Plasmonics in the infrared and vibrational signal enhancement

Prof. Dr. Annemarie Pucci

Kirchhoff-Institut für Physik, Universität Heidelberg

For about 50 years, since the observation of the "anomalous transmission", infrared (IR) vibrational signal enhancement (by up to three orders of magnitude) is considered as a phenomenon that involves adsorbates on metal-particle aggregates and, as it became clarified about 30 years later, can be modelled by effective media theories if the particles are small enough. The observed vibrational line-shape asymmetry in these surface-enhanced IR absorption (SEIRA) spectra can be simulated in that way perfectly. Less than 10 years ago, the much higher "SEIRA" (by almost six orders of magnitude) from molecules on the apex of metal nanowires with plasmonic resonances at the vibrational frequencies was detected and identified as a Fano effect with the plasmonic excitation spectrum as the background. The Fano-type coupling between this background and the vibrationally induced dipoles becomes obvious upon detuning of both the excitation spectra, which changes the line-shape asymmetry and the signal size up to a vanishing signal at complete detuning. The huge signal enhancement enables sensing with a chemical identification by means of the rich vibrational fingerprints of the molecules, whereas the tiny absorption cross sections of molecular vibrations usually hamper the sensing applications. The IR-signal enhancement and the vibrational line shape strongly depend on the IR-optical properties of the metal particles. Related to the size of the particles and the intrinsic electronic damping, the resonant plasmonic scattering plays an important role for the SEIRA enhancement.