物性研究所　表面セミナー
「走査型非弾性トンネル分光の最前線」
7月31日（木）午前10時～12時：物性研究所6F講義室

上羽弘　教授　（富山大学工学部）

Relation between inelastic tunneling current and vibrational heating of single adsorbates on metal surfaces

Relation between inelastic tunneling current (ITC) and vibrational heating, i.e., effective vibrational temperature due to vibrational excitation of single adsorbates by tunneling electrons with canning tunneling microscope (STM), is studied on the basis of the kinetic equation for the vibrational population number of adsorbates using the Keldysh Green's function method and an adsorbate-induced resonance model for an inelastic electron tunneling. The solution of the kinetic equation gives the stationary nonequiblium vibrational distribution function, from which a general formula of the vibrational heating due to inelastic electron tunneling is derived. It is shown that the vibrational generation rate as a function of the bias voltage is given by the absolute value of the inelastic tunneling current under some extreme conditions. Based on the numerical calculations including self-consistently determined vibrational distribution function and the vibrational density of states characterized by the vibrational relaxation due to electron-hole pair excitations, the influence of vibrational relaxation on ITC and on the vibrational generation rate is discussed in conjunction with a possible deviation from a simple power-law dependence on the bias voltage or the tunneling current in the vicinity of the threshold for the vibrational excitation.

米田忠弘　教授（東北大学多元科学研）

Inelastic tunneling spectroscopy of adsorbed molecules; The variation of vibration peaks with the change of bonding configuration and target molecular orbitals

T. Komeda*, Y. Kim, Y. Sainoo, H. Fukidome, M. Kawai RIKEN (* currently IMRAM, Tohoku Univ.)

Inelastic tunneling spectroscopy (IETS) using scanning tunneling microscopy (STM) can be an ultimate analytical tool which gives vibrational spectroscopy of a single molecule. However, the detection of vibrational modes is case sensitive, and a clear selection rule is not established yet. In this paper, we combine the molecule manipulation technique and IETS measurement to understand the correlation of the molecule's bonding configuration and the detection of the vibrational mode.

Hydrocarbon molecules were dosed on Pd(110) surface and the IETS measurements were done at 4.7 K in the ultra high vacuum chamber with the use of lock-in amplifier technique. IETS spectra obtained on butyne (CH_3-C=C-CH_3), trans-2-butene (C_4H_8), and cis-2-butene (C_4H_8) molecules have been measured. The spectra on the molecule show distinct feature at the marks whose energy corresponds to the ν(C-H) mode. These distinct ν(C-H) stretching features are, however, easily reduced in intensity with the change of the bonding configuration. The STM image of the butyne has a dumbbell-like feature.

By pushing this molecule by the STM tip with reducing the tip-substrate distance, it can be converted into a ball-like feature. We consider this is due to the bonding site change of the molecule from the short bridge site (C=C parallel to the surface) to the μ_2 site (pseudo three-fold hollow site, C=C inclined) or the trough site. The change of IETS spectra corresponding to the bonding-site change was clearly observed. Apparently the intensity of ν(C-H) is much reduced in the ball-like molecule compared to the dumbbell-like molecule. We consider that the main contribution to the reduction of ν(C-H) mode is the inclination of C=C in the ball-like molecule, which allows the s-like electronic state of the tip can be couple with the LUMO state of the molecule (b_2 symmetry in C_{2v} configuration) which change the interfering condition with other molecule orbitals followed by the reduction of the ν(C-H) feature. Next we show intriguing IETS spectra revealing unusually strong features on an isolated water molecule on Pd(110) surface, which shows an strong evidence of the coupling between the vibration modes and electronic state of molecules. The conductance of the water monomer shows qualitative change when electrons are dosed into the contours of the different molecular orbitals.