

# Spectroscopy of ultrathin molecular films

## using tapered optical fibres

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### Introduction

The guided modes of ultrathin air-clad optical fibres with a diameter smaller than the wavelength of the guided light exhibit a pronounced evanescent field surrounding the fibre. Due to the strong radial confinement of these modes, the intensity of the evanescent field on the surface can reach the intensity of a maximally focussed beam. Therefore, molecules adsorbed on the surface of sub-wavelength optical fibres couple strongly to the evanescent field and can be detected by monitoring the changes of the fibre transmission. For a given surface coverage, the corresponding absorbance is significantly enhanced with respect to free-beam techniques [1], because the high intensity of the evanescent field can be maintained over the whole length of the ultrathin fibre which is typically on the order of a few millimetres. This allows us to perform high-sensitivity surface spectroscopy of molecules deposited on the fibre waist. For this purpose, 3,4,9,10-perylene-tetracarboxylic dianhydride molecules (PTCDA) were used due to their stability under evaporation at ambient conditions, their high quantum yield and the experimental and theoretical knowledge concerning their spectral characteristics. Moreover, PTCDA molecules significantly change their spectral properties depending on their arrangement on the surface. Therefore, these organic molecules are suitable as a model system for sensitivity studies.

### Experiment

For our experiments, we use the nanofibre waist of a tapered optical fibre (TOF). We fabricate the TOFs by stretching a standard optical single mode fibre while heating it with a travelling hydrogen/oxygen flame. Our computer controlled fibre pulling rig allows us to produce TOFs with a homogeneous waist diameter down to 100 nm and a typical extension of 1-10 mm. In the taper sections, the mode of the unstretched fibre is adiabatically transformed into the strongly guided mode of the ultrathin section and back, resulting in a highly efficient coupling of light into and out of the taper waist. For the presented measurements we used a 320 nm diameter nanofibre with a length of 1 mm yielding maximum sensitivity for absorption spectroscopy in the visible.

The measurements were performed at ambient conditions in a simple experimental setup as schematically depicted in Figure 1. The molecules are deposited on the fibre waist by placing a crucible with PTCDA crystals below the fibre and by heating it up to 300°C. By convection, the air carries sublimated molecules to the fibre waist where they are adsorbed.

## Application Note

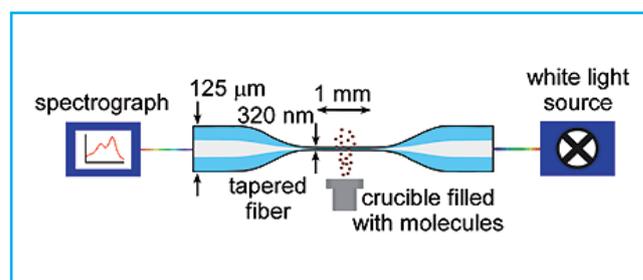


Figure 1: Scheme of the absorption spectroscopy setup.

The transmission of the fibre is measured using a conventional absorption spectrometer configuration with a tungsten white light source and a Shamrock SR 303i spectrograph with a Newton DU920N-BR-DD camera (both Andor Technology) as a detection system. After recording a reference spectrum without molecules the absorbance mode of the Andor Solis software can be used to take the absorption spectra of the deposited molecules.

### Results

Figure 2 displays a series of absorption spectra of molecules adsorbed on the fibre waist during deposition, recorded with an integration time of 1 s. We show representative spectra for six different surface coverages, ranging from 0.07 % to 0.86 % of a compact monolayer (ML) of flat lying PTCDA molecules. The surface coverages have been calculated directly from the measured absorbance [1].

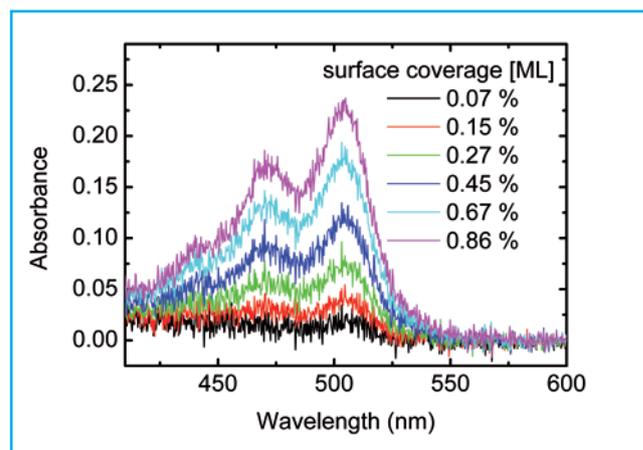


Figure 2: Absorption spectra of PTCDA molecules during deposition.

The absorption spectra show the typical vibronic progression for excitation between the ground and first excited electronic states of PTCDA.

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Due to the small value of the absorbance for low surface coverages, a high signal to noise ratio is required in order to measure the small changes in the fibre transmission. The back illuminated deep depletion sensor of the Newton camera yields a high quantum efficiency, while thermoelectrical cooling of the sensor reduces the dark noise. This improved the sensitivity of our method by about a factor of 5 in comparison to our previous results [1].

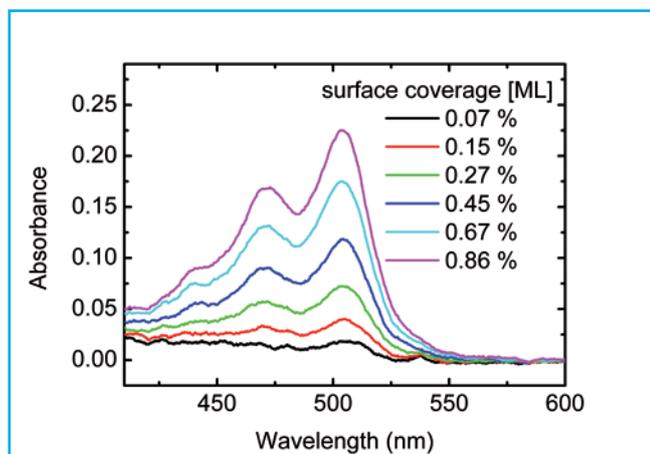


Figure 3: Smoothed absorption spectra of PTCDAs molecules during deposition.

Since the spectral resolution of 0.8 nm provided by the Shamrock spectrograph with a 300 l/mm grating is much higher than what is needed for resolving the characteristic features of the absorption spectra, smoothing the data to 6 nm effective spectral resolution averages out the residual fluctuations, as shown in Figure 3.

Beyond that, the possibility to adjust the resolution of the spectrograph by exchanging the grating opens the route to fibre-based high resolution spectroscopy as well.

### Reference

[1] F. Warken, E. Vetsch, D. Meschede, M. Sokolowski, and A. Rauschenbeutel, *Opt. Express*, 15, 11952-11958 (2007)

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