



Deliverable number 9 Addressing of Molecules

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Towards addressing and manipulation of single molecules, we learned to simultaneously measure, with ultra-high sensitivity, the fluorescence and absorption of molecules adsorbed on the fiber surface via the fiber guided mode at ambient conditions. Moreover, we managed us to design and to fabricate nanofibers with a transmission exceeding 80 % over a wavelength range of several hundred nanometers ["Design and optimization of broadband tapered optical fibers with a nanofiber waist", A. Stiebeiner, R. Garcia-Fernandez, and A. Rauschenbeutel, *Opt. Express*, **18**, 22677 (2010)].

Our method yields absorption and fluorescence spectra with a good signal to noise ratio for down to $\sim 10^6$ PTCDA molecules at room temperature. Under these conditions, thermal effects lead to strongly broadened molecular transitions. When cooling the fiber to cryogenic temperatures below 4 K, this thermal broadening could in principle be eliminated and much narrower lines should be obtainable with organic dye molecules embedded in organic crystals. Under these circumstances, our method would thus also allow us to carry out spectroscopic studies on single molecules ["Optical nanofibers and spectroscopy", R. Garcia-Fernandez, W. Alt, F. Bruse, C. Dan, K. Karapetyan, O. Rehband, A. Stiebeiner, U. Wiedemann, D. Meschede and A. Rauschenbeutel, accepted for publication in *Appl. Phys. B* (2011)]. With the purpose of reaching this single molecule sensitivity, we therefore set up a new apparatus integrating the ultrathin fiber in a cryogenic environment. Furthermore, we developed and implemented an immersion method for coating the nanofiber at ambient conditions with organic crystals doped with dye molecules. Spin coating cannot be used with nanofibers for technical reasons while crystal growth by sublimation might be an alternative if the quality of the host matrix should eventually turn out to be unsatisfactory. The dye molecule / matrix-system is the well-studied terylene embedded in p-terphenyl crystals.

The detection of single molecules requires a stable and reproducible method for cooling the coated nanofiber to cryogenic temperatures. We use a bath cryostat for this purpose and assure the thermalization of the nanofiber by means of helium buffer gas. However, the process turned out to be technically challenging. For almost one year, the nanofibers showed severe transmission drops when approaching liquid helium temperatures. Moreover, the nanofibers often broke during cooling

due to thermal contraction in combination with the different thermalization time constants of the nanofiber and of its mount. We solved these problems by using ultra-pure helium buffer gas which is slowly introduced when the rest of the setup has thermalized. Furthermore, we operate at a very low buffer gas pressure. This procedure recently enabled us to cool a coated nanofiber to 4 K while maintaining good optical properties.

This sample now allows us to record stable fluorescence excitation spectra of the molecular ensemble which exhibit narrow ($\approx 5 \text{ cm}^{-1}$ FMHM) spectral lines and which agree very well with what can be found in the literature. A first statistical analysis of the wings of the inhomogeneously broadened spectral lines allowed us to obtain preliminary results on the number of molecules interacting with the excitation laser (≈ 10) as well as on their homogenous linewidth ($\approx 1 \text{ GHz}$ FWHM). These very encouraging findings show that the realization of two of the main overall objectives of the workpackage, i.e., the development of single molecule detection methods and the realization of single molecule addressing within a molecular ensemble, are now within reach.

In addition to the above work carried out at JOGU Mainz, FHI also accomplished work toward the addressing of molecules within a molecular ensemble:

At FHI, we have coupled a coherent source of millimeter-wave radiation to our chip decelerator and measured a rotational spectrum of CO molecules that are less than $50 \mu\text{m}$ above the chip surface with a resolution of about half a MHz ["Driving rotational transitions in molecules on a chip", G. Santambrogio, S. A. Meek, M. J. Abel, L. M. Duffy, and G. Meijer, *Chem. Phys. Chem.* **12**, 1799 (2011)]. This radiation was then used to drive the transition in the $a^3\Pi_1, v=0$ state of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$. By applying a small magnetic field (≈ 10 Gauss), the individual M_F levels and the hyperfine structure of the ^{13}CO isotopologue can be resolved. This enabled us to switch the quantum state of molecules initially in a specific hyperfine and M_F state.

In this experiment, it was necessary to release the molecules from the traps to perform the pumping because the addressed levels have different Stark shifts and, as a result, the transition between them would be broadened by several hundred MHz in the inhomogeneous electric fields in the trap. However, we identified and are currently investigating the possibility of avoiding this shortcoming by using vibrational transitions instead of rotational transitions. In this case, the coupled vibrational states have similar Stark shifts (differing from one another by only ≈ 10 MHz over the relevant range of electric field strengths) and it should be possible to drive the transitions while the molecules are trapped.