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Correlations between the Catalytic Activity of Heteropoly Acids and the Special Features of Their Tunneling Spectra

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Abstract—The electronic-vibrational spectra of phosphomolybdic acid, a classic heteropoly acid with a Keggin anion, were measured in an ultrahigh vacuum with the use of scanning tunneling microscopy. The dependences of the resonance characteristics of the spectra, so-called negative differential resistances (NDRs), on the vacuum gap, the polarity of applied voltage, and the direction of tunnel current were determined. A new mechanism of the formation of NDRs was proposed based on the quantum effect of the localization of the electronic states of multicenter systems in strong electric fields. The character of correlations between NDRs and the catalytic properties of heteropoly acid catalysts was established.

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INTRODUCTION

Catalysis occupies the most important place among the various well-known areas of application of heteropoly acids (HPAs) and their salts [1]. There are broad potentials for the modification of the composition and structure of HPA catalysts; in this context, the problem of their optimization appears. In solving this problem, correlations between the physical and chemical properties of compounds should be considered. A search for possible correlations can be performed with the use of ambient scanning tunneling microscopy and spectroscopy (STM and STS, respectively). Song and coauthors [2–5] found that the spectra of HPAs measured by STS in air exhibited resonance special features, so-called negative differential resistances (NDRs). They were observed in the sections of current–voltage curves where the tunnel current J decreased rather than increased with increasing voltage V (in absolute magnitude). Regardless of the type of HPAs, all of the NDRs were located on the negative semiaxis in the range of V_0 from 0.5 to 2 V and correlated with the catalytic activity and the oxidation potential of the HPA [2–5]. More active HPAs always corresponded to smaller values of V_0 (in absolute magnitude). Published data [3, 5–7] clearly indicate the existence of such correlations. More recently, correlations of V_0 with optical absorption and emission spectra were found [6, 8]. Obviously, these correlations suggest the dependence of V_0 on forbidden band gaps ε_g (so-called HOMO–LUMO gaps). Smaller V_0 correspond to smaller ε_g. The correlation dependences established in publications [2–6, 8] determined the new possibilities of the fine selection of effective HPA catalysts with a wide variety of applications [8]. However, the nature of correlations between NDRs and the catalytic activity of HPAs, as well as the mechanism of formation of the resonance special features of the tunneling spectra of these compounds, remains unexplained.

The correlations between the activity of metal oxide catalysts and forbidden band gaps have been repeatedly discussed earlier. It is well known that the activity decreases with the width of forbidden bands (for example, see [9]); therefore, the problem of a correlation between the special features of the tunneling spectra of heteropoly compounds and their catalytic activity is reduced to the explanation of the nature of correlations of NDRs with ε_g.

Here, we propose a solution to the above problems based on the results of the analysis of the tunneling spectra of single phosphomolybdic acid molecules obtained in an ultrahigh vacuum (UHV). New information on the shapes of resonance NDR lines, the dependences of NDRs on the polarity of the applied voltage, the size of a vacuum gap, and the scales and possible types (single, paired, and multiple) of observed NDRs made it possible to establish the determining role of strong electric fields, which are typical of STM experiments, in the formation of these special features in the spectra of HPAs. Below, we will formulate new ideas on the mechanism of electron transport in tunnel nanocontacts with the participation of single HPA molecules. These ideas are based on the quantum-confined Wannier–Stark localization effect [10, 11]. As applied to the STM spectra of HPAs, the effect of localization can be described as the rupture of weak interionic bonds, which form HOMO and LUMO states, in strong fields. The model of localization makes it possible to establish simple correlations between NDR parameters and forbidden band

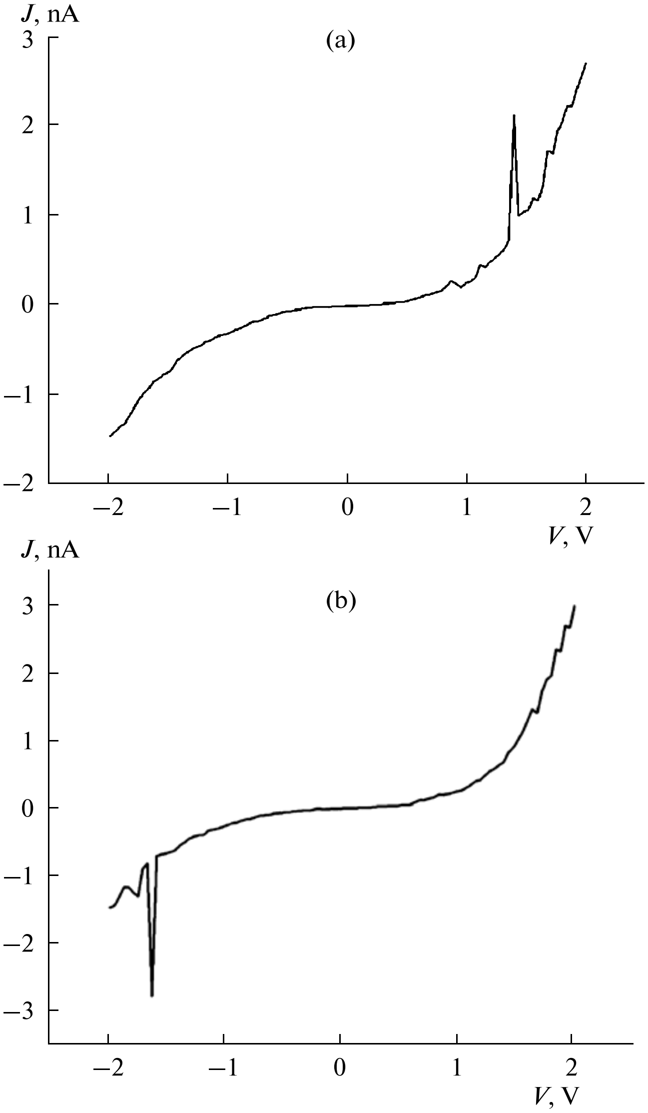

Fig. 1. Examples of the tunneling spectra of phosphomolybdic acid containing resonance maximums (NDRs) on the (a) positive and (b) negative semiaxes of voltage.

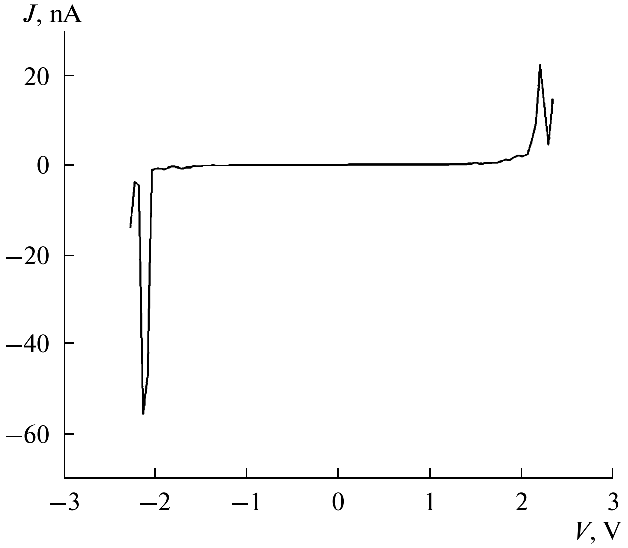

Fig. 2. Example of tunneling spectra containing paired symmetric NDRs.

gaps and to explain the entire set of data obtained in ambient (in air) [2–8, 12–14] and UHV experiments, the first results of which were published by Dalidchik et al. [11].

EXPERIMENTAL

The experiments were carried out at room temperature on a setup that included an Omicron VT STM instrument, a sample preparation chamber, and equipment for the cleaning of surfaces and tips by ionic bombardment and heating (800 K). The surface was pyrolytic graphite, and the tips were prepared by a standard (electrolytic) procedure from polycrystalline tungsten wire and cleaned by argon ions (1-keV Ar^+) and current pulses with a voltage of 10 V. For measuring the spectra, tips that made it possible to achieve atomic resolution and to obtain standard U-shaped $J(V)$ curves in measurements on the test surfaces—the defect-free regions of the graphite face (0001)—were used. Two complementary measuring procedures were used: a standard procedure, in which phosphomolybdic acid molecules were deposited onto graphite from a 0.01 M aqueous solution [2–5] and an inverted procedure, in which deposition was performed on a tip [4, 15].

Within the framework of the standard procedure, the samples with deposited phosphomolybdic acid molecules were dried in air, transferred into a high-vacuum system (pressure lower than 10^{-9} Torr), and kept for several hours; then, they were topographically scanned in selected areas to obtain $J(V)$ curves for the selected point grid. With the use of the inverted procedure, the cleaned tips were immersed in a solution of phosphomolybdic acid, dried in air, and transferred into the STM chamber. Then, after prolonged keeping in UHV, a set of $J(V)$ curves was obtained at different points of the defect-free surface region. In both cases (in the spectroscopic studies that accompanied topographic measurements and in the measurement of the conductivity of a nanocontact formed by the fixed tip), identical results were obtained.

Figures 1–4 show the examples of spectra that make it possible to judge the most significant dependences and characteristics of NDRs established for the first time in UHV experiments. The following conclusions can be made from these results:

(1) Single special features like NDRs can appear not only on the negative but also on the positive semiaxis of voltages (Fig. 1).

(2) In specific cases, the pairs of single NDRs arranged either symmetrically (Fig. 2) or asymmetri-

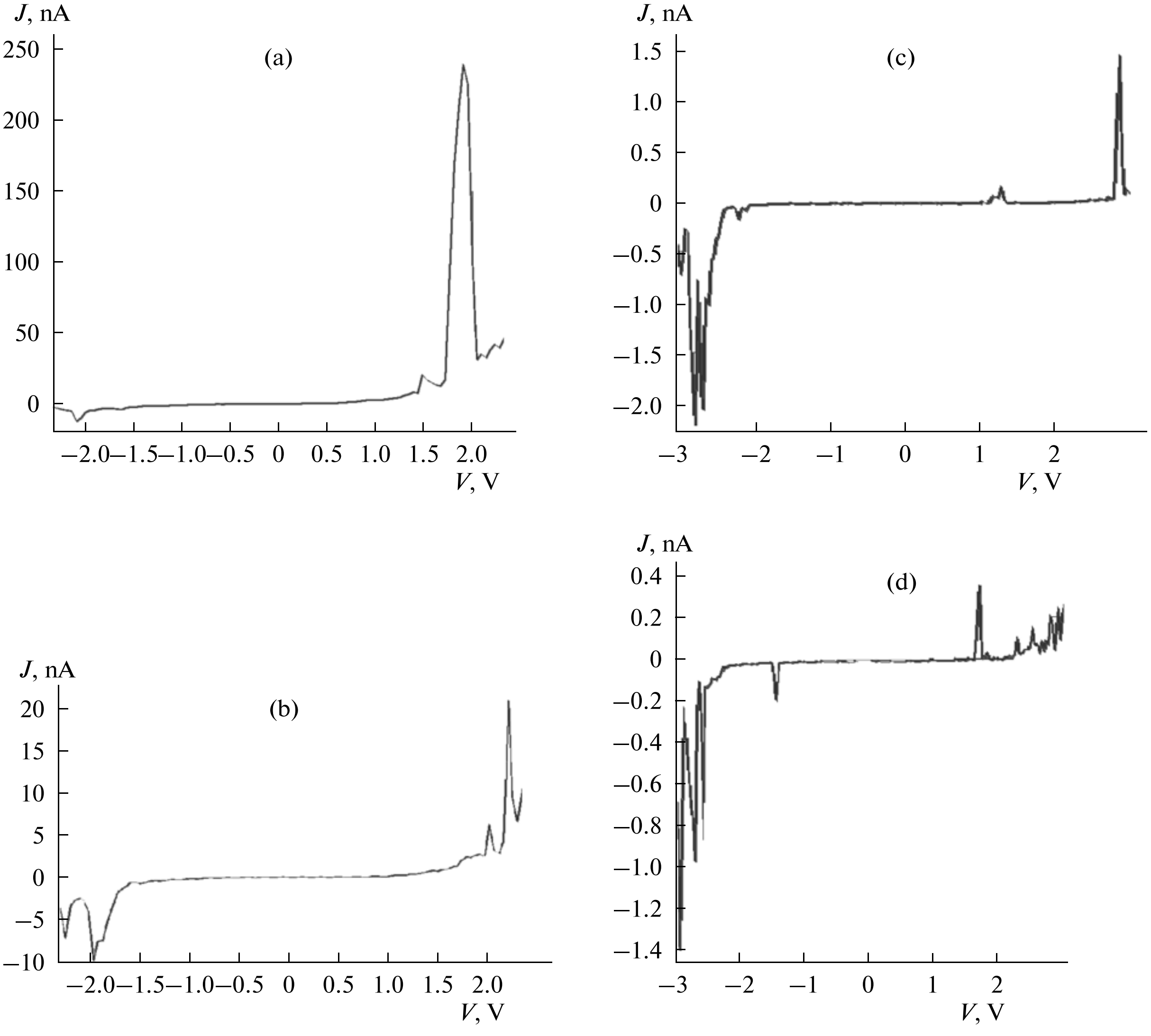

Fig. 3. Examples of spectra illustrating NDR shifts upon changing the average value of tunnel current J_0, nA: (a) 150, (b) 15, (c) 1.5, and (d) 0.15.

cally (Fig. 3b) relative to the point $V = 0$ were present in the spectra.

(3) The voltages at which NDRs were observed depend on the average values of tunnel current, whereas, in turn, the current exponentially depends on vacuum gap z. As z was increased, that is, as the current was decreased, NDRs shifted toward greater (in absolute magnitude) voltages. In this case, $dV_0/dJ \approx -0.03$ V/nA (Figs. 3a–3d).

(4) In particular spectra, the series of equidistantly arranged NDRs (with distances $\delta V_0(z) \approx 0.2$ V between peaks) with diminishing (Fig. 4a), growing (Fig. 4b), and bell-shaped (Fig. 4c) enveloping curves were observed.

(5) The lines of resonance NDR maximums had a symmetrical nearly Lorentzian shape.

RESULTS AND DISCUSSION

Extensive literature has been devoted to the nature of NDRs, which is closely related to the general problem of the tunnel transport of electrons in molecular structures [16, 17]. NDR is the key element of many molecular electronic devices; in the last decade, this fact stimulated an intensive search new systems, in which NDRs can be observed, and new mechanisms of their appearance [18]. The two-center resonant tunneling, which causes the quantum effect of the exponential clarification of potential barriers, is one of the most common mechanisms, which can be easily identified based on line shapes [19, 20]. The above results of our experiments suggest the participation of the pairs of electronic states localized in spatially separated regions with the energy levels $E_{1,\ 2}$, which depend on the vacuum gap, that is, on the field strength F in the nanocontact, in the formation of the NDRs of the tunneling spectra of HPAs. It is reasonable to relate the possibility of the symmetrical arrangement of NDRs relative to the point $V = 0$ (see Fig. 2) to the symmetry of the arrangement of the localization areas of resonant states relative to the center of the molecule. The formation of equidistant NDR series suggests the participation of vibrational degrees of freedom, which are responsible for the excitation of multiquantum transitions. In accordance with the theory of inelastic resonant tunneling [21], these transitions are possible only at sufficiently strong interactions of electronic and vibrational subsystems, that is, at sufficiently high values of the $e–v$ interaction parameter (the Huang–Rys parameter $\alpha \approx 1$ [22]), which corresponds to a high (apparently, close to atomic) degree of localization.

At first glance, states of this type are absent from nanocontacts containing HPAs. The atomic and electronic structure peculiarities of the molecules of HPAs and their salts are well known [23]. The molecules of these compounds contain characteristic groups—metal oxide polyhedrons (with a metal atom in the center), which are joined to each other through vertexes, edges, or faces. The electronic spectra of all of these compounds have much in common, in particular, sufficiently large gaps between occupied and unoccupied states $\varepsilon_g = 2–3$ eV, which correspond to the oxygen or metal orbitals. At $V = 0$, all electrons are delocalized on equivalent metal and oxygen atoms. The exchange integrals (g), which determine the exchange splitting of states localized at different centers and evaluated from characteristic electronic frequencies, do not exceed 0.1 eV.

However, it should be considered that strong fields with $F \approx 10^7$ V/cm ($F \approx V/L$, where $V = 2–3$ V; the distance between the surface and the tip is $L = (z + D) =$ 1–3 nm; D is the molecular size) act in STM nanocontacts in the course of STM experiments, in particular, in the UHV measurements of the tunneling spectra of HPAs. In these fields, the Wannier–Stark localization parameter is commensurablee with atomic dimensions ($\lambda \approx g/F \approx 0.02$ nm). Hence, it follows that, in experiments with the use of STM, the energy spectra of the electronic states of HPAs will have the form of Stark ladders:

$$\varepsilon_i^n(V, R_i) = \varepsilon^n(F = 0, R_i) + FR_i, \quad (1)$$

where n is 1 for oxygen ions or 2 for the metal, and R_i are the coordinates of ions. Paired resonances appear in the system at the voltages $V_{ij}^{1,2}V_{ij}^{1,2}$ equal to the roots of the equations

$$\varepsilon_i^1(V, R_i) = \varepsilon_j^2(V, R_i). \quad (2)$$

At these voltages, the contact is exponentially "clarified" [21]; that is, local maximums (NDRs) appear in the functions $J(V)$. Under these conditions, tunnel resonant transitions result from the occurrence of the following three sequential acts with an increased prob-

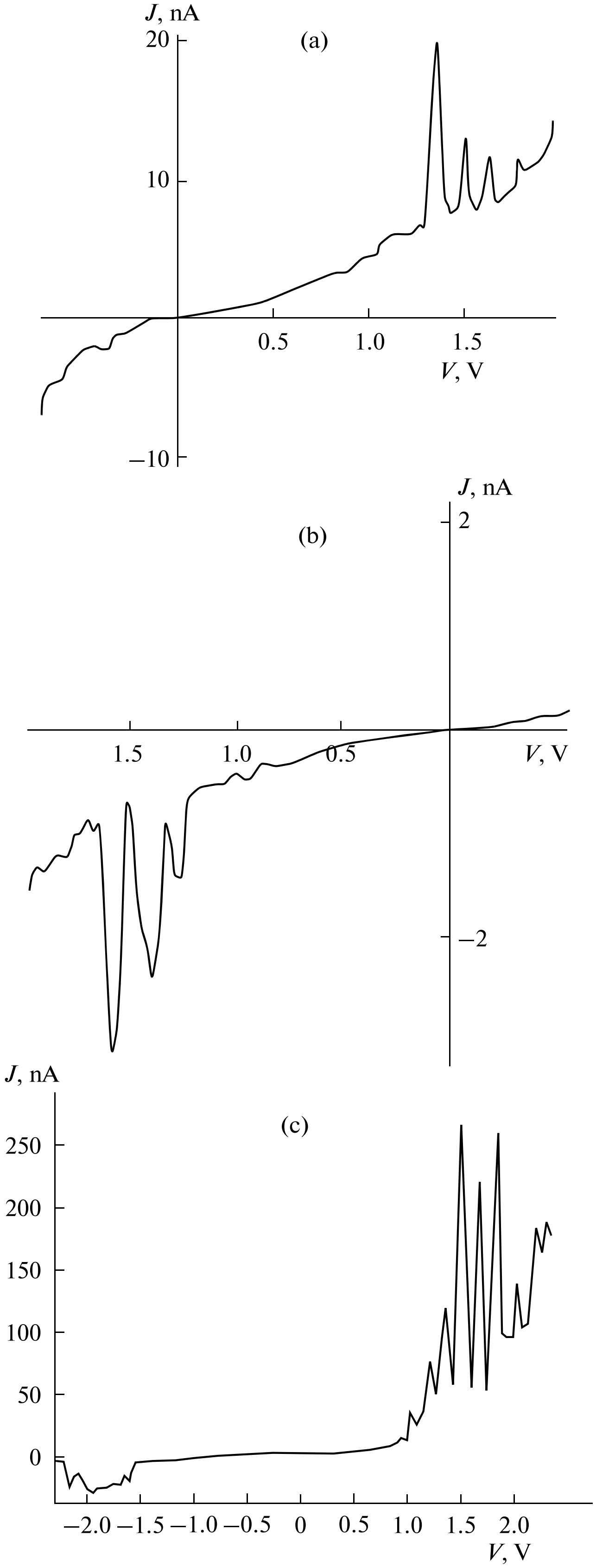

Fig. 4. Examples of spectra containing the series of equidistant NDRs with (a) decreasing, (b) increasing, and (c) bell-shaped enveloping curves.

ability: electron transfer from the contact with a negative potential to the nearest oxygen ion (with the probability Γ_{in}), the subsequent electron transfer to the metal ion nearest to the opposite contact (with the probability $w_{ij} \approx g^2$), and the final electron transfer to the contact bearing a positive potential (with the probability Γ_{out}). Note that the surprising possibility of visualization of metal ions on the topographic scanning of heteropoly compounds, which was demonstrated previously by Dykhne et al. [12], that is, the increased conductivity of a nanocontact above the ions whose levels lie above the Fermi level (at $V = 0$), is obviously related to with the final stage. According to Eqs. (1) and (2), the voltages V_0, which correspond to NDRs nearest to the origin of coordinates, are related (if we use a simple one-dimensional model of transitions) to the size of HOMO–LUMO gaps ε_g and the vacuum gap z by the relationship

$$V_0 \approx \varepsilon_g(1 + z/L). \qquad (3)$$

Shifts in NDRs upon varying z, that is, upon changing the base values of current and voltages, and also correlations between V_0 and the optical spectra of HPAs [6, 7], directly follow from equality (3).

On condition that $g \ll (\Gamma_{\text{in}} + \Gamma_{\text{out}})$, the contribution of resonant electrons to the total current $J_r(V)$ is described by the expression [11]

$$J_r \approx \int\limits_{-\infty}^{+\infty} \Gamma_{\text{in}}\rho(E,V,d) g \rho_2(E,V,d)\Gamma_{\text{out}} \mathrm{d}E, \qquad (4)$$

$$(e = h = m = 1),$$

where Γ_{in} and Γ_{out} are the probabilities of tunnel transitions between trapping centers and the corresponding contacts, and

$$\rho_n = \left\{[E - E_n(V,d)]^2 + \Gamma_n^2\right\}^{-1}\Gamma_n \qquad (5)$$

are the densities of states. At voltages that are the roots of the equations

$$E_1(1,V,d) = E_2(0,V,d) \quad \text{at} \quad V = 0 \qquad (6)$$

and

$$E_1(0,V,d) = E_2(1,V,d) \quad \text{at} \quad V > 0 \qquad (7)$$

there are intersections in the system of discrete levels corresponding to the localization of electrons on metal or oxygen atoms. In other words, the function $J(V)$ exhibits Lorentzian-shape maximums at these voltages:

$$J_r \approx g^2 \frac{(\Gamma_{\text{in}} + \Gamma_{\text{out}})}{[(E_1(V) - E_2(V))]^2 + (\Gamma_{\text{in}} + \Gamma_{\text{out}})^2}. \qquad (8)$$

Thus, in linear approximation (3), all of the lines of single NDRs are of Lorentzian shape. The half-widths of resonance lines are determined by the probabilities of electron transitions between the contact bearing a negative potential and the nearest oxygen ion and also between the contact with a positive potential and the nearest metal ion. It is easy to understand that a change in the polarity of voltage leads to only a change in the ion pairs that participate in the process of two-center resonant tunneling. This is manifested in the spectra as the absence of the precise symmetry of $J(V)$ curves, that is, by different scales and arrangements of NDRs on the axis of voltage. In special cases, when the system is axisymmetrical, that is, when the STM tip and the ions that participate in the tree-step resonant tunneling are in line, the spectra should contain the pairs of symmetrically arranged ($V_0^- = V_0^+$) equally scaled NDRs. Figure 2 shows an example of this spectrum found among several hundreds of $J(V)$ curves, which correspond to different surface points.

The detection of the series of equidistant NDRs in tunneling spectra is a new interesting result of UHV experiments with HPA molecules. Comparing the spectra obtained at different J, we can detect how these series gradually manifested themselves as the tunnel current decreased (Fig. 3), that is, as the vacuum gap was increased and the probability of electron transfer through the vacuum barrier correspondingly decreased. The dependence of the shape of the enveloping curves of resonance lines on the current and the applied voltage, that is, on the field F, which acts in the nanocontact can be found. In weak fields, the enveloping curves most frequently have the shape of monotonically decreasing functions. In this case, the number of NDRs in each series is relatively small (usually, these series contain one high peak and two or three satellites, see. Figs. 4a and 4b). In strong fields (Fig. 4c), the enveloping curves are bell-shaped. The number of NDRs in such series can be noticeably greater (to 5–7).

The equidistance of NDRs suggests the participation of the vibrational degrees of freedom of the test molecules in the processes of tunnel electron transfer. If we consider the intracontact distribution of voltage V between the vacuum gap and the localization centers of tunneling electrons, the vibrational quanta ω can be estimated at 0.1–0.2 eV, which is close to the characteristic values of photoabsorption quanta in the IR spectra of phosphomolybdic acid molecules [3]. According to the theory of inelastic resonant tunneling [21], the most complete resolution of lines in the vibrational spectra can be reached at the small probabilities of tunneling transitions, when the characteristic residence time of an electron in intermediate states is longer than the period of oscillations $\Gamma \leq \omega$ (Γ is the total width of the resonance line). In the cases under consideration, Γ depends on z. It is obvious that $\mathrm{d}\Gamma/\mathrm{d}z < 0$; this fact can explain the observed effect of the buildup of vibrational series in the $J(V)$ curves.

The field dependences of the enveloping curves of the resonance lines of vibrational spectra can be considered as evidence for the strength dependence of the electron-vibrational coupling constant α. Indeed, it is well known that the Huang–Rys parameter α, which determines the probability of multiquantum vibrational transitions

$$W_u = \exp(-\alpha)\alpha^u/u! \qquad (9)$$

(u is the number of the vibrational level to which the vertical transition from the ground state takes place), depends on the measure of changes in interionic forces with changing the electronic states of trapping centers. In the case under discussion, the localization regions of the Wannier–Stark states play the role of these centers. The sizes of these regions λ depend on the field: the weaker the field, the greater these sizes ($\lambda \approx g/F$). In this case, it is obvious that $d\alpha/dL < 0$. Hence, it follows that,in the case of weak localization, which most frequently occurs in weak fields (at small currents), the Huang–Rys parameter is small. According to Eq. (9), in these cases, the enveloping curves take the shape of monotonically decaying curves (with increasing u). In strong fields, when the sizes of localization regions are commensurable with atomic sizes, the parameter α is substantially greater. Hence, and also from Eq. (9), it follows that the enveloping curves will become bell-shaped in the case of high currents, at which the values of $\alpha > 1$ are possible. The results of UHV experiments, which are shown in Figs. 1–4, are completely consistent with the conclusions that follow from the Wannier–Stark localization model, which makes it possible to explain the mechanism of NDR formation in the tunneling spectra of HPAs.

The dependence of V_0 on ε_g (see relationship (3), which directly follows from the model of the rupture of weak interionic bonds under the action of a field) serves as a reason for a correlation between tunneling spectra and the widths of forbidden bands. In turn, as noted above, these latter correlate with the catalytic properties of metal oxides: the smaller ε_g, the higher the activity of these catalysts. Thus, if HPA is characterized by smaller values of ε_g, special features like NDRs will manifest themselves at lower voltages. This was observed experimentally.

The dependence of the activity of metal oxide catalysts on ε_g allowed us to make an important conclusion on the determining influence of electronic factors on the catalytic activity of HPAs. The activity of HPAs, which are effective acid catalysts [23], is determined by the rate of intramolecular interionic electron transfer [3, 24]. As shown in this work, these transitions can be studied at the level of single molecules with the use of STM.

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