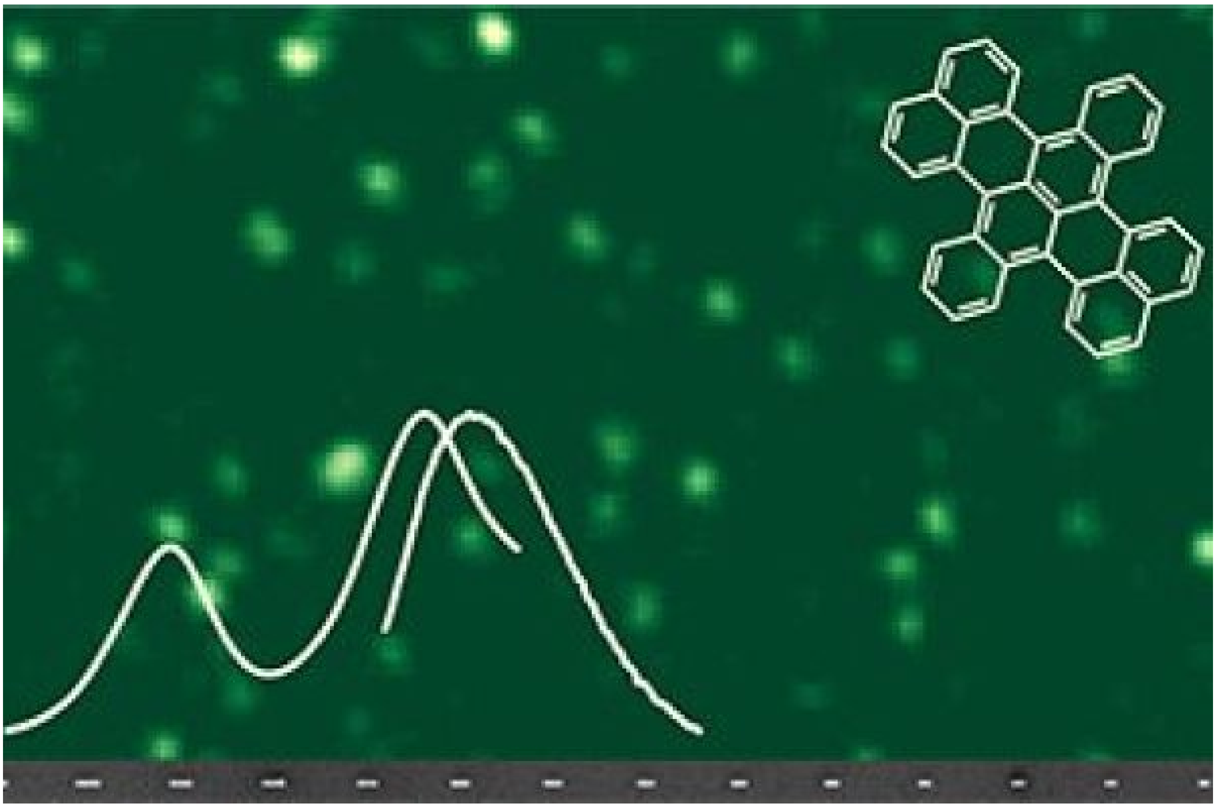

PhD Thesis Defense ESTHER GELLINGS 'Spectral Response of Individual Molecules and Nanoantennas with Two-Beam Excitation'

ESTHER GELLINGS

February 21, 2020

11:00

ICFO Auditorium

Friday, February 21, 2020, 11:00. ICFO Auditorium

ESTHER GELLINGS

Molecular Nanophotonics

ICFO-The Institute of Photonic Sciences

At room temperature, individual molecules can be found in different conformations due to intrinsic and extrinsic factors which are reflected in spectral variability. When detecting single molecules, the ensemble average is lifted and the spectral variability no longer obscured by the inhomogeneously broadened ensemble spectrum. Yet, only about one in every 10^7 photons interacts with the molecule, so that detection necessarily relies on background-free fluorescence. Fluorescence emission spectra only contain information about the ground state of molecules. In this thesis two new detection techniques are introduced to overcome this limitation: fluorescence excitation spectroscopy and stimulated emission detection. Moreover, the latter method is adapted to probe individual plasmonic nanoantennas.

First, Fourier transform excitation spectroscopy is introduced as a sensitive and robust method to probe the excited state manifold of single molecules. Fluorescence excitation and emission spectra complement each other, the former probing the excited state, and the latter the ground state manifold. Both spectra are routinely measured at cryogenic temperatures, though excitation spectroscopy has only recently reached single molecule sensitivity at room temperature. Here, Fourier transform spectroscopy is adapted to measure excitation spectra of single molecules. The working of the technique is demonstrated on synthetic dye molecules, where a spectral variability of more than 100nm has been uncovered. It is then applied to photosynthetic light-harvesting complexes LH2 that exhibit near-unity energy transfer efficiencies despite large environmental differences. Excitation spectra were routinely measured alongside emission spectra and it was found that variations in the two absorption bands B800 and B850 are uncorrelated, while the Stokes shift between the B850 and emission band becomes larger for more red-shifted complexes. The single complex Stokes shift was found to be about 20% larger than the ensemble result.

Second, a stimulated emission pump-probe setup with single molecule sensitivity is developed, which does not rely on fluorescence detection and can directly probe excited state dynamics. The necessary steps to achieve shot noise limited sensitivity will be explained. Stimulated emission depletion measurements are performed to verify the alignment of the setup and to find the best experimental parameters. The stimulated emission measurements achieved sensitivities of up to 10^-8, which in principle is sufficient for single molecule detection.

Third, single molecule techniques are applied to study the scattering and absorption of single plasmonic nanoantennas in focused Gaussian beams using the stimulated emission setup. In photothermal microscopy, the contribution of the scattering component and focal position to the signal has been largely ignored. Here, a comprehensive model including all relevant parameters is developed and systematically probed on nanoantennas of various lengths, positions in the focus, and surrounding media. It will be shown that the interaction of an antenna with a single probe beam results in a dispersive interference signal that mainly depends on the antenna dimensions, and that flips sign when passing through the antenna resonance. Adding a modulated pump beam that heats the antenna's environment leads to a combination of the probe beam scattering off the refractive index gradient around the nanoantenna, and the antenna resonance shifting, which affects the interference between the incident and scattered light. It will be demonstrated that both effects are relevant for antennas with a significant scattering cross-section and that photothermal measurements strongly depend on the photothermal properties of the surrounding medium and the antenna dimensions, which lead to strong signal variations around antenna resonance.

Friday, February 21, 2020, 11:00. ICFO Auditorium

Thesis Advisor: Prof Dr Niek van Hulst

Esther Gellings' Thesi Cover