Nanoplasmonics and surface enhanced spectroscopy

Absorption by molecule adsorbed on surface of crystal: Many particles approach

A.M. Yaremko¹, V.V. Koroteev¹, Yu.A. Romanyuk¹, V.O. Yukhymchuk¹

¹ Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine. *E-mail: Romanyuk_yu@ukr:net*

During many years SERS method is very actively used for study of the surface solids. This method is characterized by very high sensitivity but up to now many discussions take place concern to nature of this phenomenon.

Almost all early studies were performed with pyridine on roughened silver electrodes [1] but then in work [2] it was shown that for gold and copper the SERS can be also great. Now such effect has been reported for approximately a hundred molecules adsorbed on silver, gold, copper and other metals, though for some of them the enhancement have been not so great. The most significant enhancement was observed for metals Ag, Au, Cu.

In the present work we note that excitations arising in metal are not restricted only by plasmons. There are more high frequencies interband transitions therefore the influence of the metal electrons on adsorbed molecule depends on both the molecule parameters and the studied frequency region. One can note that interband transitions in metal are similar to ones in semiconductors such as Ge , Si etc., therefore the effect of strong intermixing of states at resonance conditions between excitations in molecule and interband electrons transitions of metal must occur too.

We first study the influence of crystal surface on the absorbability of molecule adsorbed on its surface by study the influence of different parameters complex molecule-crystal on the absorption value. It was shown that all molecules adsorbed on surface can interact one with another by electron system of crystal, what result in to significant enhancement of response molecule on the incident EM field. Because molecules are arbitrary distributed on the crystal surface the symmetry system "molecule-crystal" is low enough, (C_1) , therefore all excitations can be

observed both in Raman and absorption spectra. Theoretical results are compared with experiment and parameters responsible for SERS are estimated.

1. Fleischmann M., P.J. Hendra and A.J. McQuillan, Raman spectra of pyridine adsorbed at a silver electrode // Chem. Phys. Lett. -1974.-26.-P. 163-166.

2. *U. Wenning, B. Pettinger and H. Wetzel,* Angular-resolved Raman spectroscopy of pyridine on copper and gold electrodes // Chem. Phys. Letters-1980.- **70.-** P. 49-54.