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Fluorescent organic dye in a molecular monocrystal. Studies at the single-molecule level

In contrast to standard bulk experiments, which provide average parameters of a system under study experiments with single molecules remove ensemble averaging and enable observation of interactions between a molecule and its nano-environment.

Thesis refers to single molecule experiments and it consists of seven chapters. First Chapter presents a historical outline and methodology of single molecule experiments. Second Chapter contains main goal of the thesis. Third chapter contains description of the experimental apparatus. Chapters from 4 to 6 present experimental results. Thesis is briefly summarized in Chapter seven.

Chapter 4 presents study on spin-lattice relaxation (SLR) in single molecule of terrylene (Tr) embedded in *p*-terphenyl (*p*-T) crystal. SLR process has never been studied before at the single molecule level. The triplet state of Tr molecule is split in three sublevels (T_x, T_y i T_z) even in absence of an external magnetic field. Each sublevel has different population and depopulation rates, consequently, the fluorescence intensity correlation function of a single molecule in liquid helium temperature decays non-exponentially. When thermally activated SLR couples the spin sublevels the fluorescence intensity correlation function decays mono-exponentially. Lifetimes of the triplet spin sublevel in temperature range from 5 to 30 K were determined from the analysis of the fluorescence intensity correlation function. For a typical molecule this function (with a dominating short-lived component) changed from double-exponential to mono-exponential decay in a narrow temperature range between 15 K and 17,5 K. The fluorescence intensity correlation function for two untypical molecules (with a dominating long-lived component) changed in the range of temperatures between 19,5 and 20,5 K. Possible explanation for its anomalous correlation decay could be enhancement of a new intersystem crossing channel that selectively populates the spin sublevel T_{1Z} which suggests that untypical molecules may be distorted from the planar D_{2h} symmetry. The temperature-dependent SLR rate of such a molecule were estimated and it was shown that the SLR process can be governed by Orbach or Raman process.

Chapter 5 presents study on anomalous doping of molecular p-T crystal by Tr molecules, obtained by co-sublimation of both components. Confocal fluorescence images of Tr in *p*-T crystals, where the concentration of Tr is very low (10^{-12} M) consists of bright spots attributed to single molecules. Surprisingly similar image (bright spots on the dark background) was observed when Tr concentration was around $5 \cdot 10^{-8}$ M. Fluorescence excitation spectra recorded from the bright spots contained several new (not recorded before) additional lines, indicative of the presence of new sites occupied by Tr molecules in the crystal whose transition-dipole moments are aligned parallel in respect to the electric field vector of the excitation laser beam. Observed polarization of the fluorescence excitation spectra, blinking and bleaching in one step allowed us to attribute these spots to single molecules of terrylene anomalously embedded in the host crystal. The above conclusion was supported by quantum chemistry calculations.

Chapter 6 presents two new systems for single molecule studies: Tr molecules embedded in 2,3-dicholonaphtalene (2,3-DCN) and 2,3-dibromonaphtalene (2,3-DBN). 2,3-DCN and 2,3-DBN were synthesized, purified and its crystallographic structures were

determined. Single crystals of 23-DCN and 2,3-DBN doped with Tr were grown and spectroscopic studies were performed for both systems. It was found that the external heavy atom effect (resulting from the presence of the heavy atoms: chlorine and bromium) has little impact on the possibility of detection of single Tr molecules. Fluorescence excitation spectra of single Tr molecules in both systems had an extra vibronic line of ~180 cm^{-1} frequency, not observed before. Quantum-chemistry calculations indicated that this new line was the fingerprint of deformation of Tr molecules in the crystal structure, which lowered their symmetry from D_{2h} to C_{2h}, where the long axis of Tr resembles the shape of letter "S".