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Tunnel electron-vibrational spectroscopy of adsorbed complexes on the surface of ultra-small metal nanoparticles

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Ultra-small nanoparticles (USNP) with sizes less than 10 nm have unique physical, chemical, and biochemical properties and presently attract an increased general interest.

These nanoobjects are intensively studied by many methods, including probe ones with the use of a scanning tunnel microscopy (STM.) In the STM experiments, the structural and dynamical information on the nanoparticles (NPs) is contained in the tunneling spectra, specifically in the V-dependences of dnJ/dVn for n = 0 or 1, where J is current, V is the nanojunction voltage, and z=const is the distance between the tip and NP. For the properly choosen measurement conditions, these dependences show characteristic features, e.g. steps, bends, and maxima, which contain information on the energy E_n of electronic levels, vibrational quanta, electron-vibration interaction constant, etc. [1,2].

In the tunneling spectra of the USNP, the one-electron tunneling effects (Coulomb blockade and Coulomb staircases (oscillations)) can be observed even at room temperatures [3]. In the tunneling spectra of atomic particles adsorbed on the surface of USNPs, which are intensively studied with the object of solving nanocatalysis problems (see e.g. [4]), the resonance and Coulomb features often coexist. In those cases, the known concepts of resonance electron-vibrational tunnel spectroscopy may be insufficient on explaining this fact. The physical nature of the tunnel- current oscillations that can be associated both with vibrational transitions of adatoms and changes in the USNP charge state cannot be recognized. It should be keep in mind that, due to the fact that the ranges of characteristic vibrational energies of adatoms (0.1-0.6 eV) and the charging energies of nanoparticles with sizes from 2 to 10 nm coinside, the equidistant series of resonance singularities, e.g., Coulomb staircases (oscillations) and vibrational spectra, are indistinguishable in the absence of an additional information.

The model of tunnel resonant electronic transitions occurring in a nanojunction, with the A-USNP complex (A-adsorbed particle) situated under the STM tip, provides a simple explanation for the principal experimentally established features and dependencies of the tunneling spectra of metallic nanoparticles (Au, Pt, Ni, Cu) deposited on pyrolytic graphite. As a consequence, this model makes it possible to formulate simple algorithms for recognizing the Coulomb and vibrational oscillations that occur in the tunneling spectra by the biresonance (in the case of a metallic NP) or three-resonance mechanism (for a semiconductor NP). As follows from the model developed by us, the spectra in both cases have the form of equidistant bipolar series of negative differential resistances.

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