Resonance tunneling electron-vibrational spectroscopy of polyoxometalates

F. I. Dalidchik,^{a)} S. A. Kovalevskii, and E. M. Balashov

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ul. Kosygina 4, Moscow 119991, Russia

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The tunneling spectra of the ordered monolayer films of decamolybdodicobaltate (DMDC) compounds deposited from aqueous solutions on HOPG were measured by scanning tunnel microscopy in air. The DMDC spectra, as well as the tunneling spectra of other polyoxometalates (POMs), exhibit well-defined negative differential resistances (NDRs). The mechanism of formation of these spectral features was established from the collection of revealed NDR dependences on the external varying parameters and found to be common to all systems exhibiting Wannier–Stark localization. A model of biresonance tunneling was developed to provide an explanation for the totality of experimental data, both the literature and original, on the tunneling POM probing. A variant of the tunneling electron-vibrational POM spectroscopy was proposed allowing the determination of the three basic energy parameters—energy gaps between the occupied and unoccupied states, frequencies of the vibrational transitions accompanying biresonance electron-tunneling processes, and electron-vibrational interaction constants on the monomolecular level. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983486>]

I. INTRODUCTION

Molecular metal oxides (polyoxometalates, POMs) represent a rich variety of “natural” nanoparticles (NPs) whose physical and chemical properties, depending on their composition and architecture, vary over a wide range and allow fine tuning.¹ Although POMs have long been known as active catalysts,² in the last decade they have come to be studied as the most promising nanomaterials of the 21st century.^{3,4} The area of possible applications of POMs, which by now extends from catalysis and molecular electronics to nanobiology and nanomedicine, is steadily expanding. The variety of POMs increases rapidly, and it now becomes possible to synthesize POMs with the predetermined functional characteristics. It appears that the world of POMs differs little from the organic world, as regards to the variety of their forms and diversity of physicochemical properties. The synthesis of living-cell prototypes containing no carbon and composed of only metal oxides was reported recently in Ref. 5 and generated fantastic notions of inorganic living forms.

An important role that is assigned today to POMs in science, technology, and medicine necessitates thorough fundamental studies of their structure and properties on the modern “monomolecular” level. As to all other NPs, such as nanocarbons (tubes and fullerenes), semiconducting nanocrystals (quantum dots), metal clusters, etc., the monomolecular level of spectroscopic studies was mastered immediately after the development of the methods for synthesizing and/or discovering these nanostructures. In this case, a crucial role was played by the probing methods, first of all by the tunneling methods with the use of the scanning tunneling

microscope (STM). Today these methods can be employed to gain information both on the specific features of the electronic structure of NPs, on their vibrational spectra, and on the parameters of electron-vibrational interactions, which characterize the role of polaron effects in the tunneling electron transport in nanomaterials.^{6,7} However, such a level of spectroscopic measurements is as yet rather inaccessible for POM because, at first sight, the results of tunneling POM probing are contradictory to the canonical concepts of STM physics. For instance, it is known that when using the current-induced tunneling spectroscopy method in the experiments with POMs ($[\text{Cu}_{20}\text{Cl}(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{P}_8\text{W}_{48}\text{O}_{184})]^{25-}$) with negative bias, the occupied states of oxygen ions can be confused with the unoccupied states of Cu ions.⁸ The shapes of resonance features in the tunneling spectra of these compounds are anomalous, i.e., their current–voltage characteristics exhibit maxima $I_m(V_0)$, the so-called “negative differential resistances” (NDRs),^{9–16} where V_0 is the position of the local tunnel-current maximum I_m on the voltage axis.

The reasons for such significant distinctions between the POM’s spectra and the spectra of the majority of other NPs have long been unknown. Correspondingly, a possibility to extract the energy parameters of POMs from the results of their tunnel probing was as yet not discussed. The solution to these problems was suggested in Refs. 17–19, in which a model was developed for the electron-tunneling resonance transport through the nanostructures containing weak exchange bonds that break in a strong electric field. The model offered a simple explanation for a great body of experimental data, both the literature^{9–16} and original,^{17–19} on the STM-aided POM probing. The ultrahigh-vacuum (UHV) STM data on the POM molecules were obtained for the first time in our works^{17–19} devoted to the Keggin’s compounds.

^{a)}Email: domfdal@mail.ru

It should be pointed out that under UHV conditions, the ordered monolayer films do not form because of a weak POM's bonding to graphite, so that one cannot attain high spatial resolution in the STM experiments. It is shown in this work that the spectroscopic measurements with weak background currents ($I \leq 20$ nA) under ambient conditions allow one not only to attain good resolution for the ordered POM-formed structures on the HOPG graphite surface but also investigate their tunneling spectra in detail. The results presented below show that the tunneling spectra under ambient and UHV conditions exhibit the same resonance features and provide information allowing for the reproduction of electronic and vibrational parameters of the probed POMs. This is demonstrated with recently synthesized decamolybdodocobaltate (DMDC) compounds that are promising for use in heterogenic catalysis.²⁰ The structure and properties of DMDCs were previously investigated solely by macroscopic methods.²¹ The results obtained in our experiments, namely, the "band gaps," the vibrational spectra, and the electron-vibration coupling constants agree well with the results of macrospectroscopic measurements, thereby demonstrating wide possibilities of the proposed variant of tunneling electron-vibrational POM spectroscopy and confirming reliability of the results obtained by this method.

II. EXPERIMENTAL

Experiments were performed on an "Omicron" HV STM at room temperature in air. We used the Pt/Ir tips tested at the defect-free graphite (0001) surface. The selected tips made it possible to achieve atomic resolution and obtain reference U-shaped spectroscopic dependences (dI/dV - V curves).

To prepare samples, a 0.01M aqueous solution of $(\text{NH}_4)_6[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4]$ was deposited on a freshly cleaved HOPG surface and allowed to dry in air for 40 min at room temperature for STM measurements. At the first step of measurements, the area containing an ordered layer of a deposited POM was found at the sample surface. Thereafter the I - V dependences were measured over this area at different points.

III. RESULTS AND DISCUSSION

These experiments revealed that the topographic images of the ordered monolayer DMDC films deposited on HOPG show the formation of well-ordered arrays with rhombohedral unit cells (Fig. 1 in Ref. 19) similar to that obtained in Ref. 12.

A. Negative differential resistances in the tunneling spectra of polyoxometalates

When comparing the results of spectroscopic STM measurements for POMs in UHV¹⁷⁻¹⁹ and in air at a high current,⁹⁻¹⁶ the following important distinctions should be pointed out.

1. In air with background currents $I \sim 10^2$ nA, the spectra show NDRs only on the negative semiaxis of voltages. The high-vacuum (HV) spectra exhibit NDRs on both semiaxes. In many cases, the NDRs are observed in pairs, which are often situated strictly symmetrically about the origin of coordinates. In air, the scale of NDR is almost

two orders less than in the HV experiments. In the weak-current HV experiments,²² "giant" NDRs with characteristic values of peak-to-valley ratio K_{NDR} of up to 10^2 are observed [$K_{\text{NDR}} = I_{\text{m}}/I_{\text{b}}$, where I_{b} is the background current and $I_{\text{m}} = I(V_0)$].

2. In air, the NDR position does not depend on the chosen base current I^* and voltage V^* that specify the width of the tunnel gap.²³ It should be noted that the correlations between the NDR and the catalytic activity of POMs, which were established in the literature,⁹⁻¹⁶ would be improbable if the tunneling spectra depend essentially on the tip-surface separation z . In the HV experiments, the resonance features noticeably shift toward the lower V with increasing I .²⁴
3. In air, the shapes of resonance peaks are often unsymmetrical about V_0 . In these cases, the characteristic prestructures ("shoulders") are clearly seen on the low-voltage wing of the spectrum (see, e.g., Fig. 6 in Ref. 6). In the HV experiments, a series of equidistant peaks (electron-vibrational resonances) with ascending, descending, or bell-shaped envelopes are observed in such cases.
4. The well-resolved peaks in the HV spectra are symmetrical about V_0 and have a lineshape close to Lorentzian.

These distinctions can be understood when it is taken into account that in the experiments in air with sufficiently high currents the nanocontacts can close by water bridges.²⁵ In the closed nanocontacts, the voltage drop ΔV_1 on the water bridge is negligibly small, so that the spectra measured in air at sufficiently high currents change only slightly with varying I^* and V^* . For a sufficiently weak current, i.e., for large tip-POM separation, the bridges do not form, and the tunneling spectra become essentially dependent on I^* and V^* . In this case, the characteristic spectral features depending on the voltage drop on the probing molecule shift toward higher voltages as z increases. The NDR shifting with an increase in z has not been discussed and reported so far in the literature, though it is clearly demonstrated by the results of spectroscopic measurements presented in Fig. 1 in Ref. 15.

Examples demonstrating main features of the DMDC spectra measured in air are presented in Figs. 1 and 2. By comparing these spectra with the UHV spectra of the Keggin's compounds (Figs. 1-3 in Ref. 17 and Figs. 2-4 in Ref. 18), one can notice that the characteristic features of these spectra coincide. The HV spectra obtained for the Keggin's structures (phosphomolybdic acid) contain single, pair, and multiple NDRs, as also do the spectra obtained for the DMDC in air. In both cases, the NDRs can be situated on both voltage semiaxes (see Figs. 2 and 3 in Ref. 18 and Fig. 1 in this work).

The anomalously great NDRs arranged symmetrically about the origin of coordinates are possible both for the Keggin's anions (see Fig. 3 in Ref. 22) and for DMDC (see Fig. 1(b)). Note finally that the appearance of equidistant NDR series with various envelopes (ascending, descending, and bell-shaped) is possible in both cases (in air and in the HV experiments).

Two conclusions can be drawn from the above. First, the mechanisms of NDR formation in the tunneling spectra of

FIG. 1. Tunneling spectra of the DMDC containing (a) single and (b) pair NDRs. Bias symmetric features are observed in the case of axial symmetry of nanocontacts. The ratio between the amplitudes of the NDR peaks located on the positive and negative semi-axes depends on the position of the STM tip above the POM cluster.

the POMs with different composition and architecture are identical. Second, the mechanism of resonance electron transport in the HV experiments is similar to that for the in-air spectroscopic measurements with weak currents, i.e., with sufficiently large z eliminating the possibility of water bridge appearing in the tunnel gap.

B. Biresonance tunneling with the Wannier–Stark localization

The mechanisms of NDR formation in the tunneling spectra of nanostructures have been actively discussed in the last decade. The NDR-exhibiting nanosystems are considered as key elements of the nano- and molecular-electronics because they allow fabrication of the molecular amplifiers, logical elements, memory elements, commutators, etc.²⁶ The prospects for diminishing sizes of electronic devices to the nanometric level have stimulated in the last years an intensive search for the molecules and complexes suitable for these purposes. Of special interest are the large-scale NDRs with high peak-to-valley ratios ($K_{NDR} > 3$) persisting at room temperature. Examples of the NDRs with $K_{NDR} > 10$ (Fig. 1(a)) that were observed in our experiments point to a possibility of fabricating monomolecular nonlinear elements in the POM-based nanoelectronics.

One of the well-known mechanisms readily identifiable by the Lorentzian lineshapes rests on the potential-barrier

bleaching effect in the biresonance (e.g., two-center) tunneling.²⁷ In the last years, this effect was repeatedly invoked to interpret the STM experiments exhibiting NDR (see, e.g., Ref. 28). One usually assumes in these cases that the under-barrier trajectory contains two isolated electron-capture (e.g., redox) centers whose energy levels $\varepsilon_{1,2}(V)$ become isoenergetic, i.e., $\varepsilon_1(V_0) = \varepsilon_2(V_0)$ in the strong electric fields.

At first sight, the conditions necessary for the two-center bleaching of an STM nanocontact containing POM molecule cannot be realized. For each pair of the resonance states, the NDR can, obviously, be observed only on either of two voltage semiaxes. However, in many cases the POM tunneling spectra contain the NDR pairs symmetrically arranged about the origin of coordinates (Fig. 2(b)). No redox centers (capture centers) are also seen in this case. For $V = 0$, the spectrum of POM electronic states near the Fermi level consists of two rather dense manifolds of the delocalized molecular HOMO and LUMO states.

To recognize the nature of NDR in the POM tunneling spectra, one should take into account that the electronic spectrum near the Fermi level undergoes significant changes, the so-called Wannier–Stark localization²⁹ in the strong electric fields. For the POM molecules, the Wannier–Stark localization can occur for the electric-field strengths $F \geq g/a$ (g is the exchange-interaction constant between the peripheral ions and a is the characteristic interion distance), i.e., at $V \geq 1$ V. The character of the restricting of POM electronic

FIG. 2. Examples of tunneling spectra of the DMDC exhibiting vibrational NDR series.

FIG. 3. Energy diagram of a POM-containing nanocontact; (a) levels of delocalized electronic states of the POM in the absence of the field ($V = 0$); (b) energy diagram for the nanocontact shown in (a) at $V \neq 0$ taking into account Wannier-Stark localization at which the discrete levels are localized on the ions. 1 and 2 are the centers of capture of tunneling electrons; n is the index of centers that does not participate in three-stage resonance tunneling, $n \geq 3$; no vacuum gap is shown; ε_f^t and ε_f^s are the Fermi levels of the tip and the substrate. Two-center resonance blooming of the nanocontact forming NDR appears when voltages satisfy Equation (1).

states near the Fermi level in strong fields is schematically illustrated in Fig. 3. The spectrum splits into two “Stark ladders,” as a result of which the possibility arises of multiple pseudocrossings (PCs) between the electronic levels bleaching the tunneling nanocontact. It is easy to see that the pair of electronic levels adjacent to the HOMO and LUMO band edges corresponds to the NDR closest to the origin of voltage coordinates V .

Near the PC points, i.e., for voltages $V = V_0$, where V_0 are the roots of equations

$$\varepsilon_i(V_0) = \varepsilon_j(V_0) \quad (1)$$

(i and j label the electronic states), the resonance tunneling transition occurs with the participation of two electronic states $|i\rangle$ and $|j\rangle$. The amplitude $A_{12}(\varepsilon)$ of the biresonance tunneling transition is given by the two-pole expression¹⁹

$$A_{12}(\varepsilon) = \frac{\gamma_{1i}g_{ij}\gamma_{j2}}{(\varepsilon - \varepsilon_i(V_0) + i\Gamma_{1i})(\varepsilon - \varepsilon_j(V_0) + i\Gamma_{j2})}. \quad (2)$$

Here, $\gamma_{1i}(\gamma_{j2})$ is the probability amplitude of the tunneling transition occupying (depleting) the i th (j th) state, g_{ij} is the probability amplitude of the electronic transition between the i th and j th states, and $\Gamma_{1i}(\Gamma_{j2})$ are the decay widths.

For the resonance component of tunneling current, one has from Eq. (1) in Ref. 17

$$\begin{aligned} J(V) &= \text{const} \int_{-\infty}^{\infty} \Gamma_{1i} \rho_{1i}(\varepsilon_i(V)) g_{ij}^2 \rho_{j2} \varepsilon_j(V) \Gamma_{j2} d\varepsilon \\ &= \text{const} \frac{\Gamma_{1i} g_{ij}^2 \Gamma_{j2}}{(\varepsilon_i(V) - \varepsilon_j(V))^2 + \Gamma^2} \end{aligned} \quad (3)$$

under conditions

$$|(\varepsilon_{i,j}(V_0) - \varepsilon_f^{s,t}(V_0))| \gg \Gamma_{1i}(\Gamma_{j2}) \quad \text{and} \quad \Gamma_{1i}(\Gamma_{j2}) \geq k_B T,$$

where $\Gamma = \Gamma_{1i} + \Gamma_{j2}$, $\rho_{1i} = [(\varepsilon - \varepsilon_i(V))^2 + \Gamma_{1i}^2]^{-1} \Gamma_{1i}$, and $\rho_{j2} = [(\varepsilon - \varepsilon_j(V))^2 + \Gamma_{j2}^2]^{-1} \Gamma_{j2}$ are the densities of states, $\varepsilon_f^{s,t}(V_0)$ are the Fermi levels of the tip and the substrate, k_B is the Boltzmann constant, and T is the temperature.

With allowance for the symmetry of atomic structure of the POM molecules, the scheme of electronic levels in strong

fields shown in Fig. 4 provides, together with Eq. (2), a simple explanation for one of the basic features of the POM tunneling spectra: namely, the NDRs appear in pairs and are symmetrical about the origin of coordinates. To describe the mechanism for the appearance of a series of equidistantly arranged NDRs in the tunneling spectra, one should invoke the possible vibrational transitions.

C. Inelastic biresonance tunneling

The resonance tunneling processes are often accompanied by the vibrational, including multiquantum, transitions. In the STM experiments, such transitions are observed almost

FIG. 4. (a) The results of IR measurements of DMDC from Ref. 19 and (b) DMDC vibrational quantum distribution obtained in our STS experiments.

for all nanoparticles studied to date.^{30–32} However, all the processes known to us relate to the one-resonance inelastic tunneling. The corresponding theory was developed in Ref. 33. To generalize Eq. (3) to the processes of inelastic biresonance tunneling, one must take into account the multiquantum vibrational transitions accompanying the occupation and depletion events for the $|\varepsilon_{1,2}(V)\rangle$ states. By using the formalism of multiple-scattering theory and including the vibrational degrees of freedom, we obtain for the total current in the simplest approximation ($\Gamma \ll \hbar\omega$, where $\hbar\omega$ is the vibrational quantum),

$$J(V) = \text{const} \sum_{\{v_i, v', v_f\}} f(v_i) \frac{\Gamma_{v_i v'(i)} g_{v v'}^2 \Gamma_{v' v_f(i)}}{(\varepsilon_{iv}(V) - \varepsilon_{jv'}(V))^2 + \Gamma_{ij}^2}. \quad (4)$$

Here, $\Gamma_{v_i v'(i)} = \Gamma(i) \langle v_i | v' \rangle^2$ is the partial width of the i th (or j th) state, $\langle v_i | v' \rangle^2$ are the Franck-Condon factors, $v(v')$ are the vibrational quantum numbers of the resonant states, $\varepsilon_{iv}(V) = \varepsilon_i(V) + \hbar\omega(v + 1/2)$ and $\varepsilon_{jv'}(V) = \varepsilon_j(V) + \hbar\omega(v' + 1/2)$ are the electron-vibrational levels of the resonant states, $\Gamma_{ij} = \Gamma_{v_i v'(i)} + \Gamma_{v' v_f(i)}$, and $f(v)$ is the vibrational distribution. The summation in Eq. (4) goes over all vibrational quantum numbers: initial (v_i), intermediate (v and v'), and final (v_f). According to Eq. (4), the possibility of vibrational NDR series occurring in the STM experiments is dictated by the value of electron-vibrational interaction parameter α , which increases (in the framework of the shifted harmonic-oscillator model) as the shift in the nuclear coordinates increases with changing the POM's charge state. The smaller the area of electron localization in the captured state, the stronger is the interaction. Hence it follows that the Wannier–Stark localization enhances the parameter α and, correspondingly, enhances the probability of many-quantum vibrational transitions that form the equidistant (vibrational) NDR series. Examples of the spectra containing vibrational NDR series revealed by us are demonstrated in Figs. 2(a) and 2(b). Let us discuss the similarity of these spectra and the distinctions between them. In both cases, the background currents for the moderate peaks are close to 5 nA; in both cases, the vibrational NDR series closest to the origin of coordinates are placed on the negative semiaxis at voltages $|eV_0(u)| \geq \varepsilon_g$ ($u = 0, 1, 2, 3, \dots$) and characterized by the ascending envelopes. It would appear reasonable that both these series correspond to the PCs of the same electronic states adjacent to the HOMO and LUMO band edges at $V = 0$.

The electronic terms to which the vibrational states involved in the resonance electronic transition belong can be established from the shape of envelope. It can be shown that the ascending envelopes correspond to the vibrational levels adjacent (at $V = 0$) to a level at the HOMO band edge, while the descending envelopes form when the electronic HOMO term intersects the vibrational series of the level adjacent to the LUMO manifold.

The most essential distinctions between the spectra under consideration relate to the values of $V_0(v)$ and $\delta V_0(v, v \pm 1)$. First, the voltages for which the vibrational NDR series are observed differ noticeably (-3 and -2 V for the first maxima in Fig. 5) and, second, the separations δV (0.3 V and 0.2 V) between the vibrational lines change synchronously. Hence,

FIG. 5. NDR-voltage distribution obtained in the STS experiments.

one has

$$\delta V_0(v, v \pm 1)/V_0(v) \approx \text{const}, \quad (5)$$

for the spectra exhibiting electron-vibrational series corresponding to the PCs of the same electronic states.

D. Determination of the electronic and vibrational POM parameters from the NDR spectra

When analyzing the tunneling spectra containing single and pair NDRs, as shown in Fig. 1, one can state a wide spread of voltages V_o for which the resonance peaks are observed. The histogram of the observed values of V_o is given in Fig. 5.

Such scatter can naturally be attributed to the uncontrolled variations of the tunnel gap z that determines the voltage drop V_1 on the probed molecule ($U = U_1 + U_z$, where U_z is the voltage drop outside the POM). The shift in the crossing levels E_1 and E_2 involved in the biresonance electronic transition also depends on V_1 . As can be seen from Fig. 5, the maximum $\tilde{U}_0 = U_0^*$ of the distribution occurs at $U_o = 2$ V, which corresponds to the energy gap between the HOMO and LUMO levels ($U_0^* \approx \varepsilon_g \approx 2$ eV). The spectra for which $U_0 \geq U_0^*$ can be assigned to the nanocontacts with $z \geq 0$. However, numerous spectra with $U_0 \leq U_0^*$ must be of a different nature that is unrelated to the HOMO and LUMO states. One of the explanations for the nature of these levels consists in the assumption that the HOMO+1 state participates in the electron transport. We carried out the density functional theory (DFT) calculations with the *openmx* program package to verify that the HOMO+1 level is indeed observed in the DMDC spectrum 1.23 eV higher than the HOMO band edge. The numerical calculations were performed in the density functional theory (DFT) approximation using the OpenMX 3.7 program package.

The numerically calculated atomic-centered orbitals were taken as a basis.^{34,35} The pseudopotentials generated following the scheme³⁶ corresponded to the valence states of the P-, Mo-, H-s1-, and Co-atoms. The exchange correlation functional of the PBE type³⁷ was used in the generalized gradient

approximation without the inclusion of spin polarization. The initial approximation for the geometry of the system was determined from the literature X-ray structural data²⁰ followed by the quantum-chemical optimization of the equilibrium structure.

We now describe the algorithm for determining vibrational quanta $\hbar\omega$ and electron-vibrational interaction parameter α from the equidistant NDR series. Note first that the spectra with ascending envelopes correspond to the PCs of the electron-vibrational levels

$$\varepsilon_{nv}(V) = \varepsilon_n(V) + \hbar\omega(v + 1/2),$$

$$(v = 0, 1, 2, \dots), \text{ and with } \varepsilon_n(0) < \varepsilon_m(0).$$

Let us represent the dependence $\varepsilon_n(V)$ on V in the form

$$\varepsilon_n(V) = \varepsilon_n(0) + K_n(V)eV.$$

Then at the voltage V_0^{nm} corresponding to the PC of two electronic terms (n th and m th), one obtains exact (6) and approximate (7) equalities,

$$\Delta_{nm} = K_{nm}(V_0^{nm})eV_0^{nm}, \quad (6)$$

where

$$\Delta_{nm} = \varepsilon_n(0) - \varepsilon_m(0), \quad \text{and} \quad K_{nm}(V_0^{nm}) = \hbar\omega/e\delta V_0^{nm}. \quad (7)$$

In these equations, the vibrational quantum ω is equal to the separation between the neighboring maxima in the vibrational NDR series. The corrections to Eq. (7) are on the order of $\delta V_0^{nm}/V_0^{nm} \approx 0.1$.

The spectrum of the POM electronic states can be considered as being known. Knowing V_0^{nm} , one can select the $\varepsilon_n(0)$ and $\varepsilon_m(0)$ levels determining the value of Δ_{nm} . Then, using the equality

$$\omega = \delta V_0^{nm} \Delta_{nm} / \hbar V_0^{nm},$$

one can determine the vibrational quantum ω from the experimental values of δV_0^{nm} . The results of thus reproduced vibrational quanta of ammonium DMDC, as obtained by processing the spectra with ascending envelopes under the assumption that $\Delta_{nm} = 1.23$ eV, are presented in Fig. 5. A comparison of the resulting distribution with the known IR spectra of these compounds suggests that the states involved in the process of biresonance tunneling correspond to the oxygen–metal and N–H stretching modes.

IV. CONCLUSIONS

To conclude, let us summarize the main results of the work and identify their place in the physical chemistry of polyoxometalates.

1. The structure and electronic conduction of decamolybdo-dicobaltates (DMDCs) were studied by the probe methods for the first time. The topographic images of the two-dimensional ordered structures formed by the DMDC salts deposited from aqueous solutions onto the HOPG surface were obtained and used to reveal two characteristic sizes. Measurements were carried out for the tunneling DMDC spectra containing multiple NDRs (single and pair, asymmetrical and symmetrical, large-scale and grouping into the vibrational series with the

ascending, descending, and bell-shaped envelopes) on both voltage semiaxes.

2. The mechanism of NDR formation in the tunneling spectra of polyoxometalates was established and found to be common to all nanostructures with weak exchange coupling breaking in the strong electric fields.
3. The algorithm was proposed for extracting the energy parameters (such as the energy gap between the occupied and unoccupied states and vibrational quanta) of the isolated POM molecules from the NDR-containing spectra.

The proposed variant of the tunneling resonance electron-vibrational spectroscopy of the nano-objects with weak intramolecular exchange coupling is of great interest in connection with the rapid development of the chemistry of POMs, whose possible areas of application encompass today almost all the avenues of inquiry in nanotechnology.

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