Near-Field Optical Spectroscopy of Individual Molecules in Solids

W. E. Moerner,* Taras Plakhotnik,† Thomas Irngartinger, and Urs P. Wild
Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

Dieter W. Pohl and Bert Hecht
IBM Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

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Near-field single-molecule spectroscopy was performed on a crystal of pentacene-doped p-terphenyl using an Al-coated optical fiber tip with 60 nm diam aperture as a near-field light source. Individual molecules located ≅400 nm from the tip had linewidths of 10–20 MHz at 1.8 K. The background fluorescence provided a useful distance-sensing signal, as it increased exponentially during approach with a characteristic length of ≅100 nm. Single molecules closest to the tip were identified by Stark shifts.

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The new field of optical spectroscopy of individual molecular impurities in solids at low temperatures (single-molecule spectroscopy or SMS) has recently been utilized for a large array of experiments to study dynamics of local environments in crystalline and amorphous materials, local field effects, vibrational modes, and magnetic resonance of a single molecular spin [1]. Single molecules have also been imaged with a low-temperature, fluorescence excitation microscope [2], but the spatial resolution of this and all other previous SMS has been limited to ≅3–5 μm. By contrast, the *spectral* resolution of SMS has not been instrument limited, i.e., the standard cw laser linewidth of a few MHz (at an optical frequency of 500 THz or 600 nm) is negligible compared to the observed molecular linewidths of 10–100 MHz. Such narrow lines provide highly detailed information about external field perturbations and interactions with the surrounding matrix.

Very recently, scanning near-field (NF) optical microscopy (SNOM or NSOM [3,4]) employing tiny apertures as light sources has been used [5] to image the fluorescence from single molecules. The maximum spatial resolution of SNOM is given by the diameter of the aperture, generally 50–150 nm, well below the diffraction limit of $\lambda/2$ but still large compared to molecular dimensions. Hence the emission characteristics of single molecules serve as a probe for the NF distribution of radiation close to the aperture. The observed *spectral* linewidths from a recent SNOM study of single-molecule luminescence [6] were about 25 nm (20 000 GHz), mostly due to the room temperature operation.

Here we combine for the first time SMS and the optical tips commonly used for SNOM to perform near-field fluorescence excitation spectroscopy of single pentacene molecules (NF-SMS) located near the surface of a p-terphenyl host crystal. The use of low temperatures yields spectral widths on the order of 10 MHz, and we utilize this extremely high resolution to observe Stark shifts of individual molecules. Tip voltages V_T as small as only 10 V, producing electric fields on the order of 10^6 V/cm, cause significant changes in the single-molecule spectra. Simultaneous dithering of the position of the tip in the transverse plane causes a broadening of the single molecule lines which allows estimation of the actual tip-molecule distance R (in this work ≅400 nm). For approach control, we have utilized a novel surface-sensitive optical signal with range on the order of 100 nm, namely, the (spectrally averaged) background fluorescence increase (BFI). Our high-resolution single-molecule spectra in the NF regime at a fixed transverse position can be combined with 2D imaging in future studies.

The NF optical fiber tips were prepared according to the standard technique [4] of pulling a heated fiber to a small diameter until it breaks, Al coating the sides of the tip, and final inspection with scanning electron microscopy to observe the aperture in the Al coating, which was generally 60 ± 10 nm in diameter. The optical transmission of the tips was in the range 10^{-5} to 10^{-6}. A tip was mounted inside an xyz piezoelectric tube scanner made of PZT-5A to provide fine approach (z) and dithering (x or y). Coarse z positioning of the assembly was achieved by a coupled spring and steel plate similar to that described earlier [7]. Interference fringes between light emitted from the tip and its mirror image in the sample surface were used to position the tip within ~1 μm from the surface and to calibrate the approach of the z-piezo (which was ≅1 ± 0.2 nm/V). Final approach with the z-piezo was monitored by the BFI signal, described below. The entire insert was held at 1.8 K in superfluid He.

Thin, optically clear crystals of p-terphenyl doped with pentacene ~1 μm in thickness were grown by sublimation from a 2.3×10^{-5} mole/mole starting composition. This concentration is larger than usual in SMS in order to ensure the presence of sufficient numbers of pentacene molecules in the volume closest to the tip, but it was not large enough to produce severe optical broadening by dipole-dipole interactions [8]. As shown in Fig. 1 (inset),

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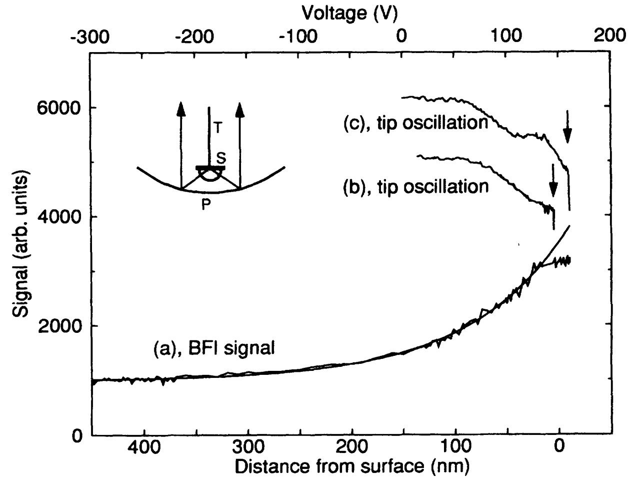

FIG. 1. Approach signals versus z piezovoltage and estimated distance from surface d for (a) BFI signal ($\lambda = 592.187$ nm), (b), (c) tip oscillation amplitude with (c) measured 20 min after (b). All scales have the same zero. Inset: Optical schematic showing tip (T), sample (S) on glass hemisphere, and paraboloidal mirror (P).

a thin sublimation plate was optically contacted to the flat surface of a glass hemisphere 3 mm in diameter in order to prevent loss of the emitted fluorescence by total internal reflection. The hemisphere was located at the focus of a parabolic mirror of numerical aperture 0.98 to collect the emitted fluorescence and direct it out of the cryostat. As is usual in excitation spectroscopy, the scattered pumping light was blocked by a long-pass filter and the resulting total Stokes-shifted fluorescence emission was detected with a photomultiplier as a function of the optical frequency of the pumping laser.

Figure 1 shows an example of the signals which were used to control the approach to the surface, with the abscissa labeled both with the z-piezo approach voltage and the estimated tip-surface distance d. We show that the BFI signal is independent of d in the far field, while in the near field the BFI signal increases, an effect which may be used to provide an early warning of the surface. The BFI signal [Fig. 1(a)] is produced by selecting a laser wavelength near the center of the inhomogeneous line, scanning the laser rapidly (0.25 s/scan) over several GHz, and detecting the (Stokes-shifted) fluorescence at 1 s intervals with a modest laser power incident on the fiber coupler, P_C, of ~ 100 μW. These conditions integrate over any of the fine spectral features which arise from all the molecules in the sample approximately within a conical section emanating from the tip. In the far field ($d > \lambda$), the BFI signal is independent of d, because the higher irradiance at closer positions (scaling as $1/d^2$) is compensated by the smaller volume excited (scaling as d^2). However, in the NF regime ($d < \lambda$), the fluorescence increases above the far-field value for two main reasons: (i) radiation from the tip can now excite waves which propagate inside the sample at angles larger than the critical angle, thus increasing the total volume generating fluorescence; and (ii) the irradiance in the near field increases faster than $1/d^2$. The BFI signal increase is related to the near-field appearance of transmitted light from the tip in the angular range normally forbidden by total internal reflection [9].

The BFI signal increases exponentially as shown by the solid curve in Fig. 1(a), in this case with a range (characteristic length of the exponential fit) of ~ 90 nm. Hence, it is quite easy to move to the NF region without crashing into the surface using this signal. In the case shown, the curve flattens near the position where the BFI signal has tripled, suggesting surface contact.

The maximum increase in the BFI signal expected at $d = 0$ depends upon the radial diameter of the sample that is effectively pumped by the light from the tip, which can vary due to sample imperfections (cracks, etc.) in the molecular crystal (hence, a separate BFI curve was acquired for each sample). To confirm the zero position, we utilized the standard shear force method [10], in which the tip was dithered transversely with a 10–20 nm amplitude at mechanical resonance. The resulting tip motion was detected outside the cryostat by measuring the intensity modulation of a HeNe laser beam reflected off the tip sidewall. Traces (b) and (c) of Fig. 1 display tip oscillation signals recorded 20 min apart. The slow decrease of the signal over the last ~ 100 nm is an artifact which changed from approach to approach and from sample to sample and should be ignored. The first indication of frictional interaction during approach is an abrupt decrease of amplitude [see arrows in traces 1(b) and 1(c)]. The tip oscillation in general recovered during slow further approach of a few nm distance, then decreased again by a larger amount if the approach was continued. In our experiment, the approach was stopped when the amplitude of a downward spike reached the 10% level in order to prevent tip damage [11]. The difference in end point between traces 1(b) and 1(c) demonstrates slow drift of the position of the surface. The downward spikes might indicate brief temporary stiction and release. Such behavior, while reasonable for a soft molecular crystal, is poorly suited for distance control; therefore, the shear force curves were used only to determine the $d = 0$ position for the BFI approach curves to within ± 20 nm [12].

Figure 2 shows fluorescence excitation spectra during an approach to the near field. In trace (a), ~ 1.2 μm from the surface, highly repeatable statistical fine structure [13] begins to appear as N_H, the number of molecules in resonance per homogeneous linewidth, becomes small enough to make the $1/\sqrt{N_H}$ number fluctuations larger than the shot noise. Closer to the surface [trace 2(b)], the average fluorescence is constant as it should be in the far field, but the statistical fine structure clearly increases in relative size due to the smaller N_H. Finally, trace 2(c)

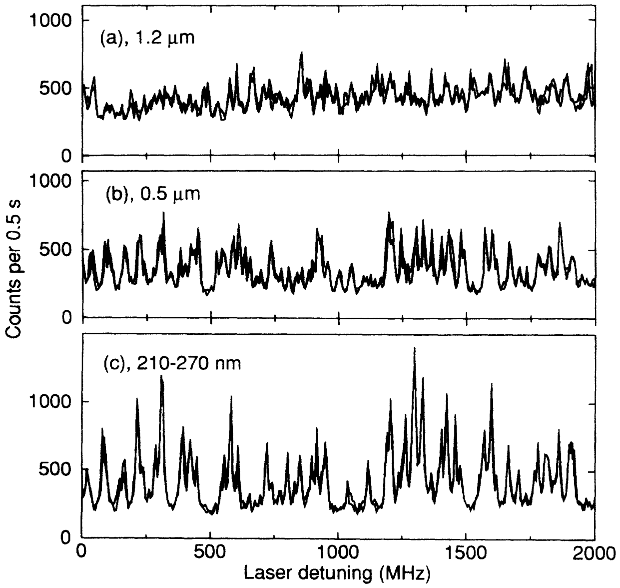

FIG. 2. Statistical fine structure and single-molecule features upon approach to the NF. Approximate distances from the surface: (a) 1.2 μm, (b) 0.5 μm, and (c) 210–270 nm. Each panel shows two spectra taken ≅5 min apart to show reproducibility. Zero detuning = 592.066 nm, $V_T = 0$, all traces from the same sample.

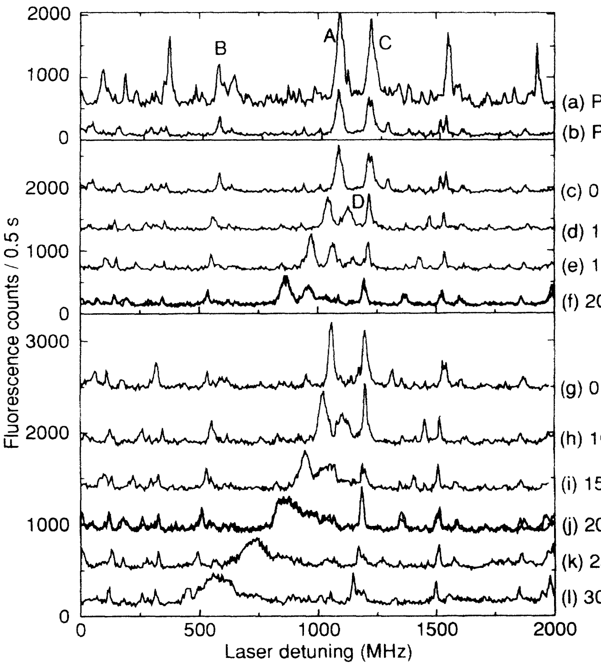

FIG. 3. Excitation spectra showing three methods to identify molecules close to the tip with $d \cong 250$ nm. Upper panel: saturation method; spectra taken with (a) $P_c = 100$ μW, and (b) 25 μW. Middle panel: static Stark shift method, traces labeled by V_T. Bottom panel: Stark shift with transverse dithering method, traces labeled by V_T. The scale is exact for the lowest trace in each panel with the other traces shifted vertically upwar. (Zero detuning = 592.067 nm.)

(210–270 nm from the surface) shows the spectrum at the transition to the NF regime. Single-molecule features now appear with increased intensity indicative of the high NF irradiance and its confinement which reduces N_H to values less than 1.

In the NF region, single-molecule spectra can readily be observed, and some examples are shown in Figs. 3(a) and 3(b). The single-molecule features are 10–20 MHz in width at the optical frequency of 507 THz, thus demonstrating the extremely high spectral resolution of NF-SMS. We have observed many stable molecules as well as some molecules whose resonance frequencies shift from scan to scan as observed in previous far-field SMS [1]. It was not determined whether these spectral shifts arose from spontaneous or light-induced processes nor if the shifting was induced by the tip. We note that if far-field SMS techniques had been used to probe a $5 \times 5 \times 1$ μm^3 volume of our high concentration sample at similar wavelengths close to the inhomogeneous line center, only statistical fine structure would have been observed.

Even though the tip was placed ≅250 nm from the surface, the molecules producing the strong signals in Fig. 3 could have been fairly deep inside the μm thick sample. The rest of the figure shows three techniques used to identify molecules with small R: (i) saturation, (ii) static Stark effect, and (iii) Stark effect with lateral dithering. In the saturation technique (upper panel), a moderate laser power was selected and a large spectral range was scanned in order to locate strong single-molecule features broader than the average width. Trace (a) shows a 2 GHz region of such a scan at $P_C = 100$ μW. Features A and C and perhaps B appear power broadened, presumably by the extremely large irradiance near the tip. By reducing the laser power by a factor of 4 [trace 3(b), and all other traces], the unsaturated features were observed to decrease in peak amplitude approximately linearly while the features A, B, and C did not, thus selectively increasing the contrast for these features. By also systematically varying the laser power and fitting the saturation behavior in the usual way [1], the emission from molecule A showed saturation at a laser power 5 times lower than for molecule B, indicating that molecule A was closer to the tip. The low power linewidths were 20 ± 2 MHz (A) and 13 ± 2 MHz (B), both larger than the lifetime-limited value of ≅8 MHz due to the high doping level. Molecule C showed an anomalous saturation behavior suggesting that this feature may have been composed of more than one molecule (see below).

To further select molecules with small R, we performed a static Stark-effect study [Figs. 3(c)–3(f), middle panel] by applying a voltage V_T to the Al coating of the tip. Molecule *A* dramatically moves to lower frequency as V_T is increased, consistent with the proximity to the tip suggested by the saturation behavior. Molecule *D* appears at $V_T > 0$ and also redshifts at higher fields; this molecule was probably obscured at $V_T = 0$ by superposition with another molecule to form feature *C*. Some weaker single-molecule features (e.g., at 1500 MHz) also show Stark shifts, while many other molecules shift little or not at all; hence the electric field is much smaller at the position of these molecules. Trace (*f*) is composed of two separate scans at the same voltage to illustrate the high degree of repeatability of the spectra.

Molecule *A* shifts quadratically with field as expected for the centrosymmetric pentacene molecule, while molecule *D* seems to have both a quadratic and linear term resulting from a local electric field. These behaviors have been observed before in far-field SMS [14]; here the Stark shift may be used to determine the field at molecule *A* and to estimate *R*. Using the previously observed [14] quadratic shift coefficient of -3.3×10^{-8} MHz/(V/cm)^2 to estimate the field at molecule *A* and assuming the tip to be a sphere of 100 nm radius and the counter electrode (ground) to be effectively at infinity, we obtain the estimate $R \cong 400 \pm 50$ nm.

Finally, the single molecules near the tip can be used to sense the spatial gradient of the static applied electric field as illustrated in Figs. 3(g)–3(l), bottom panel. Here an *X* dither of the tip of about 20 nm peak to peak is established at the tip resonance frequency near 7 kHz. This motion produces a time-varying electric field at the single molecule, which increases in amplitude as V_T increases. Since the photon counting time of 0.5 s averages over the time-varying Stark shift, we see a fascinating broadening of the excitation spectrum for molecules closest to the tip (i.e., *A* and *D*). This effect was completely reversible and repeatable [trace (j) contains two scans at the same V_T]. Using the simple spherical tip model again, one may relate *R* to the polar angle θ at the location of the molecule, because the shift and broadening both scale as the field squared. This yields an upper bound for the distance between the tip and the molecule of ~400 nm, independent of the actual Stark shift coefficient.

We have shown that it is possible to combine near-field optical excitation with the extremely high resolution characteristic of low-temperature single-molecule spectroscopy. NF-SMS can be achieved even in samples that are thicker than the optical wavelength. This method has the potential to provide highly local information on spatial scales less than $\lambda/2$ at high spectral resolution. It will clearly be possible to produce scanned images, possibly using the fluorescence background increase as a feedback control signal. Perturbations by extremely large electric fields up to the breakdown limit can easily be applied. Alternatively, since the molecule can be used to measure various spatial derivatives of the static electric field, detailed mapping of the field distribution around nm-sized tips should be possible. Single molecule spectra at low temperatures are also extremely sensitive to uniaxial stress so that the actual forces produced by the tip can be measured.

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*Present address: IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120.

†Present address: Institute of Spectroscopy, Troitsk, Moscow Region, Russia.

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