

## Optical near-field enhancement at a metal tip probed by a single fluorophore

A. Kramer, W. Trapesinger, B. Hecht,<sup>a)</sup> and U. P. Wild  
*Physical Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum,  
 CH-8092 Zurich, Switzerland*

(Received 27 July 2001; accepted for publication 17 December 2001)

The optical near-field in the vicinity of a metal tip is mapped using a single-molecule optical probe. We observe an enhancement of the fluorescence signal by a factor of  $5.7 \pm 0.3$ , clearly larger than the fourfold enhancement that can arise from constructive interference if the tip acts as a simple mirror. Considering the tip apex as a nanoparticle of nonregular shape, we suggest that, in the case of gold tips, the enhancement is due to resonant plasmon excitation. Consistently, no enhancement has been observed using Pt/Ir tips. © 2002 American Institute of Physics.  
 [DOI: 10.1063/1.1453479]

Manipulation and tailoring of optical fields on the nanometer scale is a key technology for the field of nano-optics and in particular for high-resolution optical microscopy and spectroscopy. In order to engineer and optimize a particular nano-optical field distribution, procedures have to be developed that allow mapping of optical fields with nanometer scale resolution while exerting the least possible influence on the mapped field itself. An important property of nano-optical fields is their spatial confinement to subwavelength dimensions. Strong field confinement can be achieved in the vicinity of small particles and sharp tips.<sup>1,2</sup> Recently, these phenomena have been successfully exploited for tip-enhanced near-field optical microscopy and surface-enhanced Raman scattering.<sup>3–10</sup> Currently, these techniques rely on optical signals which are emitted from a spatially extended region of the sample. Model-based estimates and extrapolation have to be applied to determine the magnitude of the field enhancement factor on the surface of the tip.<sup>6–10</sup> In order to gain a deeper understanding of the field enhancement, not only the knowledge of an enhancement factor, but also the spatial distribution of the electromagnetic vector field around a tip or any other structure of interest, should be assessable.<sup>11</sup>

In this letter, we demonstrate that a single fluorescent molecule can be used to measure the field distribution in the vicinity of an illuminated metal tip (Fig. 1). Employing a single molecule as field sensor guarantees the highest possible spatial resolution while mapping a well-defined component of the optical field.<sup>12</sup>

The setup consists of a sample-scanning confocal optical microscope on top of which a scanning probe microscope is mounted.<sup>13</sup> Linearly polarized light from a tunable dye laser ( $\lambda = 578.5$  nm) is focused to a nearly diffraction-limited spot on the sample by a microscope objective (num. apert.: 0.9, magnification:  $80\times$ ). Experiments are performed at room temperature. Nevertheless, the setup can also be operated at superfluid Helium temperature.<sup>14</sup> For this reason, the use of an immersion objective with high numerical aperture and

index matching liquid is excluded. The sample fluorescence is focused onto a single photon counting avalanche photodiode. A holographic notch filter and a subsequent cutoff filter block the Rayleigh-scattered light. Sample scanning ( $x-y$ ) is accomplished by a piezobimorph scanner, tip scanning ( $x-y-z$ ) by a piezotube. Shear force interaction between tip and sample is used for the gapwidth control. The shear force detection relies on a quartz tuning fork as a sensing element.<sup>15</sup> Depending on the feedback parameters and environmental conditions, the shear force interaction typically leads to a gapwidth between 2 and 20 nm.<sup>16,17</sup>

The sample is a 20 nm thick polymer film of poly(meth-

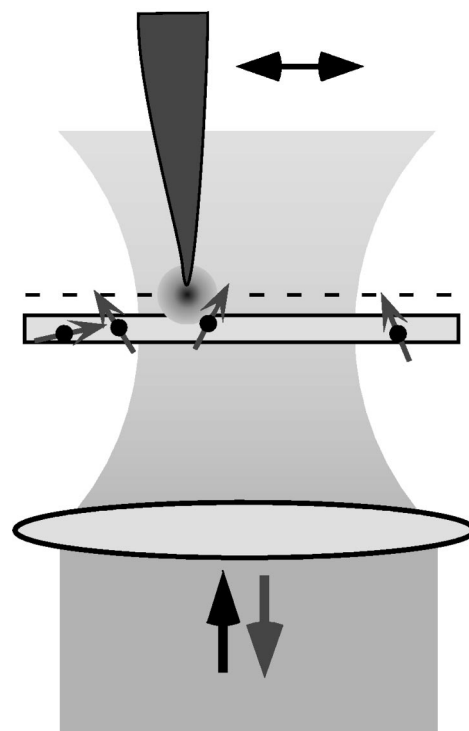


FIG. 1. Scheme of the experiment: A sharp metal tip is scanned across a single fluorescing molecule embedded in a polymer film on glass. The optical field in the vicinity of the tip apex is strongly enhanced. The molecular fluorescence as a function of the tip position allows assessing the electric field distribution around the tip.

<sup>a)</sup>Author to whom all correspondence should be addressed at: Institute of Physics, University of Basel Switzerland; electronic mail: bert.hecht@unibas.ch

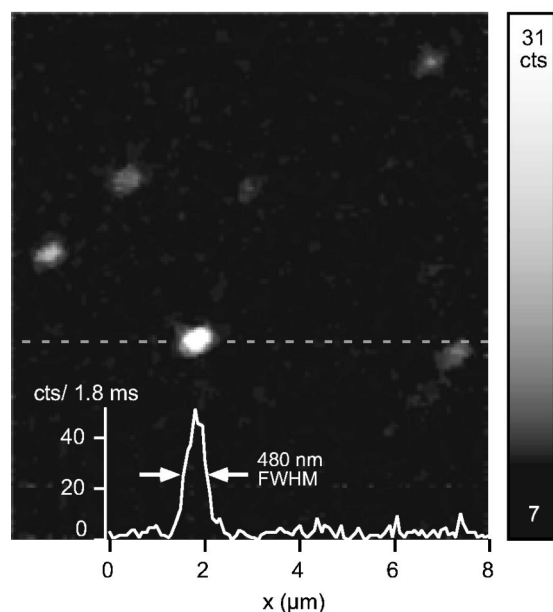


FIG. 2. Scanning confocal micrograph of single terrylene molecules in PMMA (without tip). The image is generated by scanning the molecules through the focus. The apparent width of a single-molecule fluorescence spot is 480 nm. The signal-to-background ratio is 20. ( $128 \times 128$  pixel, integration time 1.8 ms/pixel,  $I_{\text{exc}} = 20 \mu\text{W}$ .)

ylmethacrylate) (PMMA) prepared by spin casting onto a cover slip. The film is doped with a low concentration of terrylene molecules, resulting in an areal density of  $\approx 0.1$  molecules/ $\mu\text{m}^2$  in the film. The excitation intensity is approximately  $20 \mu\text{W}$ . From recorded saturation curves, we have clear evidence that the molecules were excited far below the saturation intensity. Under these conditions, a linear relation between the observed count rate and the excitation intensity holds. In order to decrease the probability of photochemical destruction of the molecules, the gap region was kept exposed to a continuous, laminar  $\text{N}_2$  stream. We thus achieve continuous single-molecule fluorescence for 10–20 min at a count rate of  $R \approx 4000$  c/s for selected molecules.

Tips used in this experiment are manufactured by electrochemical etching of thin wires of gold and Pt/Ir (90:10), respectively. Gold tips are etched in HCl (25%) with an ac voltage of  $1 \text{ V} < U_{\text{ac}} < 2 \text{ V}$  ( $\nu = 50 \text{ Hz}$ ).<sup>18</sup> Pt/Ir tips are etched in 5 M KOH ( $2 \text{ V} < U_{\text{ac}} < 10 \text{ V}$ ,  $\nu = 50 \text{ Hz}$ ) and sharpened according to the method of Lindahl *et al.*<sup>19</sup> Scanning electron microscopy (SEM) images of freshly etched tips revealed nanoscale structures of irregular shape at the tip apex. The size of the tip apex varies between 20 and 200 nm.

A typical confocal fluorescence image of the dye-doped PMMA film is shown in Fig. 2, where six molecules are clearly visible. The obvious variation of the fluorescence rate among the molecules arises mainly from different orientations of their absorption dipole with respect to the excitation polarization. A line section across the brightest molecule illustrates a favorable signal-to-background ratio of about 20. The full width at half maximum (FWHM) of the spot is 480 nm.

In order to map the field distribution at the tip, a single molecule is identified by its fluorescence spot in the confocal image and moved into the focus. The sample is kept at a fixed position in the following, whereas the tip is now

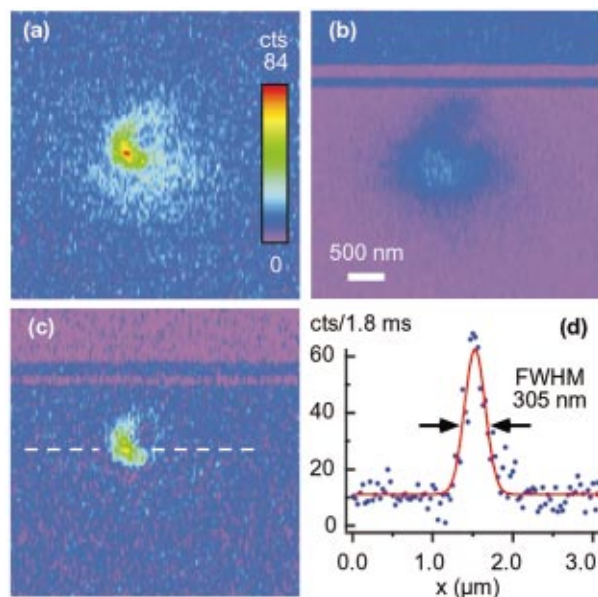


FIG. 3. (Color) (a) Fluorescence emitted by a single terrylene molecule held fixed in the focus as a function of the tip position (integration time 1.8 ms/pixel). (b) Recorded subsequent to (a). Photobleaching of the molecule is evident after the first couple of lines (top-to-bottom scan). Background fluorescence shows up in the center of the image (integration time 9 ms/pixel). (c) Image obtained by subtraction of (b) from (a). (d) Cross section along the dashed line in (c). The fluorescence increase by a factor of  $5.7 \pm 0.3$  evidences a tip enhancement of the optical field. (Dots: measured count rate. Line: Gaussian fit. Images same length and intensity scale and  $128 \times 128$  pixels: in all images).

scanned across the focal region containing the molecule. Five molecules which exhibited a rather stable and high fluorescence rate have been investigated. As an example, we discuss the results obtained with the molecule that showed the strongest field enhancement. Figure 3(a) illustrates the variation of the fluorescence rate of the molecule as a function of the tip position. The polarization direction of the linearly polarized excitation light relative to the tip scan direction (fast axis) is not known.

We observe a strong, spatially confined fluorescence signal on top of a broad background. While the fluorescence of the molecule finally ceases due to photobleaching [top of Fig. 3(b)], the background is constant over time and likely due to direct reflection off the tip. The tip scan including the photobleaching event of the molecule [Fig. 3(b)] can thus be used to subtract the background from the total signal [Fig. 3(a)]. This allows extracting the pure distribution of the optical near field in the vicinity of the tip. The resulting slightly oval pattern is displayed in Fig. 3(c). In order to extract quantitative results, the cross section along the dashed line in Fig. 3(c) is fitted by a Gaussian [Fig. 3(d)]. The enhancement pattern of the molecular fluorescence exhibits a FWHM of  $305 \pm 15$  nm. The maximum fluorescence is by a factor of  $5.7 \pm 0.3$  larger than the reference level. The reference level is the constant molecular fluorescence in absence of tip. This value corresponds to the offset parameter of the fit. A topography image is recorded simultaneously (data not shown). It reveals a flat PMMA film [root-mean-square (rms) roughness  $\Delta z \approx 3$  nm] without any topographic feature at the site of the enhancement. It is thus certain that the enhancement does not arise from a crosstalk between topography and optical imaging.

The apparent, oval pattern in Fig. 3(c) is likely connected to the particular shape of the tip. The spatial confinement of  $305 \pm 15$  nm is clearly smaller than the width of the focal spot (480 nm). The enhancement factor of  $5.7 \pm 0.3$  is clearly larger than the fourfold enhancement that can arise from constructive interference if the tip acts as a simple mirror. This indicates that a true, tip-induced near-field interaction with the molecule has been observed.

It is not surprising that the observed size of the enhancement area is larger than the range of tip diameters found by SEM. The width of the enhancement area depends strongly on the tip–molecule distance. Theoretical work has shown that the intensity confinement area is calculated to be generally larger than the size of the tip apex.<sup>20–22</sup>

Note that some phenomena have to be taken into account which might affect the measurement of the field enhancement and field distribution: (i) The fluorescence map corresponds to the projections of the electric field vector onto the absorption dipole of the molecule in a plane perpendicular to the tip axis. Generally, the absorption dipole of the molecular probe is not parallel to the electric field. We measure the fluorescence count rate  $R$ , where  $R \propto \mathbf{E}^2 \cos^2 \alpha$  and  $\alpha$  is the angle between the electric field  $\mathbf{E}$  and the molecular dipole. Thus,  $R$  provides a lower limit of the squared electric field  $|\mathbf{E}^2|$ . (ii) It is well known, that the nonradiative decay rate of a molecule near a metallic object is increased at distances of  $z \leq 10$  nm (“quenching”).<sup>23</sup> (iii) It has been shown that the emission pattern of a molecule sitting at an interface can be modified by the proximity of a metal object.<sup>23,24</sup> As a result, the fluorescence collection efficiency may change as a function of the tip position. Effects (ii) and (iii) play an important role only if the molecule–tip distance is small ( $\leq 10$  nm). Taking into account both the film thickness and the shear force gap width, we assume that these phenomena cause a minor disturbance in our case.

We suggest that, in the present study, the enhanced fluorescence is due to localized plasmon fields and not due to a nonresonant enhancement (lightning rod effect) at the tip apex. This is supported by three observations. (i) A wavelength dependence: For gold-coated glass tips a resonance at  $h\nu = 2.11$  eV ( $\lambda = 588$  nm), close to our wavelength, was reported.<sup>6</sup> When performing similar experiments with gold-coated atomic-force-microscope tips at an excitation wavelength of  $\lambda = 532$  nm, we observe no significant field enhancement ( $\leq 2$ ).<sup>25</sup> (ii) For material properties: Using Pt/Ir (90:10) tips instead of gold tips in our experiment, no significant enhancement was observed ( $\leq 2$ ). (iii) Considerable nonresonant enhancement only occurs at very sharp tips in the presence of the excitation field components along the tip axis.<sup>20–22</sup> Both criteria are not met in our experiment.

Further experiments will include a complete mapping of the field by performing tip  $x$ – $y$  scans at various tip–sample distances. However, this is complicated by the limited number of photons the molecule emits before photochemical

damage. A more practical approach would be the recording of tip  $z$  scans at selected sites of the sample. Moreover, the acquisition of further parameters is envisaged which would provide a more precise assessment of the field distribution and field enhancement. These include the orientation of the molecular absorption dipole,<sup>12</sup> the fluorescence lifetime, and the tip–molecule distance.

In conclusion, we demonstrated mapping of the complex field distribution around a metal tip. By employing a single molecule as local field sensor, we experimentally provide evidence for near-field enhancement at a metal tip. Since the spatial extension of the enhanced field can be tailored down to the nanometer-scale, these results may be of use for future developments in high-resolution near-field microscopy at molecular length scales. Furthermore, our results may be interesting for comparison with theoretical models, which calculate the near-field in the vicinity of nanometer-scale scatterers.

The authors gratefully acknowledge discussions with J.-M. Segura, A. Renn, L. Novotny, and M. Kreiter. They also thank Y. D. Suh for help with etching the gold tips and A. Bouhelier and J. Toquant for SEM support. This work was funded by the Swiss National Foundation (NFP 36) and the ETH Zurich.

<sup>1</sup>J. Wessel, *J. Opt. Soc. Am. B* **2**, 1538 (1985).

<sup>2</sup>A. V. Zayats, *Opt. Commun.* **161**, 156 (1999).

<sup>3</sup>F. Zenhausern, Y. Martin, and H. K. Wickramasinghe, *Science* **269**, 1083 (1995).

<sup>4</sup>B. Knoll and F. Keilmann, *Appl. Phys. Lett.* **77**, 3980 (2000).

<sup>5</sup>E. J. Sanchez, L. Novotny, and X. Sunney Xie, *Phys. Rev. Lett.* **82**, 4014 (1999).

<sup>6</sup>M. Ashino and M. Ohtsu, *Appl. Phys. Lett.* **72**, 1299 (1998).

<sup>7</sup>H. F. Hamann, A. Gallagher, and D. J. Nesbitt, *Appl. Phys. Lett.* **76**, 1953 (2000).

<sup>8</sup>J. Azoulay, A. Debarre, and P. Tchenio, *J. Microsc.* **194**, 2 (1999).

<sup>9</sup>R. M. Stöckle, Y. D. Suh, V. Deckert, and R. Zenobi, *Chem. Phys. Lett.* **318**, 131 (2000).

<sup>10</sup>N. Hayazawa, Y. Inouye, Z. Sekkat, and S. Kawata, *Chem. Phys. Lett.* **335**, 369 (2001).

<sup>11</sup>E. Betzig and R. J. Chichester, *Science* **262**, 1422 (1993).

<sup>12</sup>B. Sick, B. Hecht, and L. Novotny, *Phys. Rev. Lett.* **85**, 4482 (2000).

<sup>13</sup>A. Kramer, J.-M. Segura, A. Hunkeler, A. Renn, and B. Hecht (unpublished).

<sup>14</sup>J. M. Segura, A. Renn, and B. Hecht, *Rev. Sci. Instrum.* **71**, 1706 (2000).

<sup>15</sup>K. Karrai and R. D. Grober, *Appl. Phys. Lett.* **66**, 1842 (1995).

<sup>16</sup>K. Karrai and I. Tiemann, *Phys. Rev. B* **62**, 13174 (2000).

<sup>17</sup>R. Brunner, O. Marti, and O. Hollricher, *J. Appl. Phys.* **86**, 7100 (1999).

<sup>18</sup>Y. D. Suh, V. Deckert and R. Zenobi (personal communication).

<sup>19</sup>J. Lindahl, A. T. Takanen, and L. Montelius, *J. Vac. Sci. Technol. B* **16**, 3077 (1998).

<sup>20</sup>L. Novotny, E. J. Sanchez, and X. S. Xie, *Ultramicroscopy* **71**, 21 (1998).

<sup>21</sup>O. J. F. Martin and C. Girard, *Appl. Phys. Lett.* **70**, 705 (1997).

<sup>22</sup>J. P. Kottmann, O. J. F. Martin, D. R. Smith, and S. Schultz, *J. Microsc.* **202**, 60 (2000).

<sup>23</sup>L. Novotny, *Appl. Phys. Lett.* **69**, 3806 (1996).

<sup>24</sup>H. Gersen, M. F. Garcia Parajo, L. Novotny, J. A. Veerman, L. Kuipers, and N. F. van Hulst, *Phys. Rev. Lett.* **85**, 5312 (2000).

<sup>25</sup>W. Trabsinger, A. Kramer, M. Kreiter, B. Hecht, and U. P. Wild (unpublished).