Single-Molecule Vibrations, Conformational Changes, and Electronic Conductivity of Five-Membered Heterocycles

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Abstract: Using an ultrahigh vacuum scanning tunneling microscope (STM), we have explored the interactions of isolated five-membered heterocycles, pyrrole, thiophene, pyrrolidine, and tetrahydrothiophene, with the Cu(001) surface at 9 K. Pyrrolidine was also studied on the Ag(001) surface. Important distinctions in bonding, vibrational spectra, and vibrationally mediated negative differential resistance were observed with the aid of single-molecule inelastic electron tunneling spectroscopy (STM-IETS).

Introduction

Extensive theoretical and experimental investigations into the conformational and dynamical properties of five-membered heterocycles have been carried out[1,2] due, in part, to their important structural roles in nucleic acids and proteins. Together with their aromatic analogues, tetrahydrofuran, tetrahydrothiophene, and pyrrolidine form a series of molecules which provide contrasts in chemical bonding. Most of the previous work on these molecules has focused on the examination of their gas-phase properties. However, recognizing the importance of surface interactions for heterogeneous catalysis and other surface chemical reactions, some work characterizing the adsorption of these heterocycles has been carried out (ref 3 and references therein).

The scanning tunneling microscope (STM) with its spatially localized tunneling electrons provides a unique window for visualizing surface chemical interactions. Imaging (elastic tunneling) single molecules on surfaces often yields insights into orientation and bonding. In addition, by losing energy to a molecular bond, the electrons can tunnel inelastically to induce single-molecule chemistry[4−8] and to enable vibrational spectroscopy.[9] This inelastic electron tunneling spectroscopy (IETS) makes it possible to probe the effects of surface interactions on individual molecular bonds.

In the present work, we examine the molecule−surface interactions of five-membered heterocycles, comparing the bonding and spectroscopy of aromatic and saturated species. We find evidence of adsorbates bonding to the surface through π-orbitals for the aromatic species or the lone pair for the saturated species. In addition, one saturated molecule, pyrrolidine, has two surface conformations between which it can switch while the related tetrahydrothiophene shows no sign of undergoing such motion. This conformational switching is critical in bringing about vibrationally mediated negative differential resistance (NDR).[10] The IETS spectrum of pyrrolidine is also more structured than the tetrahydrothiophene spectrum.

Experimental Section

All experiments were conducted with a home-built variable temperature STM housed in an ultrahigh vacuum chamber (base pressure of 2×10^{-11} Torr).[11,12] The Cu(001) sample was cleaned by repeated cycles of Ne ion sputtering and annealing to 525 °C. Etched polycrystalline tungsten tips were also sputtered and annealed prior to use. Thiophene (99% purity), tetrahydrothiophene (99%), and pyrrolidine (99.5% purity) were purchased from Sigma-Aldrich. Pyrrolidine-2,2,3,3,4,4,5,5-d_8 (pyrrolidine-d_8) came from Isotec, Inc. and had 98 atom % purity. These liquids were further purified with multiple freeze−pump−thaw cycles. The molecules were dosed in situ via a capillary array doser attached to a variable leak valve. The STM and sample were cooled to 9 K prior to dosing and held there for the duration of the experiment. Under these conditions, all molecules adsorbed molecularly; there was no evidence for desulfurization, in agreement with previously reported results.[3]

To obtain a vibrational spectrum,[11,12] the molecule was tracked on a local maximum in the topographical image. The feedback was then turned off, and an ac modulation (5 mV, 260 Hz) was added to the linearly ramped dc sample bias voltage. A lock-in amplifier was used to detect the first and second harmonics of the modulation frequency which are proportional to dI/dV and d^2I/dV^2, respectively. After each sweep of the bias voltage, the feedback was turned back on, and the molecule was tracked automatically prior to the next sweep. Spectra were averaged after each sweep. The vibrational energies are reported in units of millielectronvolts: 1 meV = 8.0655 cm^{-1}. No modulation was used when collecting $I-V$ spectra. To avoid any drifts in the tip height, a few hundred scans (a few minutes) were obtained without tracking. Then a STM image was taken and the tip repositioned over the molecule. Another $I-V$ spectrum could be taken and averaged with the previous spectra as long as the molecule was in the same conformation when the feedback was turned off, thus ensuring the same tip height.

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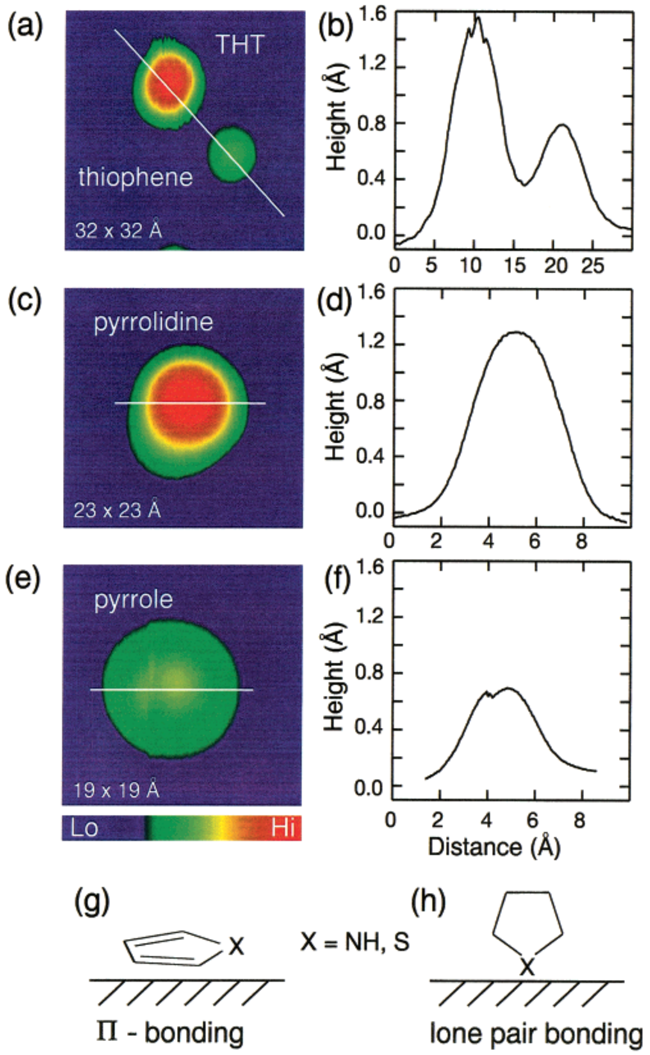

Figure 1. Constant-current STM images of (a) tetrahydrothiophene (THT) and thiophene on Cu(001) (32 Å × 32 Å, 0.1 nA and 1.0 V sample bias), (c) pyrrolidine on Cu(001) (23 Å × 23 Å, 1 nA and 250 mV sample bias), and (e) pyrrole on Cu(001) (19 Å × 19 Å, 1 nA and 250 mV sample bias). The right-hand column (b, d, f) shows cross sections of these molecules taken along the lines indicated in the STM images. (g) Proposed bonding of the heterocycles with π systems, thiophene and pyrrole. (h) Proposed bonding of the saturated heterocycles, tetrahydrothiophene and pyrrolidine.

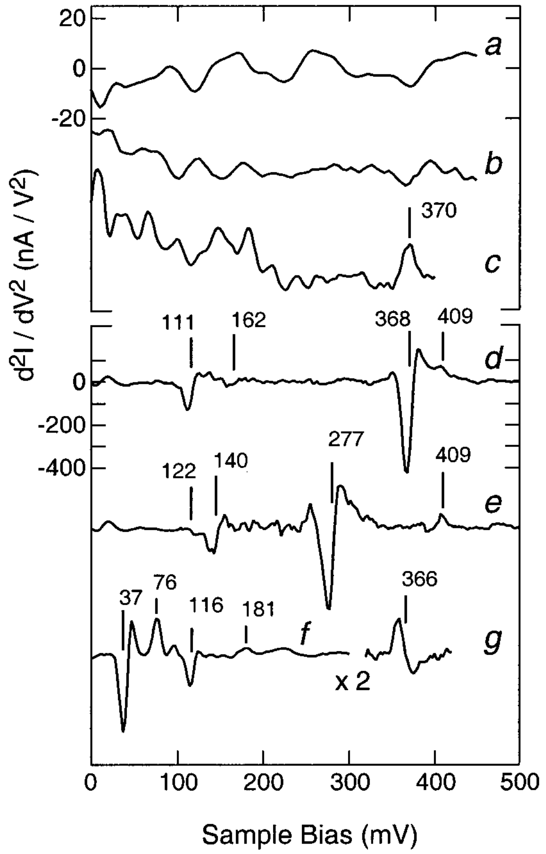

Figure 2. Single-molecule vibrational spectra obtained by STM-IETS for (a) pyrrole on Cu(001), (b) thiophene on Cu(001), (c) tetrahydrothiophene on Cu(001), (d) pyrrolidine on Cu(001), (e) pyrrolidine-d_8 on Cu(001), and (f) pyrrolidine on Ag(001). The line markers indicate the positions of the dips or peaks associated with the vibrational modes. The step size in each scan was 2.5 mV with 300 ms dwell time per step. The sample bias was modulated at 260 Hz and rms voltage of 5 mV. The spectra shown are background-subtracted and an average of multiple scans from 0 mV to the maximum bias and back down to 0 mV: (a) 381 scans, (b) 499 scans, (c) 303 scans, (d) 235 scans, (e) 533 scans, (f) 283 scans, and (g) 35 scans.

Results and Discussion

Cyclic molecules can bond to the surface in two orientations: with the ring parallel or inclined with respect to the surface plane. The STM enables direct observation of isolated molecules and provides insight into their orientations. Cross sections taken through the maximum in each molecular image (Figure 1) reveal two groups based on the apparent heights. Tetrahydrothiophene (apparent height of 1.5 Å) and pyrrolidine (apparent height of 1.2 Å) are distinctly taller than thiophene (apparent height of 0.8 Å) and pyrrole (apparent height of 0.7 Å).

Pyrrolidine bonds to the surface through the lone pair of electrons on the nitrogen. Two conformations, standing and bent, have been resolved.[10] Tunneling electrons can induce the switching between these two conformations. To make the above comparisons of the apparent height meaningful, an image (Figure 1c) was obtained with pyrrolidine in the standing conformation. The noise in the images of pyrrole and tetrahydrothiophene is tip-induced internal motion of the molecules on the surface. However, we found no evidence that these motions were similar to the conformational switching motion of pyrrolidine. The molecules remained on the same sites, which enabled imaging and spectroscopy. Furan underwent tip-induced movement; it was too mobile for spectroscopy. Tetrahydrofuran only formed a weakly physisorbed complex on the Cu(001) surface at 9 K because this species was very mobile even during imaging.

The evidence strongly suggests that surface interactions with the π system (Figure 1g) dominate for the unsaturated heterocycles (pyrrole and thiophene). Thus, they bond with the ring parallel to the surface, while the saturated heterocycles, lacking π electrons, form a heteroatom (N or S) to copper dative bond (Figure 1h). These results are in agreement with previous studies of tetrahydrothiophene on Cu(110),[13] pyrrole on Cu(001),[3] and thiophene on Cu(001).[3,14]

STM-IETS of these related molecules (Figure 2) reveals striking similarities and differences in the tunneling active vibrational modes. No vibrational modes are observed for either pyrrole (Figure 2a) or thiophene (Figure 2b). The CH_2 stretch

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mode (370 mV), assigned by comparison to spectra obtained by STM-IETS[9,5,7,15] and electron energy loss spectroscopy (EELS),[3] is the only detectable vibration for tetrahydrothiophene on Cu(001) (Figure 2c). The other features in this spectrum are tip-dependent and arise from the electronic properties of the tip and surface. Previous STM-IETS studies[15] also failed to detect any vibrational modes on benzene, another cyclic molecule π-bonded to the surface. The removal of two H atoms from the benzene molecule with tunneling electrons caused the benzene fragment to stand up on edge due to stronger bonding to the surface via the dehydrogenated C atoms. CH vibrations were detected with STM-IETS on this upright benzene fragment. Systematic studies on related molecules provide an important first step toward an experimental and theoretical understanding of selection rules and inelastic tunneling mechanisms.[16−18]

The STM-IETS spectra of pyrrolidine adsorbed on Cu(001) (Figure 2d) and Ag(001) (Figure 2f,g) are more complex. By examining the isotope effect (pyrrolidine-d_8, spectrum in Figure 2e) and previous gas- and liquid-phase studies,[19] the four observed vibrational modes on Cu(001) can be assigned: 409 mV as the NH stretch, 368 mV (277 mV) as the CH_2 (CD_2) stretch, 162 mV (140 mV) as the CH_2 (CD_2) twist or wag, and 111 mV (122 mV) as a ring mode. Five vibrational modes are detected in the d^2I/dV^2 spectrum for pyrrolidine on Ag(001): 366 mV, 181 mV, 116 mV, 76 mV, and 37 mV. By comparison with the STM-IETS spectrum on Cu(001), the first three modes can be tentatively assigned as the CH_2 stretch, the CH_2 twist or wag, and a ring mode, respectively. Comparing to the gas- and liquid-phase studies,[19] the mode at 76 mV could be either a CH_2 rocking or ring mode vibration. The mode at 37 mV is attributed to the energy barrier for conformational switching; the analogous gas-phase pseudorotation barrier is 35 mV.[20] Multiple short scans had to be collected for the CH_2 stretch region (Figure 2g) because pyrroldine is mobile on the Ag(001) surface under the conditions used to collect spectra in that voltage regime. The molecule was not stationary long enough to resolve the NH stretch vibration. This is consistent with the fact that the coinage metals (Cu, Ag, Au) decrease in reactivity with increasing atomic number.[21]

Tunneling electrons induce pyrrolidine to switch between two conformations,[10] but no thermally induced switching was observed at 9 K. When the tip height is fixed (such as during spectroscopy), the standing (bent) conformation is a high (low)-current state. Certain vibrations couple efficiently to this motion, resulting in the molecule having a higher fractional occupation time of the low-current state. This causes nonlinearities in $I-V$, most noticeably vibrationally mediated NDR, at voltages corresponding to the CH_2 (CD_2) stretch vibration in pyrrolidine, 368 mV (277 mV) on Cu(001), and the conformational switching, 37 mV on Ag(001) (Figure 3). Taking two mathematical derivatives of the dip in $I-V$ produces the asymmetric line shape in d^2I/dV^2 (Figure 2 d−g). The onset of another nonlinearity in $I-V$ for pyrrolidine on Cu(001) at ~120 mV corresponds with the ring mode vibration. The "normal" (Gaussian-like) NH stretch line shape in d^2I/dV^2 shows that this vibrational mode does not couple efficiently to the conformational switching. Since pyrrolidine bonds to the surface through the nitrogen lone pair of electrons, the NH bond is much closer to the surface than the CH bonds. Presumably electron−hole pair and phonon excitations are the dominant dissipation mechanisms for the NH vibrational energy. For a given bias voltage on Cu(001), the fractional occupation of the high (low)-current state increases (decreases) with increasing current. We do not yet understand the underlying mechanism for this current-dependent behavior.

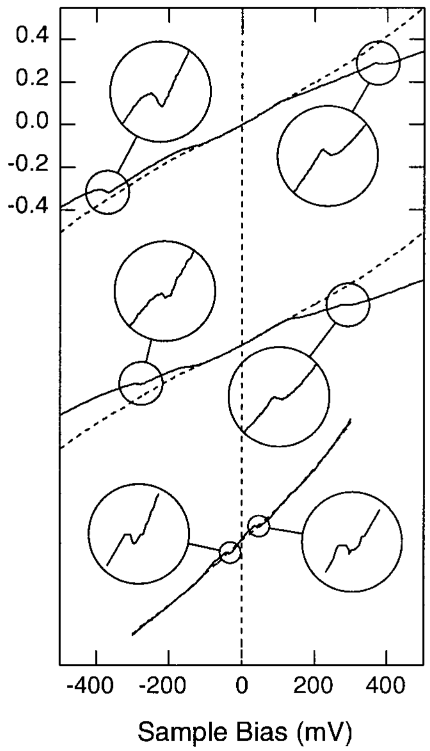

Figure 3. $I-V$ measured over pyrrolidine on Cu(001) (upper curve), pyrrolidine-d_8 on Cu(001) (middle curve), and pyrrolidine on Ag(001) (lower curve). For comparison, a spectrum was also collected over the surface, Cu(001) or Ag(001), (dashed line). The NDR regions are shown as expanded views (× 6). The spectra are averages of multiple scans from −450 mV (−300 mV) to +450 mV (300 mV) and back down to −450 mV (−300 mV): 3000 scans on pyrrolidine on Cu(001), 6000 scans on pyrrolidine-d_8, 1200 scans on Cu(001), 200 scans on pyrrolidine on Ag(001), and 600 scans on Ag(001). The step size in each scan was 2.5 mV with 2 ms dwell time per step.

Tetrahydrothiophene on Cu(001) showed no signs of NDR or any conformational switching. Tetrahydrothiophene is similar in structure to pyrrolidine with a sulfur atom replacing the NH moiety. As discussed above, both species bind to the surface through the lone pair electrons on the heteroatom. However, the sulfur atom has an additional lone pair of electrons relative to the NH moiety, which may also be involved in the bonding to the surface, thus constraining the molecule to an upright position. In addition, there may be repulsive interactions between the lone pair of electrons and nearby carbon−hydrogen bonds. The higher gas-phase pseudorotation barrier of tetrahydrofuran and pyrrolidine relative to cyclopentane has been attributed to these types of interactions.[20] The gas-phase pseudorotation barrier for cyclopentane is estimated to be about 0 cm^{-1} compared to 57 cm^{-1}, 280 cm^{-1}, and 773 cm^{-1} for tetrahydrofuran,[2] pyrrolidine,[20] and tetrahydrothiophene,[2] respectively. The more spatially extended nature of the orbitals in S compared to O may account for the higher barrier for tetrahydrothiophene compared to tetrahydrofuran.

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Conclusions

We have studied the adsorption, IETS, and conformational dynamics of single five-membered heterocyclic molecules adsorbed on Cu(001) and Ag(001) at 9 K. Our conclusions regarding adsorption geometries of these species are in good agreement with previous work. STM-IETS measurements on a series of molecules with known adsorption geometries will yield a deeper understanding of the coupling of electrons to nuclear motions and aid the development of a more complete theory for STM-IETS. The distinctions in the IETS and $I-V$ curves of the saturated compared to the aromatic heterocycles will help further the understanding of chemical dynamics at the atomic scale and its effects on the electrical conductivity of molecules. Such a fundamental understanding will be crucial as we move toward a future where a bottom-up assembly of devices may play an important role.

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