Optical Nanoscopy with Excited State Saturation at Liquid Helium Temperatures

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Optical resolution of solid-state single quantum emitters at the nanometer scale is a challenging step towards the control of delocalized states formed by strongly and coherently interacting emitters. We developed a simple super-resolution optical microscopy method operating at cryogenic temperatures, which is based on optical saturation of the excited state of single fluorescent molecules with a doughnut-shaped beam. Sub-5 nm resolution is achieved with extremely low excitation intensities; a million times lower than those used in room temperature STED microscopy. We use organic fluorescent molecules embedded in well chosen solid matrices at liquid helium temperatures which behave as simple two-level systems with a fluorescence quantum yield close to unity, thus offering optical properties of a test-bench system for quantum optics [1-5]. Compared to super-localization approaches, our technique offers a unique opportunity to super-resolve single molecules having overlapping optical resonance frequencies, paving the way to the study of coherent interactions between single emitters and to the manipulation of their degree of entanglement.

The principle of the ESSat imaging technique is presented in Figure 1. A single molecule is scanned through a focused doughnut-shaped laser beam (LG01 Laguerre-Gaussian mode) tuned to zero-phonon line resonance while its fluorescence is recorded. For laser intensities much smaller than the saturation intensity I_s, *i.e.* in the linear regime, the fluorescence signal is proportional to the light intensity and the image of the molecule reproduces the intensity distribution of the doughnut beam. When the laser intensity is increased, the saturation of the molecular transition leads to a broadening of the fluorescence image and to a sharpening of the dip at the doughnut beam center. If the resolution is defined as the FWHM of the central dip, it will be given by the diffraction limit in the linear excitation regime, while it will drop well below this limit with the onset of optical saturation. Approximating the intensity distribution of the doughnut-beam central region by $I(r) = I_D \sin^2(N.A.\pi r/\lambda)$, the optical resolution is :

$$\Delta r = \frac{2\lambda}{\pi N.A.} Arc\sin\left(\frac{1}{\sqrt{2 + I_D / I_s}}\right) \quad (1),$$

where I_D is the intensity maximum of the doughnut beam, N.A. the numerical aperture of the microscope objective, λ the excitation wavelength. At high saturations ($I_d >> I_s$), the resolution Δr decreases as $\sqrt{I_s / I_D}$.

The host-guest system chosen in this experiment consists in dibenzanthanthrene (DBATT) molecules embedded in an octadecane Shpolskii matrix [6-7], where single molecules exhibit narrow ZPL widths determined by the inverse lifetime of the excited state (Full-Width at Half-Maximum FWHM~20MHz) at 2 Kelvin, and weak saturation intensities I_s of few W.cm^{-2}. Fluorescence images of a single DBATT molecule excited with a Gaussian beam and with a doughnut beam at different laser intensities are displayed in Figure 2a .The two lower images clearly show the expected sharpening of the central dip with increasing intensities of the doughnut beam.

Figure 2b and 2c show the Excited State Saturation (ESSat) image and the cross-sectional profile of a molecule recorded at an intensity I_D=13 kW.cm^{-2}, which is four orders of magnitude larger than I_s. In this case, we achieve an optical resolution of 4.4 nm [7], close

to the expected value of 3.8 nm determined by equation (1). This resolution is about a hundredth of the diffraction limit (380 nm) and approaches the size of the molecule (~1.5 nm). It is noteworthy that these resolutions are better than the best achieved at room temperature with color centers in diamond using STED [8] and ground state depletion [9] microscopies. Furthermore these resolutions are obtained with extremely low laser intensities (about ten kW/cm^2), more than five and more than three orders of magnitude weaker than those used at room temperature, respectively.

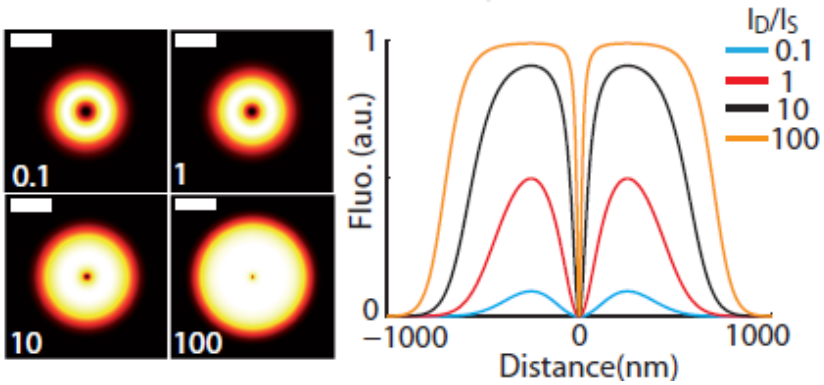

Figure 1: **Principle of ESSat microscopy** Fluorescence images and corresponding cross-section profiles calculated for a molecule excited at different doughnut beam intensities. Scale bars: 600 nm.

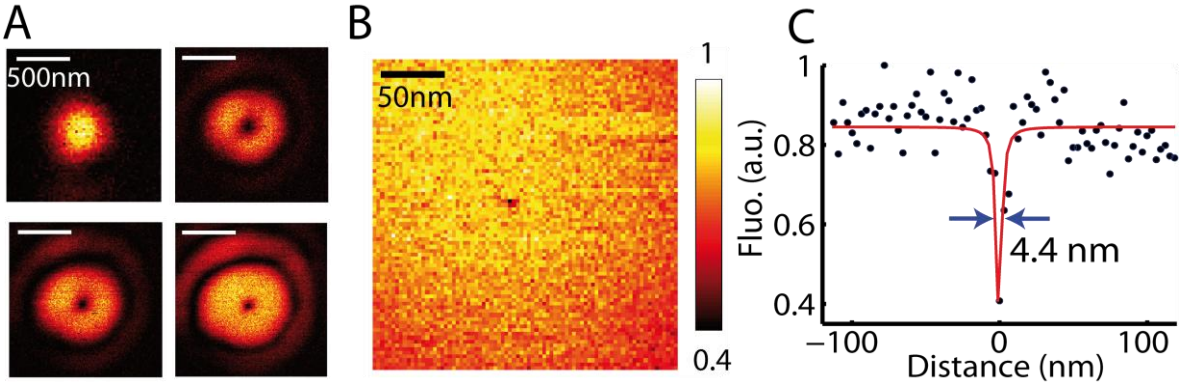

Figure 2 : **a,** Images of a single DBATT molecule obtained with a Gaussian beam (upper left image) and with the doughnut beam at different intensities (I_D = 0.8, 3.3 and 13 W.cm^{-2}, I_s= 3.8 W.cm^{-2}). **b,** Direct-ESSat image of a molecule recorded with I_D=13 kW.cm^{-2}. Pixel dwell time: 10 ms. **c,** Cross-sectional profile of the image (**b**), showing a resolution of 4.4 nm.

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