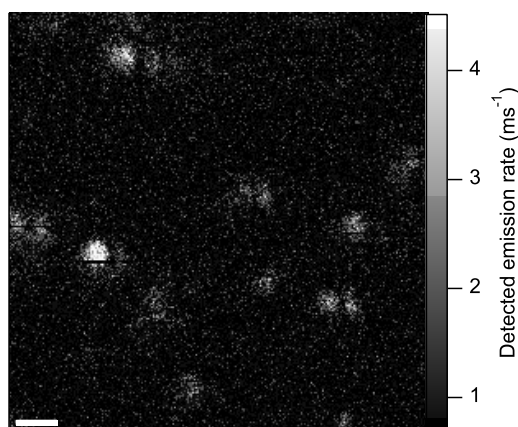


Figure 2. Scanning near-field optical microscopy of single terrylene molecules at 1.8 K. The symmetric two-lobe patterns of most spots point towards a transition dipole moment orientation perpendicular to the sample plane. However, some molecules show different patterns, indicating deviating orientations. The scale bar is $2\ \mu\text{m}$, the integration time was 2.6 ms.

were repeated at least once to check the reproducibility of the spectral positions and relative intensities of the single molecules. The excitation intensity in confocal spectra was above saturation, whereas in the near-field excitation spectra, extreme care was taken to keep the intensity below the saturation level, to prevent intensity-induced spectral instabilities. In figure 3(a), more single-molecule lines are found upon near-field excitation (upper trace) as compared to confocal excitation (lower trace). Besides that, the relative intensities of the molecules that appear in both excitation schemes are different. Although a higher number of molecules in a near-field excitation scan might appear counterintuitive, it can be well explained by the nature of the excitation and the characteristics of the sample. Since a major part of the field components of light emanating from a sub-wavelength aperture are oriented perpendicular to the sample surface and are concentrated at the aperture rims, molecules with their transition dipole moments oriented almost perpendicular to the sample plane, such as terrylene molecules in *p*-terphenyl [18, 19], can be excited efficiently if they are located close to the rim of the aperture. On the other hand such molecules are excited very inefficiently in a confocal scheme with predominant transverse polarization. However, the differences in intensity cannot be explained by this reason alone. Another important influence is the difference in excitation volume (figure 1(b)). Molecules that appear weaker in the near-field spectra can either have a relatively unfavourable orientation, depending on the relative position between aperture and molecule, or can be located further away from the tip, or a combination of both. Unfortunately, the relative position and relative orientation cannot be separated using fluorescence excitation spectroscopy only.

Figure 3(b) shows another example of near-field and confocal fluorescence excitation spectra, at the same spatial position but at a slightly different frequency. In this example fewer molecules are observed on near-field excitation. Three weak signatures can be found that are not seen under confocal excitation, whereas two intense lines in the confocal scans are almost absent in the near-field scans. The two intense

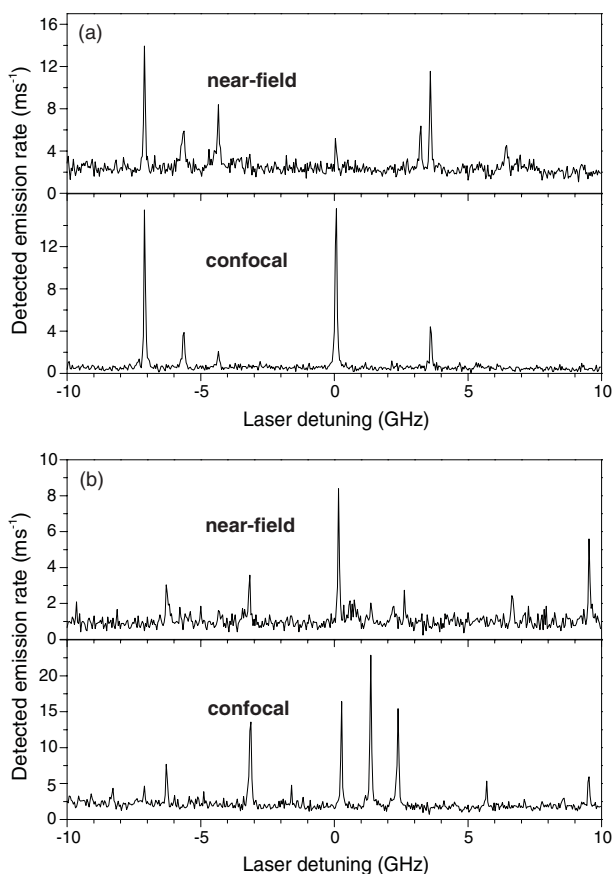


Figure 3. ((a) and (b)) Examples of near-field and confocal fluorescence excitation spectra. The excitation frequency was scanned over 20 GHz and the integration time was 16.9 ms. The intensity in the confocal spectra was above saturation. Between the spectra in (a) and (b), only the laser frequency was changed.

lines seen in the confocal spectrum but absent in the near-field spectrum can most probably be attributed to two molecules positioned far from the sample surface, such that they can be excited with confocal excitation, but not with near-field excitation (figure 1(b)). For the weaker signatures at a detuning between 6.5 and 8 GHz, the situation is different. They were found in the near-field spectrum, but not in the confocal spectrum. As the near-field excitation volume is a small part of the confocal excitation volume (figure 1(b)), the positions of these molecules cannot be the reason. Molecules that are inaccessible to confocal excitation although they reside within the confocal volume must have transition dipole moments almost perpendicular to the sample surface. In order to be visible in the near-field spectrum, these molecules must be located close to the aperture rims.

Note that in between the recording of the spectra of figures 3(a) and (b), only the laser frequency was changed, while the tip and sample were both kept at the same position, indicating the absence of any conceivable artefacts.

4. Conclusion

To summarize, we have shown the first scanning near-field optical microscopy images of single molecules at 1.8 K. These images give information on the position and orientation

of the molecules in the scanned area, as was expected from room-temperature scanning near-field optical microscopy images [4, 5]. Although the resolution is not much improved compared to far-field techniques due to the big aperture size, near-field effects are present as is reflected by the patterns from which the three-dimensional orientation of single molecules could be deduced. Besides that, we have shown for the first time a direct comparison between confocal and near-field fluorescence excitation spectra. Differences between the molecules that were found in these spectra could be explained by a combination of orientation and position with respect to the aperture probe.

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