Steric Turnoff of Vibrationally Mediated Negative Differential Resistance in a Single Molecule**

Jennifer Gaudioso and Wilson Ho*

Understanding the flow of energy through a molecule is a problem of fundamental interest to chemical dynamics and of practical importance to molecular electronics. Examples abound of vibrational energy coupling to changes in molecular conformation.[1] The scanning tunneling microscope (STM) has been used to study these processes at the single-molecule level.[2, 3] Stipe et al. discovered that the CH stretching excitation couples to the reversible rotation of an acetylene molecule in the fourfold hollow site of Cu(001) at 8 K. We previously demonstrated that tunneling electrons could be used to excite the CH_2 stretch in single pyrrolidine molecules adsorbed on the Cu(001) surface at 9 K. This excitation energy coupled to the interconversion between two conformational states of the adsorbed molecule to produce negative differential resistance (NDR) by a new vibrationally mediated mechanism.[4] In contrast, previous observations of NDR in the Esaki tunnel diode,[5] quantum wells and dots,[6] atomic impurities,[7, 8] and adsorbed monolayers[9, 10] can all be attributed to discrete states in the electronic structure. These discrete states are due to either size quantization or atomic localization. Negative differential resistance, that is, decreasing current with increasing voltage, is the basic operating principle behind a variety of high-speed semiconductor devices.[11, 12] While the development of molecular-sized versions of conventional electronics will become important as we push towards ever smaller devices,[13] these single-molecule studies also offer insights into the effects of structure and dynamics on electron transport and intramolecular and molecule–surface energy-transfer processes.

Here we report on the steric turnoff of the vibrationally mediated NDR effect by comparing *N*-methylpyrrolidine to pyrrolidine on Cu(001) at 9 K. The STM was used to further our understanding of the relationship between molecular structure and dynamics in single adsorbed molecules.

Experiments were performed with a homemade variable-temperature STM in an ultrahigh-vacuum chamber. Details of the apparatus and cleaning procedures for the Cu(001) sample and tungsten tips have been described elsewhere.[14] For experiments, the sample and STM were cooled to 9 K. Pyrrolidine (Aldrich; 99.5 % purity), [2,2,3,3,4,4,5,5-D_8]pyrrolidine (Isotec, Inc.; 98 atom % purity), and *N*-methylpyrrolidine (Aldrich; 97 % purity) were further purified by multiple freeze–pump–thaw cycles. Coverages of about 0.001 monolayers were obtained by passing the molecules from the vapors above the room-temperature liquids through a capillary-array doser attached to a variable leak valve. Neither pyrrolidine nor *N*-methylpyrrolidine diffuses away from the tip under the conditions used in this study. The vibrational energies are reported in units of millielectron volts: 1 meV = 8.065 cm^{-1}.

Both pyrrolidine and *N*-methylpyrrolidine are adsorbed through the lone pair of electrons on nitrogen and appear as protrusions in the constant-current STM images (Figure 1 a). As the tip was scanned across the molecules, the pyrrolidine molecule flipped between two states (I and II); the proposed conformations of these states are depicted in Figure 1 b.[4] The occupation of these two states is determined by the sample bias voltage and the tunneling current. *N*-Methylpyrrolidine was never observed to change states. We believe that the methyl group pins the molecule in the bent conformation (Figure 1 b). Cross sections taken through the maxima in the molecular images (Figure 1 c) show that the apparent height

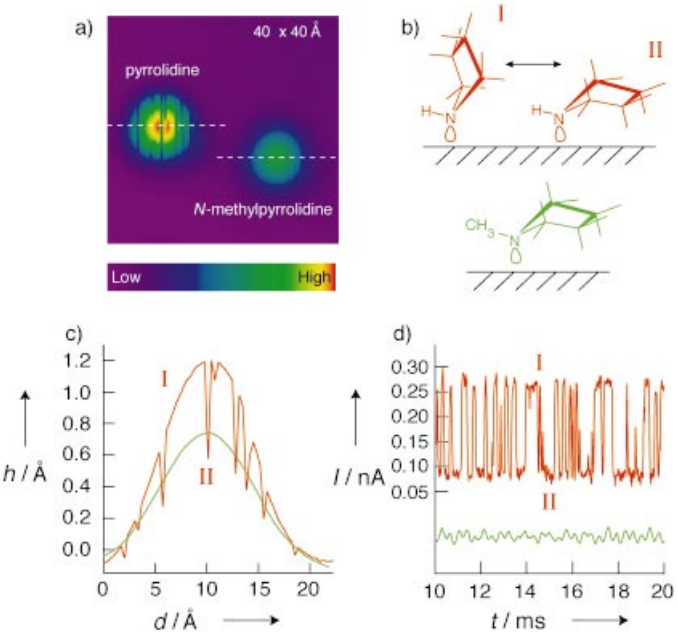


Figure 1. a) 40 × 40 Å constant-current STM images of pyrrolidine and *N*-methylpyrrolidine on Cu(001) at 9 K, taken at 50 pA and 30 mV sample bias. The pyrrolidine molecule flipped between two states (I and II) as the tip was scanned across the molecule, whereas *N*-methylpyrrolidine did not change. b) Schematic picture of the two proposed conformations of adsorbed pyrrolidine (top) and the single conformation of *N*-methylpyrrolidine (bottom). c) Cross sections of pyrrolidine (red) and *N*-methylpyrrolidine (green) images, taken along the dashed lines in (a). d) Current collected during a voltage pulse with the sample bias corresponding to 16 meV above the CD_2 (CH_2) stretching energy; the tip was positioned over the center of a [D_8]pyrrolidine (*N*-methylpyrrolidine) molecule. Two distinct current levels corresponding to states I and II are seen in the [D_8]pyrrolidine (red) current trace; only one current level is observed for *N*-methylpyrrolidine (green), with an average value of 0.14 nA (for clarity the current trace is offset from that of [D_8]pyrrolidine but shares the same *y* axis scale). The flipping rate of pyrrolidine is faster than that of [D_8]pyrrolidine.

[*] Prof. W. Ho
Department of Physics and Astronomy and Department of Chemistry
University of California, Irvine, CA 92697 (USA)
Fax: (+1) 949-824-2174
E-mail: wilsonho@uci.edu

J. Gaudioso
Department of Chemistry and Cornell Center for Materials Research
Cornell University, Ithaca, NY 14853 (USA)

[**] This work was supported by the National Science Foundation (DMR-9417866) and by the Cornell Center for Materials Research (CCMR), a Materials Research and Engineering Center of the National Science Foundation (DMR-9632275). Particular acknowledgement is made of the use of the Computing and Materials Facilities of the CCMR.

  1433-7851/01/4021-4080 $ 17.50+.50/0

of *N*-methylpyrrolidine is about 120 % of that of conformation II of pyrrolidine. Changes in the electronic structure of the molecule due to the substitution of the methyl group for the hydrogen atom on the nitrogen atom could result in the observed height differences. The apparent height of conformation I of pyrrolidine is about 194 % of that of conformation II. The conformational change in pyrrolidine can be studied by monitoring the time dependence of the tunneling current. With the tip fixed at a constant height over the maximum of the molecular protrusion, the tunneling current of the molecular junction changed as the pyrrolidine molecule flipped between the two conformations. This was evident as two levels in the current. The current trace displayed in Figure 1 d was collected over [D_8]pyrrolidine, which flips at a slower rate than pyrrolidine. For all biases studied, the current collected with the tip over *N*-methylpyrrolidine exhibited only one level (Figure 1 d), which indicates that the molecule does not change states. This difference in molecular geometry between pyrrolidine and *N*-methylpyrrolidine produces a significant difference in the molecular conductivity of the two species. The current – voltage ($I-V$) characteristic for a single pyrrolidine molecule (Figure 2) shows regions of NDR at both

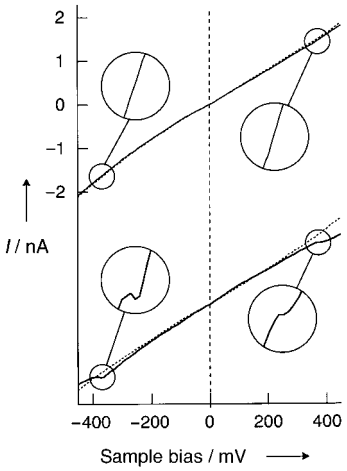


Figure 2. $I-V$ measured with the same tip over *N*-methylpyrrolidine (upper curve) and pyrrolidine (lower curve). A spectrum was also collected over the clean Cu(001) surface (dashed line) for comparison. The NDR regions for pyrrolidine and the comparable regions for *N*-methylpyrrolidine are shown as expanded views (×6). NDR was observed at voltages corresponding to the CH_2 stretch in pyrrolidine. The spectra are averages of multiple scans from −450 to +450 mV and back down to −450 mV: 200 scans on *N*-methylpyrrolidine, 1000 scans on pyrrolidine, and 200 scans on Cu(001). The step size is 2.5 mV with a dwell time of 2 ms. Because the pyrrolidine molecule switches conformations, more averaging is required to achieve a signal-to-noise ratio that is comparable to that of the *N*-methylpyrrolidine curve.

positive and negative bias. The value of the current at each bias represents an average of both the high- (I) and low-current (II) levels weighted by the fractional occupation of the two conformations. When pyrrolidine ([D_8]pyrrolidine) begins to spend more time in the low current state as the sample bias crosses the threshold voltage corresponding to the CH_2 (CD_2) stretch, the average current decreases.[4] Since the methyl group constrains *N*-methylpyrrolidine to only one state on Cu(001), the $I-V$ characteristic for this molecule increases monotonically throughout the measurement.

Stark contrasts are also evident in the inelastic electron tunneling spectra (STM-IETS[15]) collected over the single adsorbed molecules (Figure 3). Four vibrational modes are

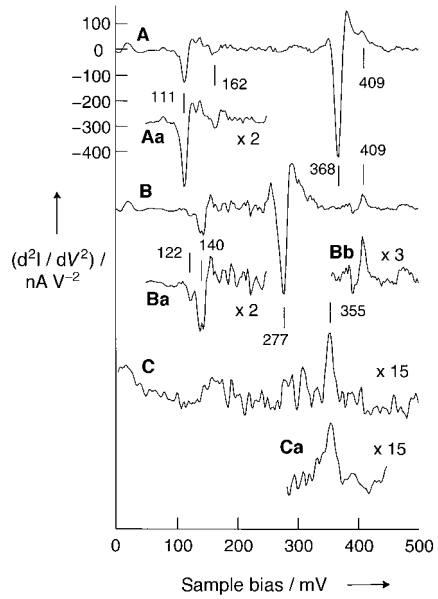


Figure 3. Single-molecule vibrational spectra obtained by STM-IETS for **A**) pyrrolidine, **B**) [D_8]pyrrolidine, and **C**) *N*-methylpyrrolidine. The vertical lines indicate the positions of the dips or peaks associated with the vibrational modes. To clarify the lineshape in d^2I/dV^2, portions of spectra for modes with smaller intensities are shown enlarged and with additional averaging. **A**) 235 scans from 0 to 500 mV and back down to 0 mV (0 – 500 mV), **Aa**) 1025 scans (50 – 250 mV); **B**) 533 scans (0 – 500 mV), **Ba**) 733 scans (50 – 250 mV), **Bb**) 533 scans (325 – 500 mV); and **C**) 112 scans (0 – 500 mV), **Ca**) 285 scans (250 – 450 mV). The step size is 2.5 mV with a dwell time of 300 ms.

observed by STM-IETS in the d^2I/dV^2 spectrum for pyrrolidine ([D_8]pyrrolidine). Asymmetric dips are observed at 368 (277), 162 (140), and 111 (122 mV) and are associated with the CH_2 (CD_2) stretch, CH_2 (CD_2) wag or twist, and a ring mode, respectively. The second derivative of the NDR region of the $I-V$ curves produces the observed lineshape for the CH_2 (CD_2) stretch. The symmetric, positive peak (409 mV) is assigned to the NH stretch. It appears in the shoulder of the CH_2 stretch but is clearly visible in the [D_8]pyrrolidine spectrum. These mode assignments were based on isotopic shifts and comparison to previous infrared studies on gas- and liquid-phase pyrrolidine.[16] A CH_2 stretch (355 mV), also a symmetric, positive peak, is the only vibrational mode detected by STM-IETS for *N*-methylpyrrolidine. This observed lineshape is indicative of an increase in the differential conductance dI/dV at the vibrational energy.[17] In contrast to *N*-methylpyrrolidine, more vibrational modes are "tunneling-active" in pyrrolidine. This increase in the inelastic cross section is attributed to the coupling of the tunneling electrons to the different conformations of pyrrolidine.

For gaseous pyrrolidines, it is well known that substitution at the nitrogen atom only marginally affects the structure of the ring but strongly affects the preferred conformation.[18, 19]

  1433-7851/01/4021-4081 $ 17.50+.50/0

Substitution of a methyl group for the *N*-hydrogen atom turns a conformationally floppy adsorbate into a sterically constrained one. This alters the process of intramolecular vibrational energy redistribution (IVR). For pyrrolidine, the CH_2 stretch excitation can dissipate by coupling to the large-scale conformational change. This dissipation path is quenched for *N*-methylpyrrolidine. For both molecules, the CH_2 stretch can transfer its energy to other lower energy vibrations, substrate phonons, and electron–hole pairs.

Like the pyrrolidines, pyridine binds to copper predominantly through the lone pair electrons on nitrogen.[20] Only the CH (CD) stretch mode of pyridine on Cu(001) at 377 (281) mV has been observed with STM-IETS,[21] and the lineshape of this mode matches the lineshape of the *N*-methylpyrrolidine CH_2 stretch. The aromaticity of the pyridine ring constrains the molecule to a planar geometry. The rigid electronic backbone of pyridine acts like the bulky methyl group on *N*-methylpyrrolidine, keeping the molecule in just one conformation.

It is evident that molecular structure can have a significant impact on the dissipation of vibrational energy. Simple substitution of a methyl group for a hydrogen atom removes the NDR from the $I-V$ curve. Thus, as we move to ever smaller devices, consideration must be given to the effect of molecular structure and conformation on the conductivity. By changing the functional groups in a molecule, different electronic functions can be realized at the molecular level. At a more fundamental level, understanding how molecular structure and dynamics alter electron transport through single molecules has important ramifications in chemical and biological systems.

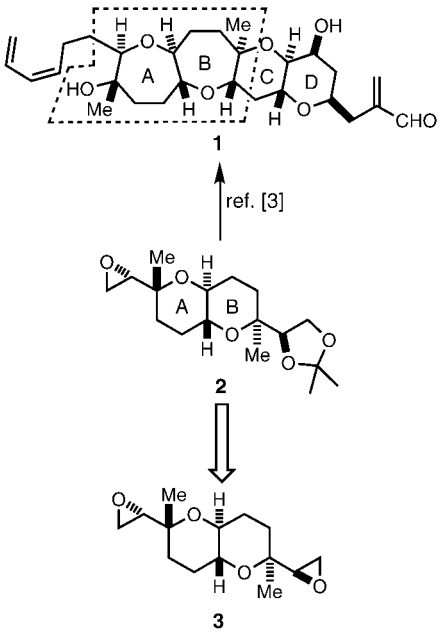
Received: May 16, 2001 [Z17121]

[1] M. Räsänen, H. Kunttu, J. Murto, *Laser Chem.* **1988**, *9*, 123.
[2] B. C. Stipe, M. A. Rezaei, W. Ho, *Science* **1998**, *279*, 1907.
[3] B. C. Stipe, M. A. Rezaei, W. Ho, *Phys. Rev. Lett.* **1998**, *81*, 1263.
[4] J. Gaudioso, L. J. Lauhon, W. Ho, *Phys. Rev. Lett.* **2000**, *85*, 1918.
[5] L. Esaki, *Phys. Rev.* **1958**, *109*, 603.
[6] *Physics and Technology of Submicron Structures* (Eds.: H. Heinrich, G. Bauer, F. Kuchar), Springer, Berlin, **1988**.
[7] I. W. Lyo, P. Avouris, *Science* **1989**, *245*, 1369.
[8] P. Bedrossian, D. M. Chen, K. Mortensen, J. A. Golovchenko, *Nature* **1989**, *342*, 258.
[9] J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **1999**, *286*, 1550.
[10] Y. Xue, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson, C. P. Kubiak, *Phys. Rev. B* **1999**, *59*, R7852.
[11] S. M. Sze, *Physics of Semiconductor Devices*, Wiley, New York, **1981**.
[12] L. L. Chang, E. E. Mendez, C. Tejedor, *Resonant Tunneling in Semiconductors*, Plenum, New York, **1991**.
[13] *Molecular Electronics: Science and Technology* (Eds.: A. Aviram, M. Ratner), New York Academy of Sciences, New York, **1998**.
[14] B. C. Stipe, M. A. Rezaei, W. Ho, *Rev. Sci. Instrum.* **1999**, *70*, 137.
[15] B. C. Stipe, M. A. Rezaei, W. Ho, *Science* **1998**, *280*, 1732.
[16] J. C. Evans, J. C. Wahr, *J. Chem. Phys.* **1959**, *31*, 655.
[17] P. K. Hansma, *Tunneling Spectroscopy*, Plenum, New York, **1982**.
[18] G. Pfafferott, H. Oberhammer, J. E. Boggs, *J. Am. Chem. Soc.* **1985**, *107*, 2309.
[19] I. F. Shishkov, L. V. Vilkov, N. F. Pyatakov, *J. Struct. Chem.* **1992**, *33*, 38.
[20] B. J. Bandy, D. R. Lloyd, N. V. Richardson, *Surf. Sci.* **1979**, *89*, 344.
[21] L. J. Lauhon, W. Ho, *J. Phys. Chem. A* **2000**, *104*, 2463.

First Desymmetrization of a Centrosymmetric Molecule in Natural Product Synthesis: Preparation of a Key Fragment in the Synthesis of Hemibrevetoxin B**

Joanne M. Holland, Mark Lewis, and Adam Nelson*

Many polyether marine natural products, such as the ciguatoxins, brevetoxins, and yessotoxins, have embedded centrosymmetric fragments.[1] For example, the AB ring system of hemibrevetoxin B (**1**) is a centrosymmetric dioxepane (see boxed fragment: **1**, Scheme 1). There are three reported syntheses of hemibrevetoxin B (**1**), but none of these approaches take advantage of this hidden symmetry.[2, 3]



Scheme 1. Retrosynthetic analysis.

Our approach to hemibrevetoxin B is outlined in Scheme 1. Desymmetrization[4] of the centrosymmetric diepoxide **3**, by selective hydrolysis[5] of one of its enantiotopic epoxides and protection, would give the known[3] acetonide **2**. The symmetry of **3** demanded that a two-directional strategy[6] be used, an approach which was expected to improve the efficiency of the synthesis of **2** considerably. The epoxide **2** has been prepared

[*] Dr. A. Nelson, J. M. Holland
School of Chemistry
University of Leeds
Leeds, LS2 9JT (UK)
Fax (+44) 113-233-6565
E-mail: adamn@chem.leeds.ac.uk
Dr. M. Lewis
Discovery Chemistry, Pfizer Central Research
Ramsgate Road, Sandwich, Kent, CT13 9NJ (UK)

[**] This work was supported by the University of Leeds (through a Brotherton Scholarship to J.M.H.) and Pfizer. We are extremely grateful to Professor T. Nakata of the Institute of Physical and Chemical Research (RIKEN), Saitama, Japan, for providing us with the NMR spectra of the epoxide **2**, the Royal Society for a grant, and AstraZeneca for strategic research funding.

  1433-7851/01/4021-4082 $ 17.50+.50/0