Vibrationally Mediated Negative Differential Resistance in a Single Molecule

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A new mechanism for negative differential resistance (NDR) has been discovered and involves a single molecule in the junction of a scanning tunneling microscope. The NDR was observed at voltages corresponding to the vibrational energies of single pyrrolidine molecules on the (001) surface of copper at 9 K. This vibrationally mediated NDR contrasts with the previously known mechanisms which all involve the electronic states of the conducting media.

Future generations of electronics may rely on single molecules to perform as nanoscopic electronic devices and to carry current between such devices [1]. The use of single molecules for tasks currently managed by larger-scale silicon-based electronics will require an understanding of electron transport on the molecular scale. Recent measurements of single molecule transport properties [2–7] represent important contributions to the eventual realization of molecular electronics, one example of which is a room temperature transistor constructed from a single carbon nanotube [8].

The basic operating principle behind a variety of high-speed semiconductor devices is the phenomenon of negative differential resistance (NDR) [9,10], first discovered by Esaki [11] in the *p-n* junction of a Ge diode. NDR on the atomic scale was first observed on a semiconductor surface in the junction of a scanning tunneling microscope (STM) [12,13]. More recently, NDR was found in self-assembled monolayers both in a nanoscale molecular device [14] and in the junction of an STM [15]. The NDR characteristics of these systems can all be attributed to electron transport involving discrete states in the electronic structure.

We observed NDR in a single pyrrolidine (C_4H_8NH) molecule in the junction of an STM. This single molecule NDR is driven by a novel mechanism: the excitation and relaxation of a localized molecular vibration. These results demonstrate how the conductivity of a single molecule can be affected by the inelastic electron-vibration coupling and structural changes in a single molecule adsorbed on a metal surface.

The variable temperature STM and sample preparation techniques used in this study have been described previously [16]. Pyrrolidine (Aldrich; 99.5% purity) and pyrrolidine-d_8 (pyrrolidine-2,2,3,3,4,4,5,5-d_8: Isotec, Inc.; 98 atom % purity) were further purified with multiple freeze-pump-thaw cycles. These molecules were dosed onto the cooled Cu(001) surface (9 K) with vapors from the room temperature liquids. Coverage was kept low to permit investigation of individual well-isolated molecules. The experiment was conducted at 9 K to provide a stable junction geometry and to minimize thermal energy broad-ening of tunneling electrons. The molecular-scale junction consisted of the STM tip, a vacuum gap of ~5-8 Å, and a single pyrrolidine molecule bound to the copper surface. Pyrrolidine does not diffuse away from the STM tip under the conditions of this study.

The current-voltage (*I-V*) characteristic for the pyrrolidine molecular junction (Fig. 1) clearly displays three regions. Near zero bias, the curves are essentially linear, indicating metallic behavior. At ~±120 mV for pyrrolidine and pyrrolidine-d_8, there is an abrupt change in slope and the curves deviate from the *I-V* curve of the clean Cu(001) surface. NDR, in which the slope of *I-V* becomes negative, is evident at both positive and negative biases [17]. This NDR effect manifests itself as a negative conductance, dI/dV, starting at ±376 mV (±283 mV) for pyrrolidine (pyrrolidine-d_8). The deviations from metallic behavior coincide with known pyrrolidine molecular vibrations in the gas and liquid phases: CH_2 stretch at 365 meV, CH_2 wag at 151 meV or twist at 161 meV, and a ring mode at 122 meV [18]. Further confirmation of the vibrationally mediated mechanism for these changes in differential resistance was obtained by observing the expected isotopic shifts of the vibration-induced features in the *I-V* curve of pyrrolidine-d_8 (Fig. 1).

To understand the observed NDR, the dynamics of adsorbed pyrrolidine must be studied. Pyrrolidine adsorbs molecularly on Cu(001) at 9 K, appearing as a protrusion in constant current STM images (Fig. 2a). The noise apparent in the image is molecular in nature. An image taken at a larger gap resistance (Fig. 2b) revealed the molecule switching between two states (I and II) as the tip was scanned across it. The tunneling current in the two states and the time dependence of this switching were studied (Fig. 2c) by placing the tip over the maxium height of the molecular image and turning off the feedback. The molecule flipped between the two states. Since the tip height was fixed, the conductance of the molecular junction changed when the molecule changed states. This produced two distinct levels in the current trace. The high (low) current state corresponds to I (II). The spectra shown in Fig. 1 are averages over both of the states. Deuterium exchange studies over transition metal catalysts suggest
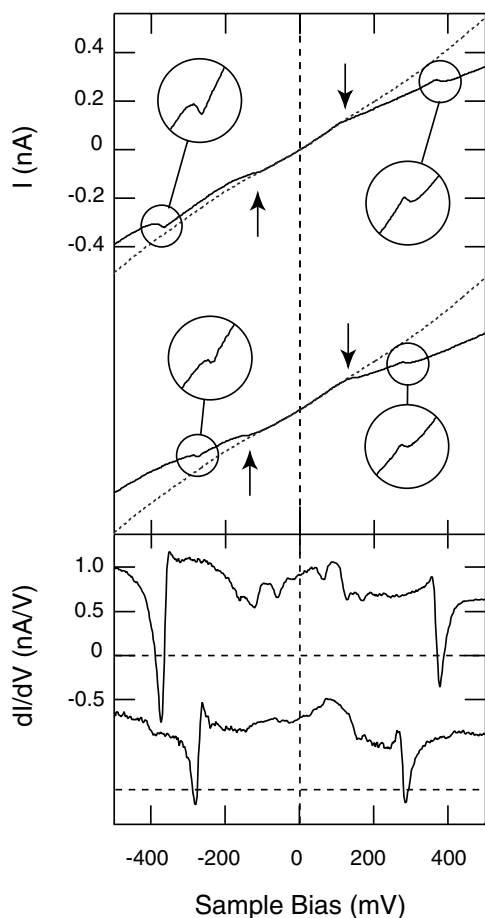
FIG. 1. I and dI/dV versus the sample bias measured with the same tip over pyrrolidine (upper curve) and pyrrolidine-d_8 (lower curve). The lower curves are offset for clarity. I-V measurements were made over the clean Cu(001) surface (dashed line) for comparison. Expanded views ($\times 6$) of the NDR regions; arrows indicate the additional nonlinear sections of the I-V curves. Before opening the feedback loop for spectroscopy, the tip height was set by choosing a gap resistance of 1.0 GΩ (0.1 nA at 100 mV). I-V measurements were obtained without modulating the dc sample bias while dI/dV was measured with a sample bias modulation of 5 mV rms, 260 Hz. The step size in each scan is 2.5 mV with a 2 ms dwell time per step for I-V and a 300 ms dwell time per step for dI/dV. The spectra displayed are an average of multiple scans from -500 mV to $+500$ mV and back to -500 mV: 3000 scans for I-V and 102 scans for dI/dV on pyrrolidine, 6000 scans for I-V and 131 scans for dI/dV on pyrrolidine-d_8, and 1200 scans for I-V on Cu(001). Portions of dI/dV below the horizontal dashed lines correspond to the occurrences of NDR.

that pyrrolidine adsorbs through the lone pair of electrons on the nitrogen [19]. The molecule can then either stand up (I) or bend (II) towards the surface as illustrated schematically in Fig. 2d. The pyrrolidine ring in proline residues of proteins and polypeptides exhibits a similar conformation change [20]. In the gas phase, these conformations interconvert through pseudorotation [21] with an energy barrier of ~ 40 meV [22]. Calculations and other experi-
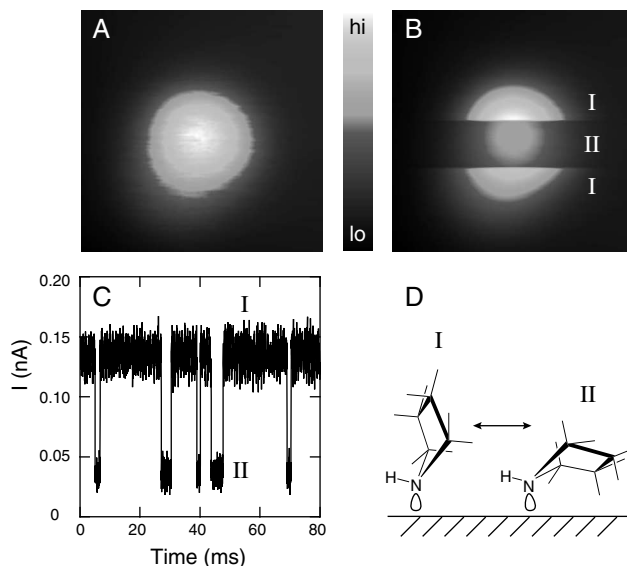

FIG. 2. (a) Constant current image (22 Å $\times$ 22 Å) of a single pyrrolidine-d_8 molecule on Cu(001) taken at a tunneling current of 1 nA and 250 mV bias. The "noise" is due to molecular motion. (b) In this constant current image (20 pA, 30 mV), pyrrolidine-d_8 flipped between the two states (I and II) as the tip was scanned horizontally across the molecule. (c) Current collected with the tip positioned over the center of the pyrrolidine-d_8 molecule. The feedback was turned off (with the tip height set at 0.1 nA and 100 mV) and a bias voltage of 144 mV was applied. Two distinct current states are seen. The high (low) current level corresponds to state I (II). Tunneling electrons induce the molecule to flip between these two states. (d) Proposed conformations of pyrrolidine on the surface for the two current states.

mental methods are needed to determine the nature of these states for pyrrolidine adsorbed on the Cu(001) surface.

By collecting current traces (e.g., Fig. 2c) at 2.5 mV bias increments, we measured the I-V curves of the two pyrrolidine states in the region of the CD_2 stretch (Fig. 3a) [23]. These state-resolved I-V curves (Fig. 3a) are linear, in sharp contrast to the state-averaged I-V curves (Fig. 1). Changes in the fractional occupation of the two states (Fig. 3b) produce the nonlinearities, including NDR, observed in the state-averaged I-V curves. The fractional occupation times at a given bias can be determined from the average times spent in the high and low current states in the current trace. Weighting the state-resolved I-V curves, I_1 and I_2 (Fig. 3a), with the fractional occupation times, t_1 and t_2 (Fig. 3b), $I_{\text{avg}} = t_1 * I_1 + t_2 * I_2$, effectively simulates the state-averaged I-V measurements (Fig. 3c).

Vibrationally mediated NDR results from an abrupt change in fractional occupation times of the high and low current states (I and II, respectively) when the CH_2 (CD_2) stretch is excited. As the bias is increased through the threshold for excitation of the CH_2 (CD_2) stretch, the fractional occupation of the low current state increases while that of the high current state decreases, resulting in a decrease of the current averaged over the two states.
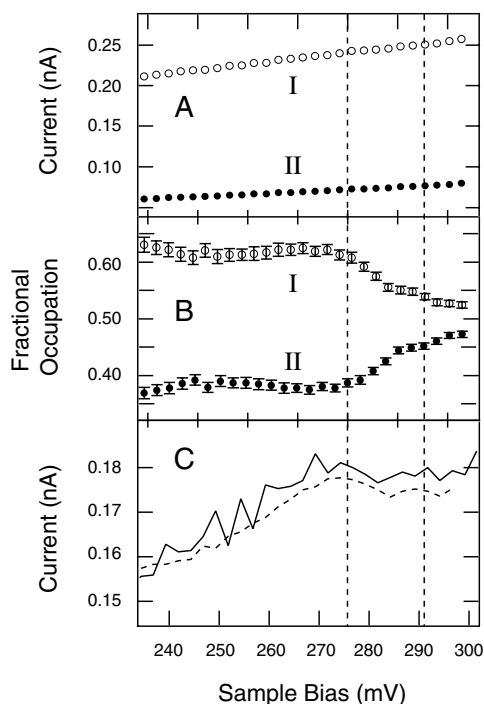
FIG. 3. (a) State-resolved I-V curves on pyrrolidine-d_8 (State I: ○ marker, State II: ● marker) determined from current traces as in Fig. 2C. All current traces were obtained with the same gap distance (set at 0.1 nA and 100 mV) and multiple traces were collected for each sample bias to obtain good statistics. The current level of each state was determined by fitting the peaks in a histogram of the current values with a Gaussian. The error from this fitting procedure is smaller than the marker size. (b) Fractional occupation as a function of bias for the two states of pyrrolidine-d_8. The error bars were determined from Poisson statistics. The vertical dashed lines show the range of biases where NDR was observed. (c) State-averaged I-V on pyrrolidine-d_8 (solid line; 200 passes) and the simulated I-V curve (dashed line).

Above and below the vibrational energy, there is no sharp variation in the occupation of the two states so the average current increases smoothly with bias. The onset of the low energy nonlinearity at $\sim\pm120$ mV in I-V corresponds with the ring mode vibration.

The magnitude of the change in fractional occupation of the two current states depends on the efficiency of vibrational excitation and the conversion of this energy into molecular motion. One possible explanation for the increase in fractional occupation of II is that the excitation cross section for the CH_2 (CD_2) stretch is expected to be greater for I due to the closer proximity of the molecule to the tip. Excitation of the ring deformation mode due to intramolecular vibrational relaxation is thus increased proportionally. Since the motion for the conformational change involves the ring deformation, a relative increase is observed in the transition rate out of I compared to the transition rate out of II. Another possible factor is that the molecule is closer to the surface in II, the bent conformation, where its vibrational excitations [in particular,

the CH_2 (CD_2) stretch and ring deformation mode] can dissipate into the substrate more efficiently. The more efficient coupling to the substrate decreases the probability of a transition back to I, the standing conformation. This, too, could contribute to the higher fractional occupation for the low current state.

Variations in the curvature of the state-averaged I-V (Fig. 1) ranged from the slight nonlinearity induced by the ring and wag (or twist) modes to the NDR due to the CH_2 (CD_2) stretch mode. Thus the degree of electron-vibrational coupling and the subsequent conversion of energy from vibrations to structural conformation changes determine the voltage-dependent conductivity of this single molecule junction. The redistribution of electronic energy to vibrational modes of a molecule is itself an active area of research [24] because it can lead not only to conformational changes but also chemical transformation.

It is worth noting that NDR in pyrrolidine occurs at energies less than 0.5 eV; molecular devices which operate at biases of a few eV may be susceptible to chemical changes as chemical bond energies are also of this order [25]. An additional benefit of low-voltage device operation is reduced power consumption. The degree to which this vibrationally mediated NDR mechanism will contribute to the development of molecular devices remains to be seen.

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