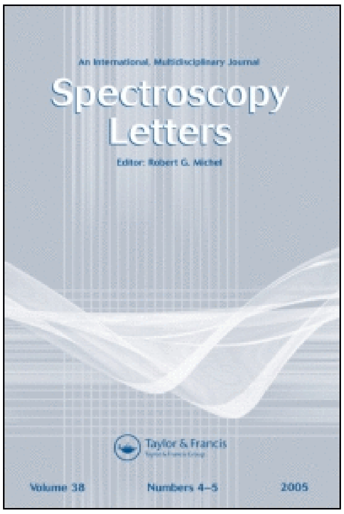

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SCANNING TUNNELING VIBRATIONAL SPECTROSCOPY

KEY WORDS: Scanning Tunneling Spectroscopy, Vibrational Spectra

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ABSTRACT

A new method for studying of vibronic transitions by scanning tunneling microscope ("intraresonator electron-vibronic scanning tunneling spectroscopy of adsorbates") is proposed. Results of experiments carried out by STM "Omicron" where electron-vibronic series of field emission resonances were observed are presented. Frequencies of the resonances correspond to ones of local vibrations of titan oxide and adsorbed hydroxil particles.

INTRODUCTION

The searching for the STM-methods for observing and studying the elementary inelastic processes such as the excitation of local modes (or local electronic transitions) is among the primary topics of the modern probe microscopy. The development of the nano-scale analogs of the tunneling inelastic spectroscopy [1], Auger spectroscopy, electron energy-loss spectroscopy [2, 3], and other well-elaborated macroscopic methods of investigation of the solid surface would enable one to gain a unique information on the structure and properties of the isolated adsorption complexes functioning as the "active centers" in catalysis [4] and reveal the dynamics of the elementary acts and transformations in such centers.

The researches into the new methods of the dynamic tunneling spectroscopy (inelastic tunneling [5–10], electron-emission [11], or "atomic resolution" EPR spectroscopy [12–14]) are in progress in many laboratories. The purpose of this communication is to formulate the basic theoretical concepts of the dynamics of electronic transitions in the scanning tunneling microscope operating in a field-emission mode [15–17] and present new experimental data that demonstrate the clearly defined effects caused by the vibrational excitation of the isolated adsorbed particles. The novel scanning tunneling vibrational spectroscopy can be based on this effects.

INTRARESONATOR VIBRATIONAL SPECTROSCOPY OF ADSORBATES

It is well-known (see. e.g., [15–17]) that the STM currents exhibit resonance features when STM operates in the field-emission mode (i.e., at the bias voltage $V > \phi$, where ϕ is the tip work function). These features can be observed by measuring either the volt-ampere characteristic (or conductivity) on V (at $d = const$ or $F = V/d = const$) or on d (at $V = const$). The resonance behavior of the nanocontact tunnel currents can be explained by the appearance of the standing electron waves in the space resonator formed by the field barrier and surface (the sample's voltage polarity is assumed to be positive).

The spectrum of standing waves (field-emission resonances (FERs)) and the V_n (or $d_n, n = 1, 2, 3, ...$ is the number of resonance) values corresponding to the peculiarities of the STM currents are determined by the geometry of the electronic STM resonator and the coefficient of electron reflection from the surface, K. These values are equal to the roots of equation

$$V = \phi + E_n(V, d), \quad e = \hbar = m = 1, \tag{1}$$

which is nothing but the condition for the coincidence of the standing wave energy levels with the tip Fermi level and $E_n(V, d)$ is the n-th resonance energy measured from the surface vacuum level. The electronic frequencies $\omega_n = E_{n+1} - E_n$ (and, correspondingly, $u_n = V_{n+1} - V_n$) are estimated at $\omega_n \sim 1 - 2$ eV for the typical values $V \sim 10$ V and $d \sim 15$ Å . The decay widths $\Gamma_n(V, d)$ of the FERs are determined by the electron residence times $\tau_n \sim \Gamma_n^{-1}$ in the resonator and can vary over wide limits

$$\Gamma_n(V, d) \sim \omega_n(V, d)(1 - K)^{-1}, \quad K < 1. \tag{2}$$

The shape of a resonance feature in the $J(V)$ curve is determined by the four time parameters, among which are the characteristic times of electron transition from the tip to the resonator ($(\Gamma_t(V,d)^{-1})$, from the resonator to the sample ($(\Gamma_s(V,d)^{-1})$, and the corresponding tunneling times $((\frac{\partial}{\partial E}\ln\Gamma_{s,t}(V,d))^{-1})$. Indeed, let us consider the function

$$f(x,a,b,\alpha,\beta) = \frac{ab\exp(-(\alpha+\beta)x)}{a\exp(-\alpha x)+b\exp(-\beta x)}\left(\frac{\pi}{2}+\arctan\frac{x}{a\exp(-\alpha x)+b\exp(-\beta x)}\right), \qquad (3)$$

that approximates the $J(V)$ dependence in the single-resonance approximation ($\Gamma_s = a\exp(-\alpha x)$, $\Gamma_t = b\exp(-\beta x)$, $|V - V_n| << V_{n+1} - V_n$). Two limiting situations differing from one another in the tunneling times are illustrated by the functions $f(x,a,b,\alpha,\beta)$ presented in Fig. 1 as an example.

One can see from these data that at short tunneling times the resonance features appear as the steps in the $J(V)$ curve. In the limit of long tunneling times, the scale of the feature in the V-axis is determined by the $\Gamma(V,d) = \Gamma_s(V,d) + \Gamma_t(V,d)$ value, i.e., by the electron residence time in the resonator.

The transition of an electron from the tip into the standing-wave state results in the electron localization in the vicinity of the surface, at a distance of $x \sim (d/V)^{1/3}n^{2/3}$ from it. For the typical values $V \sim 10$ V and $d \sim 15$ Å , one has $x \sim 2$ Å $n^{2/3}$, so that at $n \sim 1$ the electron entrapping into resonator is accompanied by an appreciable change in the force field in which the surface (or adsorbed) atoms moves, i.e., the vibrational subsystem of the contact suffers the "shake-up" at the instant of capture, thereby the vibrational transitions are induced. The second shake-up (at the instant of electron transition from the resonator to the sample) excites the vibrational subsystem a second time, so that not only the single-quantum but also many- quantum transitions can occur in the vibrational subsystem.

For the isolated electronic resonance, the effect of vibrational transitions on the volt-ampere characteristic of the tunneling nanocontact is described by equation (the difference between the electron densities at the tip and surface is ignored)

$$J(V,d) = \sum_{u_i} f(u_i) \sum_{u_f} J_{u_i,u_f}(V,d), \qquad (4)$$

where $u_{i(f)}$ is the initial (final) vibrational quantum number, $f(u_i)$ is the stationary distribution of the quantum vibrational subsystem, and $J_{u_i,u_f}(V,d)$ is the tunnel electron current corresponding to the inelastic transition accompanied by formation the vibrational subsystem in the u_f-th state,

$$J_{u_i,u_f}(V,d) = const\int^{E_F} D_{u_i,u_f}(E,V,d)dE, \;\; V \gg \omega, \qquad (5)$$

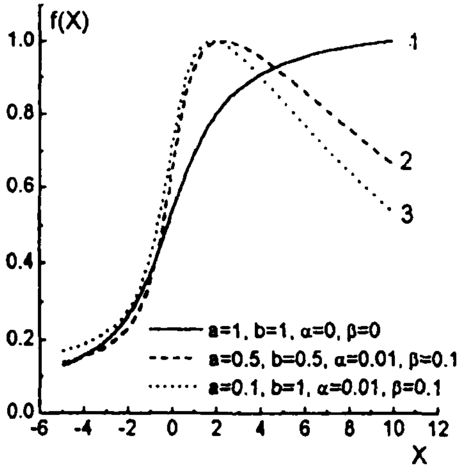

Fig. 1. The $f(x, a, b, \alpha, \beta)$ function for different values of parameters.

$D_{u_i,u_f}(E, V, d)$ is the probability of the electron inelastic resonance tunneling from the state with energy E, ω is the frequency of the local mode, and E_F is the tip Fermi level. The analytic expression for $D_{u_i,u_f}(E, V, d)$ was obtained in [18],

$$D_{u_i,u_f}(E, V, d) = \left|\langle u_i|\gamma_s(E_{u_i} - \hat{H}_u - \hat{\Omega})^{-1}\gamma_t|u_f\rangle\right|^2, \quad E_{u_i} = E+\omega(u_i+1/2). \quad (6)$$

In this expression, γ_s is the transition amplitude (dependent on the vibrational coordinates) for the electron transition from the tip to the resonator, γ_s is the same for the electron transition from the resonator to the sample, $\hat{H}_u$ is the Hamiltonian of the vibrational subsystem, and $\hat{\Omega}$ is the optical potential, whose imaginary part determines the electron residence time in the resonator, $|u\rangle$ is vibrational wave function.

The detailed analysis of the peculiarities of the function $J(V, d)$, determined by formulas (4) and (5), is beyond the scope of this work. We restrict ourselves only by two limiting situations, those of the short-lived ($\Gamma \sim \omega$) and long-lived ($\Gamma \ll \omega$) resonances.

If $\Gamma \sim \omega$, $\Gamma \frac{\partial}{\partial E} \ln \Gamma_{s,t} \ll 1$, $f(u_i) = \delta_{u_i,0}$, then it follows from equations (4)-(6) that

$$\frac{\partial J}{\partial V} \sim \sum_{u_f} D_{u_f,0}(V) \sim \mathrm{Im} A_{00}(V) \quad (7)$$

where $A_{00}(V)$ is the resonance elastic tunneling amplitude. For the model of displaced oscillators, the analytic expression for $A_{00}(V)$ is known [19]:

$$A_{00}(V) = -i\Gamma \exp(-\alpha) \int_0^\infty dt \exp(i\xi t + \alpha \exp(-i\omega t)), \; \xi = V - E_n + i\Gamma/2 \quad (8)$$

(In this expression, α is the electron-vibronic coupling constant). The function $\mathrm{Im}A_{00}(V)$ is displayed in Figs. 2 and 3 for different values of the α and Γ/ω parameters.

The results presented show that the resonance maximum takes the Lorentzian form for $\alpha = 0$. The vibrational transitions ($\alpha \neq 0$) shift and broaden the resonance maximum and give rise to the oscillatory structure (with period of $\sim \omega$) at its wings. The smaller the ratio of the decay rate to the vibrational frequency, the more pronounced the structure.

The results obtained can be compared with the experimental data presented in [15], where, in particular, the FER spectrum was measured for the disordered adsorption of oxygen on Ni(100) (Fig. 3b). One can distinguish rather regular small-scale oscillations in the first three broadened maxima whose shapes are close to the theoretical curves obtained by formulas (7) and (8). In our opinion, these oscillations can be due to the vibrational transitions of adsorbates. Smearing of this structure and narrowing of the maxima with increase in n is in agreement with the theoretical results presented in Fig.3a (calculations were carried out for $\alpha(n, F) = \alpha(1, F)/n^{4/3}, \quad \alpha(1, F) = 1$).

The other limiting case corresponds to the long-lived FERs and long tunneling times. In this case, the resonance peaks (see Fig.1) are observed in the curves corresponding to the total current. One has

$$J(V,d) = c \int^{E_F} \sum_{u_i} f(u_i) \sum_{u} \frac{\Gamma^t_n(u_i, u, V, d)\, \Gamma^s_n(u, V, d)}{(E + \omega_0(u_i + 1/2) - E_n(u, V, d))^2 + \Gamma^2_n(u, V, d)} dE, \quad (9)$$

In this expression, $c = const$, $V \gg \omega$, E_F is the tip Fermi level, ω_0 is the frequency of the vibrational subsystem of the STM resonator (surface local mode or vibrations of an adsorbed particle),

$$E_n(u, V, d) = E_n(V, d) + \omega_n(V, d)(u + 1/2), \quad u = 0, 1, 2, \ldots \quad (10)$$

are the energy levels of the complex formed by the entrapped electron and vibrational degrees of freedom of the resonator, $\omega_n(V, d)$ is the vibrational frequency of the complex, $\Gamma^t_n(u_i, u, V, d)$ is the probability of the electron

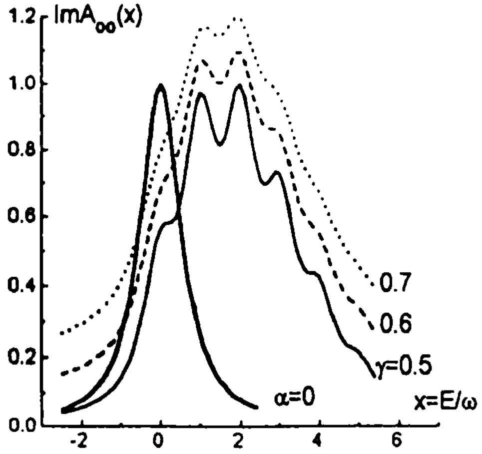

Fig.2. Imaginary part of $A_{00}(x)$ for different values of the γ parameter at $\alpha = 1$. The imaginary part of $A_{00}(x)$ at $\alpha = 0$ is given for comparision.

transition from the tip to the resonator, $\Gamma_n^s(u, V, d)$ is the probability of the electron transition to the sample, $(\Gamma_n^s(u, V, d) = \sum_{u_f} \Gamma_n^s(u, u_f, V, d)$, $\Gamma_n^s(u, u_f, V, d)$ is the partial probability of the (n, u) complex decaying as a result of the transition to the u_f state of the vibrational subsystem, $\Gamma_n(u, V, d) = (\Gamma_n^s(u, V, d) + \Gamma_n^t(u, V, d))$ is the inverse electron residence time in the resonator, and $\Gamma_n^t(u, V, d) = \sum_{u_i} \Gamma_n^t(u_i, u, V, d))$.

Obviously, the energy parameters of the complex depend on V and d. As a result, the STM currents $J(V, d)$ exhibit the resonance features whose spectra are determined by the roots of equation

$$V = \phi - \omega_0(u_i + 1/2) - E_n(u, V, d), \tag{11}$$

which specifies the condition for coincidence of the electron-vibronic level of the complex with the tip Fermi level.

The vibrational frequencies of the complex must be close to those of the local modes of the isolated sample (i.e., $\omega_0 \approx \omega_n(V, d)$), because the STM field is ordinarily much lesser than the atomic field ($F \approx V/d \leq 10^{-2}$ a.u. at $V \leq 10$ V and $d \geq 10$Å). The $E_n(V, d)$ and $\Gamma_n^{s,t}(V, d)$ dependences play the dominant role in the formation of the peculiarities of the $J(V, d)$ functions.

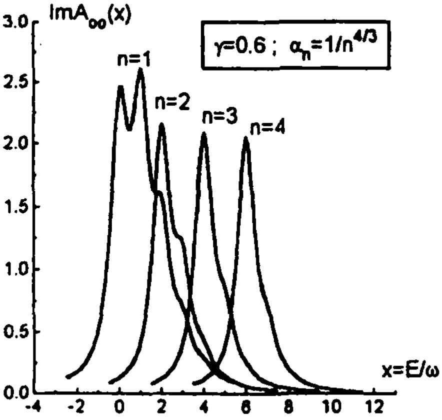

Fig.3a. Imaginary part of $A_{00}(x)$ for different n values at $\gamma = 0.6$.

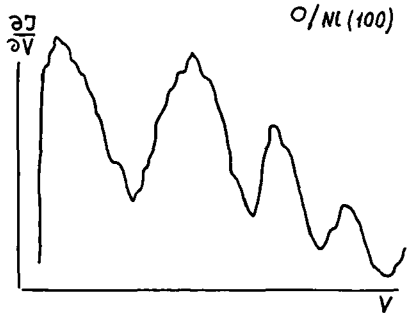

Fig.3b. FER spectrum for the Ni(100) surface covered with the disordered submonolayer of adsorbed oxygen. Data from [15].

The $E_n(V,d)$ energies are determined by the geometry of the STM resonator and coefficient of electron reflection from the surface. For the simplest 1D triangular potential well model one has

$$E_n(V) \approx \left(\frac{cVn}{d}\right)^{2/3}, \quad c \sim 1 \tag{12}$$

The functions $\Gamma_n^t(V,d)$ are determined by the permeability of the field barrier between the STM resonator and tip,

$$\Gamma^t_n(V,d) \sim \exp\left(-\frac{4\phi^{3/2}d}{3V}\right).$$

The functions $\Gamma^s_n(V,d)$ are determined by the transmission coefficient of an electron passing through the surface layers of the sample.

Let us set $d = const$ for definiteness. Then it follows from (11) and (12) that the spectrum of the resonance values of V is:

$$V_n(u,u_i) = \phi + \alpha n^{2/3} + \omega_0(u-u_i),\ V_n(u,u_i) - \phi \ll \phi \qquad (13)$$
$$(n = 1,2,\dots;\ u,u_i = 0,1,2,\dots)$$

$$\alpha \approx \left(c\frac{\phi}{d}\right)^{2/3}.$$

The frequencies ω_0 of the surface modes correspond to the energies $\sim 0.05 - 0.5$ eV, while the electrons frequencies are $\sim 1 - 2$ eV for $n \sim 1$. So when STM operates in a field-emission mode the resonance spectrum of $J(V)$-dependence takes the form of electronic-vibrational bands exhibiting both the "Stokes" ($u > u_i$) and "anti-Stokes" ($u < u_i$) lines.

VIBRATIONAL TRANSITIONS IN STM EXPERIMENTS

On searching of the electronic-vibrational FER bands we have performed systematic measurements of the $J(V)$ and $\partial J(V)/\partial V$ dependences for the polycrystalline titanium and gold samples by scanning their surfaces with the platinum tip of STM "Omicron" in air and in vacuum. The spectroscopic measurements were performed in a $d = const$ mode at different surface points 0.1 - 50 Å apart. The d values were chosen from the condition $J(V_{max}) = J_0$, and the V_{max} values varied within 10 V. The J_0 currents ranged from 4 to 20 nA. The step variations of voltage V were at intervals from 0.05 V, which sufficed to detect the bands, to 0.01 V, which was necessary for resolving the fine (vibrational) structure of the bands. In the latter case, the data were averaged over several (from two to four) neighboring V points to eliminate the small-scale current fluctuations. It was found that at small J_0 the resonance features could be detected only at sufficiently high voltages V. (At $J_0 > 7$ nA, the resonances, as a rule, were invariably observed over the whole range of V values from $\phi_{Pt} \sim 5$ eV to 10 eV). Examples of the $J(V)$ and $\partial J(V)/\partial V$ dependences measured in air and in vacuum are shown in Figs.4-6.

TOPICS IN HETEROGENEOUS CATALYSIS (NECESSITY FOR THE LOCAL DYNAMICAL METHOD)

One of the most promising applications of the nano-scale probe microscopy technique is associated with the solution of the fundamental problems of

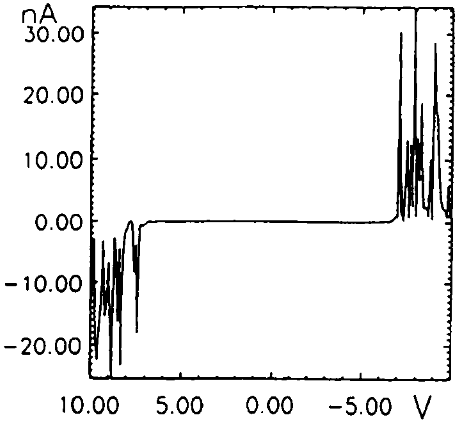

Fig.4. The $J(V)$ curve for titanium in air.

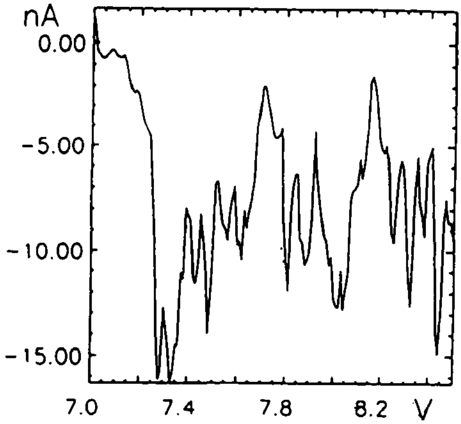

Fig.5. FER electronic-vibrational progressions (titanium in air).

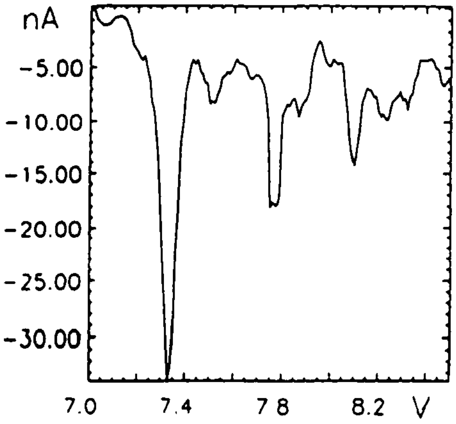

Fig.6. High-frequency FER vibrational progression (titanium in air).

heterogeneous catalysis. This is the only method that can be used for gaining the information that can be helpful in elucidating, at a microscopic level, the mechanisms of those catalytic chemical reactions which, even in the simplest systems, proceed through the intermediacy of a number of sequential elementary processes including various interaction acts that occur between the surface and gas-phase species on the solid-state surfaces.

Over the several past decades, the adsorption and desorption of particles, their migration and transformations on the surface and upon interaction with the free particles have been studied by a variety of methods. However, these method share a common and crucial disadvantage: all of them provide only the "averaged" information and refer to the macroscopic ensembles of the particles ordinarily no less than 10^{10} in number. In such ensembles, the number of heterogeneous complexes, i.e., groups of different nonequivalent atoms, is also very high. Different stages of chemical reactions can be dominated by the essentially different active centers (complexes), whose composition and structure are presently, as a rule, unknown. For this reason, the concept of a unified, for a given chemical reaction, active center, though often used in the heterogeneous macrokinetics, is, broadly speaking, meaningless.

Further progress of the local dynamical methods, to which the scanning tunneling vibrational spectroscopy also belongs, can provide a unique information on the structure and properties of the heterogeneous complexes that can take diversified, though strictly fixed (according to the data of topographic measurements), configurations. The vibrational spectra can be used not only for the "identification" of the particles, i.e., for a local chemical analysis of the surface, but also for estimating the effects of lateral (interparticle) interactions. Upon variation of the tunnel current, i.e., degree of excitation of the adparticle local vibrations, one can study the dynamics of interactions between the adsorbed particles for various levels of excitation. This opens up new possibilities in elaborating the nano-scale level-to-level kinetics, which is necessary for the utter understanding of the mechanisms of multistage heterogeneous chemical transformations.

SUMMARY

(1) The effects of inelastic electron tunneling are observed in the experiments with STM operating in field emission mode for the first time.

(2) The electronic-vibrational FER spectra are found to strongly depend on the local surface structure.

(3) Clear-cut adsorption- and desorption-induced changes in the FER spectra are observed.

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