Ultra-sensitive fluorescence spectroscopy of isolated surface-adsorbed molecules using an optical nanofiber

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The strong radial confinement and the pronounced evanescent field of the guided light in optical nanofibers allow the controlled interaction with particles which are deposited near or on the fiber surface. We have demonstrated that surface absorption spectroscopy of molecules using nanofibers is several orders of magnitude more sensitive than conventional methods based on free beam absorption [1].

Using the guided mode of the nanofiber for excitation and fluorescence collection, we present spectroscopic measurements on 3,4,9,10-perylene-tetracarboxylic dianhydride molecules (PTCDA) at ambient conditions. The fluorescence light emitted by the molecules adsorbed on the fiber surface is efficiently coupled into the guided mode of the fiber yielding a high degree of sensitivity for spectroscopic studies. Surface coverages as small as 0.1 % of a compact monolayer still give rise to fluorescence spectra with a good signal to noise ratio. We perform interlaced measurements of absorption and fluorescence spectra in order to determine the respective surface coverage.
The characteristics of our system result in self-absorption, i.e., a partial reabsorption of the emitted fluorescence by circumjacent molecules along the nanofiber. While the high sensitivity of our method allows us to perform measurements in a regime of low surface coverages where self-absorption is negligible, it is taken into account for higher surface coverages.

Moreover, upon excitation at the low energy edge of the absorption spectrum, we observe fluorescence emission at wavelengths smaller than the excitation wavelength. We attribute the occurrence of this so-called anti-Stokes fluorescence to the thermalization of the internal degrees of freedom of the molecules with the fiber surface. In order to investigate the temperature dependence of this effect, we are currently setting up an apparatus for measurements in a cryogenic environment. The new setup together with the high sensitivity of our method would allow us to perform nanofiber-based spectroscopy on the single molecule level.

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References:

[1] F. Warken et al., Opt. Express **15**, 11952-11958 (2007)