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The molecular rectifiers and negative differential resistance based on the polyoxometalates

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The STM tunneling spectra of the ordered monolayer films of decamolybdodicobaltate compounds deposited from aqueous solutions on HOPG exhibit well-defined negative differential resistances (NDRs). The mechanism of formation of these spectral features found to be common to all systems exhibiting the Wannier—Stark localization. A model of biresonance tunneling was developed to provide an explanation for the totality of experimental data, both literature and original. 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. In this work, we evaluate electron transport properties of molecular devices built from molecules of polyoxometallates Keggin's type adsorbed on HOPG and connected by an alkane chain to the tip of STM. We find that electron transport in these systems at gap voltage $\cong \pm 2$ v is mediated by the Keggin's molecular orbitals LUMO and HOMO. For higher voltage, a model of biresonance tunneling electron transitions provided the pseudo-energy levels intersection was proposed for explanation of the totality of experimental data.

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