Molecular Optoelectronics:

On the Interaction of Molecular Junctions with Light

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Development of nano-fabrication and optical techniques at nanoscale led to tremendous progress in ability to detect and manipulate molecules on surfaces and in junctions. The main signal reported in the literature for molecular devices attached to macroscopic leads for a long time was current-voltage (conductance-voltage) characteristics. Standard junction tools (such as inelastic electron tunneling spectroscopy) are complemented by techniques probing molecular conduction junctions by optical means. Light and its interaction with molecules in junctions came to the forefront of research, resulting in appearance of a new branch of electronics at nanoscale – molecular optoelectronics.

Observation of optical response of a single molecule is possible only via enhancement of the molecular signal by a much stronger field of plasmons excited on nearby metallic surfaces. Thus molecular nanoplasmronics (a combination of nanoplasmronics and molecular response to the generated field) is a natural ingredient in any theoretical study of molecular junctions interaction with light. The other challenge to theory is formulation of techniques capable of proper description of optical response in open non-equilibrium molecular systems.

Within simple models we present simulations of time-dependent transport and optical response of molecular junctions driven by external laser fields. First we present results of simulations employing combination of nonequilibrium Green functions (NEGF) for description of quantum transport and finite difference time-domain (FDTD) approach for numerical integration of Maxwell equations on a spatial grid. Employing realistic parameters we show that a self-consistent treatment of the local field formation is crucial for the proper description of the junction transport characteristics. Then we discuss a possible route for quantum description of the coupling between plasmons and molecular excitons in junctions. In particular, we employ a pseudoparticle nonequilibrium Green function (PP-NEGF) formalism to study the sensitivity of the molecule-plasmon Fano resonance to junction bias and intra-molecular interactions, and compare our predictions to previous studies.

In the second part of the talk we describe our attempts to generalize standard molecular spectroscopy tools to the realm of molecular junctions. In particular, within simple models we consider intra-molecular and charge-transfer contributions to Raman spectroscopy of molecular junction, time-dependent correlations between Stokes signal and conductance, and observation of Raman staircase during laser induced fusion of nanoparticles. We also discuss a concept of "effective temperature", its relevance in representation of bias-induced heating, and ability of Raman measurements to provide information on the latter. Finally, we present a formulation of Raman scattering in current carrying molecular junctions based on a many-body state representation of the molecule. We illustrate the presented formulation by first principles simulations of Raman response in an OPV3 molecular junction, and compare results of the simulations with available experimental data.