Nanoplasmonics and surface enhanced spectroscopy

Spectroscopy of molecules on the crystal surface: many particles approach and experiment

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In the present work we study the influence of crystal surface (metal or semiconductor) on the absorption of a molecule adsorbed on this surface. We investigate the influence of different parameters of molecule-crystal system on the absorption and Raman spectra (RS). It is obvious that micro-approach can give understanding of the most principal mechanisms responsible for SERS. In the metal the surface excitations are as a rule related to plasmons. However, there are also excitations of higher frequency that can influence on the behavior of an adsorbed molecule. These excitations correspond to interband transitions. It is known that interband transitions in metal are similar to the ones in semiconductors such as Ge, Si etc., therefore the effect of strong intermixing of states is very important. The intermixing is strong at resonance between molecular excitations and interband transitions of electrons in crystal.

In the present work the response of molecule adsorbed on the surface of crystal is studied by using the many particle approach, taking into account the interaction between electrons of a molecule with electrons in crystal as well as the interactions of electrons in crystal. It is supposed that the adsorbed molecules do not interact directly, while there is an indirect interaction of the absorbed molecules involving the electrons of a crystal. Moreover, electrons in a molecule interact with intrinsic molecular vibrations. Due to the arbitrary distribution of molecules on the crystal surface the symmetry of the system molecule-crystal film is low, C_1, and therefore all selection rules for absorption and Raman scattering processes are identical. Numerical simulation of the frequency dependence of a RS, obtained in the framework of micro-approach using Green function method showed that at certain ratios between the energy of molecular excitation, gap between electron bands of crystal film and position of Fermi level the significant enhancement of absorption can occur in a complex molecule-crystal film as compared with a free molecule. The additional experiments in which the parameters of molecule and crystal film would be correctly taken into account are necessary.