A single molecule as a probe of optical intensity distribution

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Single terrylene molecules embedded in microscopic *p*-terphenyl crystals are identified with the technique of fluorescence excitation spectroscopy. By use of the architecture of a scanning-probe microscope at $T = 1.4$ K, a single molecule is scanned through an excitation laser beam while the fluorescence signal is recorded. In this manner we have mapped the intensity distribution in a one-dimensional optical standing wave, demonstrating the potential of a single molecule as a nanometric probe. We discuss future experiments aimed at combining the high spatial and spectral sensitivity of a single molecule. © 1999 Optical Society of America

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The interaction of light and matter lies at the heart of many areas of science and technology. The vast majority of the experimental work in this area examines the interaction of an electromagnetic field with an ensemble of material particles such as atoms in a cell, a beam, or an optical trap. Over the years many clever techniques such as Doppler-free spectroscopy have been developed to overcome inhomogeneities in measurements from ensembles. However, the textbook paradigm of a single particle located at a well-defined position interacting with the electromagnetic field has been much more difficult to explore. In recent years several researchers have studied an average of one or fewer atoms at a time interacting with a single mode of an optical cavity.[1,2] However, statistical fluctuations in particle number as well as lack of knowledge of the precise position of the particle in the electromagnetic field have led to a need for averaging processes. In an ideal experiment one would like to avoid any averaging and instead manipulate and perform many repeated measurements on the same particle at a known location in the optical field. To this end it would be desirable to perform experiments with a single particle fixed in a solid matrix that one could position in the optical field with nanometer accuracy. On the other hand, in such a system one is usually confronted with poor spectral resolution caused by dephasing phenomena in the solid state that considerably reduce the coherence in the optical transition.

Since the pioneering works of Moerner and Kador[3] and Orrit and Bernard,[4] several groups have performed high-resolution spectroscopy on single molecules in a solid matrix.[5] Performed at liquid-helium temperature, these experiments show that it is possible to reduce the homogeneous linewidths of the molecules to the level of being dominated by their natural linewidths. The variation of the resonance frequencies of individual molecules sitting at different locations in the matrix allows for the identification of a single molecule in frequency space. In contrast with the detection of single molecules on a surface by use of a scanning near-field optical microscope,[6] single-molecule spectroscopy offers a large signal-to-noise ratio, but it fails to provide any precise information about the location of the molecule in position space. The most important asset in this technique is the narrow line of the molecular resonance and its sensitivity to small variations in the electromagnetic field. Indeed, the elimination of the nonradiative dephasing processes has opened the door to experiments in quantum optics.[7] In our experiment we used the machinery of a scanning near-field optical microscope together with the large signal-to-noise ratio obtained in far-field single-molecule spectroscopy to demonstrate the potential of a single molecule as a nanometric probe for the electromagnetic field.

Figure 1(a) shows a schematic of the setup. Microcrystals of *p*-terphenyl (20–50 μm in size) doped with terrylene molecules at a concentration of 10^{-6} were sublimated onto a glass slide. The sample was then attached to a three-dimensional piezoelectric scanner (3DPS) that provided a scan range of $\sim$6 μm at $T = 1.4$ K. To correct for piezo nonlinearities in the z direction of the scanner, we set up an interferometer, using a He–Ne laser as shown in Fig. 1(a). The laser beam was coupled into the cryostat from the back window. The beam was partly reflected from the glass substrate and interfered with another part that was reflected from the front end of the microscope objective. The components of the experimental setup in the cryostat were immersed in a helium-gas atmosphere of $\sim$1 mbar that acted as a thermalization exchange gas and allowed us to obtain a temperature of 1.4 K. The molecules were excited at the wavelength $\lambda \sim 578$ nm by a tunable cw ring dye laser. The laser linewidth was less than 1 MHz, and we stabilized its intensity to better than 2%, using an acousto-optical modulator (AOM). The laser beam had a diameter of 1 mm and was focused onto the sample by a microscope objective with a nominal numerical aperture of 0.8. A CCD camera with a commercial zoom lens was used to image the sample and resolve individual crystals through the microscope objective. This resolution allowed us to choose and illuminate a given crystal for spectroscopy. As is common in the technique of fluorescence excitation spectroscopy, the frequency of the excitation laser was tuned through the zero-phonon line of a given molecule, and the fluorescence signal was collected by a high-numerical-aperture optic, in our case the microscopic objective. The fluorescence light consisted

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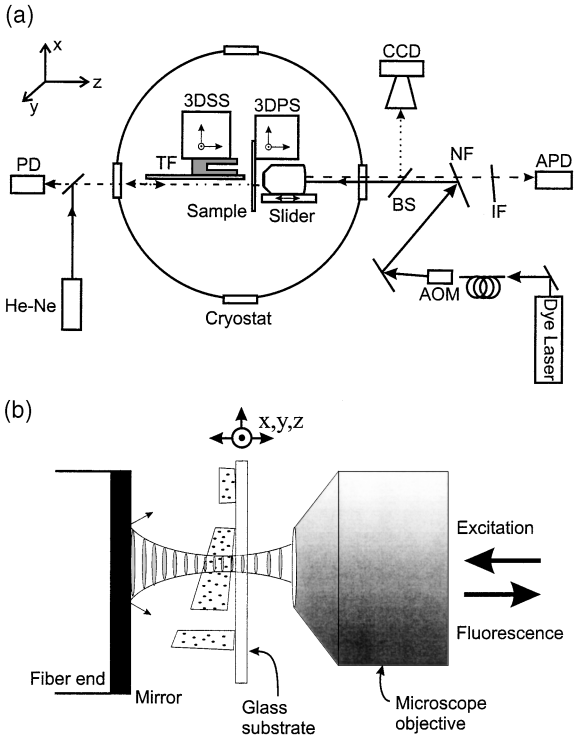

Fig. 1. (a) Schematic of the experimental setup: PD, photodector; BS, beam splitter. See text for other details. (b) Magnified view of the sample scanned through the standing wave (not to scale). The molecules are depicted as small dots in the crystal. The divergent beam after the focus is reflected by the aluminum mirror at the end of the fiber and undergoes partial interference with the incident beam. For simplicity the refraction of the laser beam at the crystal faces is not shown.

of several spectral components, since the excited state can decay to many different vibrational levels in the ground state. Light that was redshifted by more than ~10 nm was spectrally separated from the excitation light by a holographic notch filter (NF) plus an interference filter (IF) and detected by an avalanche photodiode (APD). We had count rates of the order of 100 kHz and linewidths as small as 40 MHz, which are typical of terrylene in *p*-terphenyl, which is a very photostable system with a high quantum yield.[8]

Once a single molecule was identified in frequency space, the laser frequency was left on its resonance, which was power broadened to ~200 MHz in this experiment. Next, we moved the microscope objective to position the molecule in its focus and maximize the avalanche photodiode signal. The motion of the objective was controlled by a homemade piezoelectric slip-stick slider system with total range of 10 mm, with a step size of ~200 nm.[9] Next, to find the optical axis, or the z axis in Fig. 1, we adjusted the angle of the incident excitation beam until its reflection from the glass substrate remained collinear with the motion of the objective. We then scanned the crystal laterally with the piezoelectric scanner while recording the fluorescence signal [the dashed line in Fig. 1(a)] to map the transverse intensity distribution of the excitation laser beam. In this manner we could measure the focus waist of the excitation beam to be ~1 μm and then place the molecule at the position of maximum intensity. Next, we scanned the sample in the z direction. The bars in Fig. 2(a) show the variation of the fluorescence signal as a function of the molecule's position. Each scan contained 256 points in the z direction, corresponding to a step size of ~24 nm and an integration time of 20 ms/point. To improve the signal-to-noise ratio and minimize the influence of occasional disappearance of the signal owing to transitions to triplet states,[10] we repeated each scan 64 times and averaged the data. The variations of the signal at a given pixel between the individual scans were used to estimate the error bars shown in Fig. 2. This gave a signal-to-noise ratio of ~50. The repeated measurements also served as a check on the stability of the laser frequency. The solid curve in Fig. 2(a) shows the fit obtained assuming that the z axis makes an angle of 11° with the axis of the Gaussian beam. This angle is important in explaining the slight asymmetry in the data, and it can be caused by an error in the alignment or by refraction at the first facet of the crystal. We also considered the possibility of spherical aberration that might arise when an ordinary microscope objective is cooled to $T = 1.4$ K, but we found its contribution to be negligible.

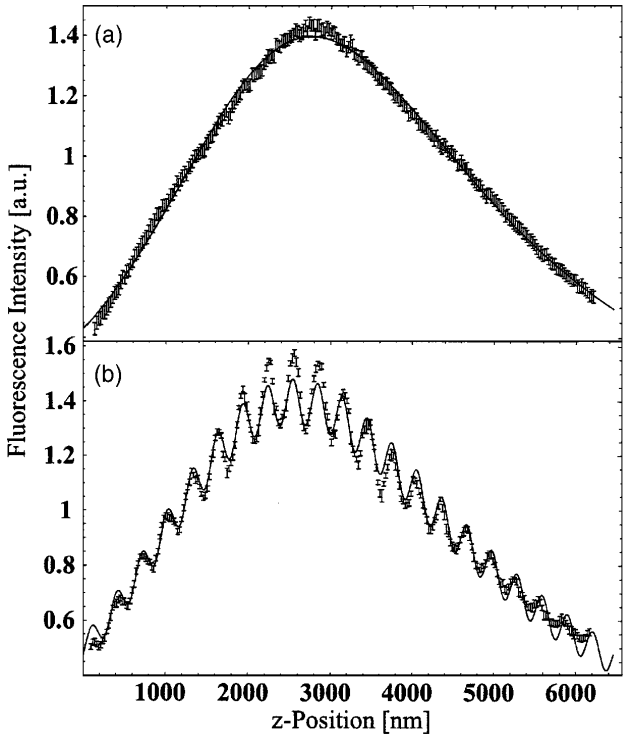

Fig. 2. (a) Bars, fluorescence signal when the molecule is scanned in the z direction (without the mirror in place). The slight asymmetry is due to an angle between the direction of travel of the molecule and that of the laser beam in the crystal. Solid curve, result of the fit (see text). (b) Bars, recorded fluorescence signal as the molecule is scanned along the z direction in the presence of the mirror; solid curve, fit assuming that the laser beam with the parameters found from the fit in (a) is reflected from a mirror (see text).

To set up a standing wave, we retroreflected the excitation beam by use of a microscopic mirror of diameter 125 μm. We formed the mirror by coating the end of a cleaved optical fiber with aluminum [see Fig. 1(b)]. The fiber was positioned in the excitation beam by use of a three-dimensional piezoelectric slip-stick slider system (3DSS), as was used in the motion of the microscope objective. We placed the mirror a few micrometers from the sample while monitoring the shear-force signal from a quartz tuning fork[11] (TF) to avoid crashing the fiber into the sample. The symbols in Fig. 2(b) show the fluorescence signal when the same molecule as that in Fig. 2(a) was scanned in the z direction. One can observe a pronounced interference pattern superposed on the intensity profile obtained in Fig. 2(a). To understand the details of the data, it is important to note several aspects of the geometry in the interaction region that we did not emphasize in Fig. 1 for the sake of simplicity. First, to minimize the background fluorescence one has to place the focus of the excitation light in the crystal, and therefore the reflected beam cannot fully overlap the incident beam. Furthermore, the excitation beam can undergo refraction at the second facet of the crystal, which in turn leads to a finite angle of incidence at the mirror. As a result, in general, the reflected beam is not parallel to the incident beam, and the intensity distribution obtained along the z axis of the setup can be complex. One indication of this is that the observed periodicity of 309 nm in Fig. 2(b) corresponds to an effective angle of $\sim 20^\circ$ between the incident and the reflected beams. We simulated the optics and fitted the data, as displayed by the solid curve in Fig. 2(b). We obtained a distance between the molecule and the mirror of 25 μm and an effective reflectivity of $\sim 50\%$. It is therefore not surprising that the visibility of the interference fringes is not very strong. To assess a quantitative value for the spatial resolution in the axial direction, we fitted a sine-squared function to the central fringe of Fig. 2(b). The center of this fringe could be located to within 24 nm, limited by visibility and noise in the signal. This result shows an improvement over recent reports.[12,13] We expect the inherent resolution in all these experiments to be limited by the size of the molecule, which is of the order of 1 nm.

In conclusion, we have demonstrated the potential of a single molecule as a nanometric probe of an electromagnetic field by mapping an optical standing wave. A particularly exciting extension of this idea is in the optical near-field imaging of a sample with a single molecule as a probe.[14,15] A novel scheme for obtaining high-resolution lateral images exploiting the spectral sensitivity of a single molecule was suggested recently in a theoretical study.[16] In this proposal the energy-level shift of the molecular line serves as a measure of the variations of the local optical contrast. Finally, the combination of the narrow spectrum of a single molecule with the positioning capability of such a probe might be of interest in quantum optics, in which the controlled coupling of a single particle with a single mode of an electromagnetic field is desired.

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