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Adsorption Geometry of 4-Picoline Chemisorbed on the Cu(110) Surface: A Study of Forces Controlling Molecular Self-Assembly

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Abstract: The adsorption of 4-picoline (4-methylpyridine) on the Cu(110) surface has been studied with time-of-flight electron stimulated desorption ion angular distribution (TOF-ESDIAD) and other methods. Using deuterium labeling in the methyl group and hydrogen labeling on the aromatic ring, it has been possible to separately monitor by TOF-ESDIAD the C−D bond directions and the C−H bond directions in the adsorbed molecule. These triangulation measurements have led to a detailed understanding of the conformation of the adsorbed molecule relative to the Cu(110) crystal lattice, allowing one to witness changes in the molecular conformation as adsorbate−adsorbate interactional effects take place for increasing coverages. At low coverages, the molecule adsorbs by the N atom at an atop Cu site with the aromatic ring parallel to the $\langle 001\rangle$ azimuth and with the molecular axis inclined 33 (±5)° along the $\langle 001\rangle$ azimuth. As rows of 4-picoline molecules form long range ordered chain structures oriented along the $\langle 112\rangle$ azimuth, the aromatic ring twists 29° about the inclined molecular axis as a result of forces between the adsorbate molecules. The initial tilting of the molecular axis at low coverage is likely due to the interaction of the positive-outward dipole with its image in the substrate. The ring twist may result from dipole−dipole forces between the adsorbate molecules in the rows formed tending to form nested parallel pyridine rings. These studies are the first to apply the TOF-ESDIAD method for the measurement of the direction of chemical bonds at more than one molecular location within an adsorbed molecule and the new method is named electron stimulated desorption-molecular triangulation (ESD-MT). The results obtained give information of importance in understanding the factors which control conformational effects during the molecular self-assembly of complex adsorbed molecules on surfaces.

1. Introduction

The study of the adsorption of simple aromatic molecules, such as benzene and pyridine, on well-defined surfaces provides insight into the formation of organic thin films that are relevant in various fields of technological importance.[1,2] By studying the structure, bonding, and orientation of simple adsorption systems, it is possible to understand structural factors which are crucial in the adhesion, growth, and use of organic thin films at metal surfaces. For example, nitrogen-containing heterocyclic molecules have been found to be highly effective adsorbed species for inhibiting corrosion for copper, nickel, iron, and other metals,[3] and it is likely that structural features of such films are of importance in their ability to inhibit corrosion. The 4-picoline (4-methylpyridine) molecule is a heterocyclic aromatic compound for which conformational changes are possible as the adsorbed layer forms. Very little is known about the interaction of 4-picoline with metal surfaces.

Electron stimulated desorption ion angular distribution (ESDIAD) has been shown to be a direct method for the determination of adsorbate orientation as a function of coverage.[4] Its principle and applications have been reviewed extensively by Ramsier and Yates.[5] Recently, the introduction of time-of-flight discrimination into the TOF-ESDIAD system has been developed by Ahner, Yates, and co-workers,[6−9] providing a powerful extension of the basic ESDIAD method for measuring the angular distribution of the desorbing species. So far, most of the research using the ESDIAD technique has concentrated on the investigation of small adsorbed molecules. In the present work, we have employed TOF-ESDIAD to study a larger molecule from which ionic fragments can originate from different positions on the adsorbed molecule. As shown in Figure 1, by using deuterium labeling in the methyl group of 4-picoline, we are able (by time-of-flight) to separate ESDIAD ionic fragments originating from different molecular positions on the molecule. This capability provides an incisive capability to monitor detailed conformational changes which the molecule

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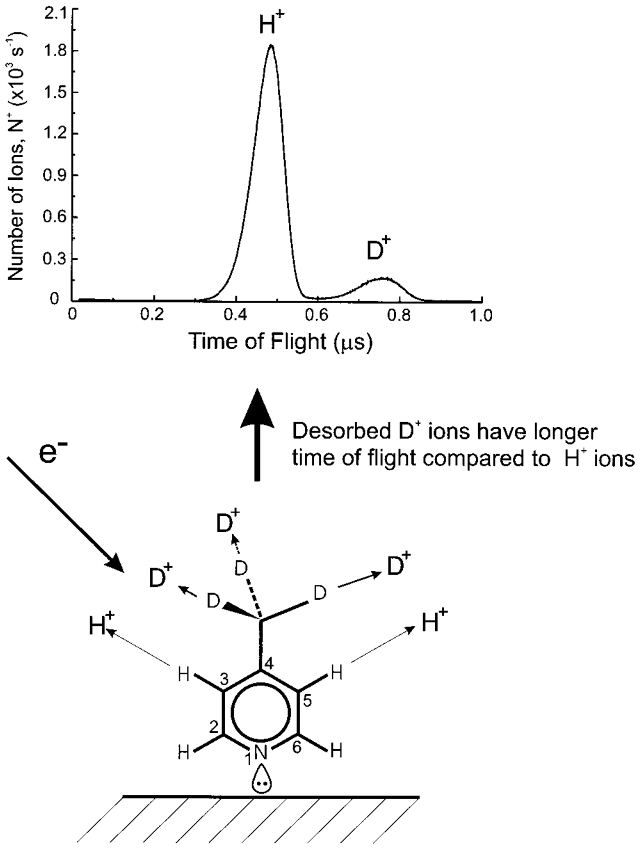

Figure 1. Schematic of separate measurements of H^+ and D^+ ions using the TOF-ESDIAD technique for 4-picoline. The molecular positions on the aromatic ring are indicated by numerals 1−6.

undergoes as adsorbate−adsorbate interactions build up during the growth of the adsorbed layer. Such growth processes have been found to be complex in pioneering studies by Scoles and co-workers.[10] The method applied to larger adsorbed molecules is termed ESD-MT (electron stimulated desorption-molecular triangulation).

In the present paper, we report the adsorption geometry and orientation of the 4-picoline molecule on Cu(110) at different coverages. At low coverage, the molecular aromatic ring plane is oriented parallel to the $\langle 001\rangle$ azimuth and the molecular symmetry axis is highly tilted along the $\langle 001\rangle$ azimuth. At high coverage, the aromatic ring plane of 4-picoline molecule is twisted toward the $\langle 1\bar{1}0\rangle$ azimuth as a result of the adsorbate−adsorbate interactions.

2. Experimental Section

The experiments described in this paper were performed in an ultrahigh vacuum chamber with a base pressure below 1×10^{-10} mbar. The Cu single crystal, a cylindrical disk 3 mm thick, with a diameter of 10 mm, was oriented to within ±0.22° of the $\langle 110\rangle$ plane. The crystal could be cooled to 80 K using liquid nitrogen and heated to 900 K by resistive heating.

The copper crystal was exposed to 4-picoline (99%, Aldrich) for temperature programmed desorption (TPD) and 4-picoline-methyl-d_3 (98 atom % D, Aldrich) for ESD-MT. Exposure was accomplished using a calibrated microcapillary array beam doser which produced uniform layers while maintaining low background pressure during adsorption.[11] Typically, the adsorbate flux employed was in the range 2.0×10^{12} to 1.0×10^{13} molecules/cm^2·s. Desorbing H^+ ions and D^+ ions were produced by electronic stimulation with electron pulses (50 ns width) containing 10^4−10^5 electrons of energy $V_e = 180$ eV, incident in a ~0.5 mm diameter beam. An accelerating voltage of +30 V was applied to the Cu crystal in all ESDIAD studies to compress the ESDIAD patterns. Damage to the adsorbed layer was minimized by using a total effective bombardment time of only about 3 s in which the total fluence of electrons was only 4.5×10^{12} electrons/cm^2.

The H^+ ESDIAD data were recorded in 3-dimensions, x, y, and t, where (x, y) are coordinates on a position sensitive detector placed behind an array of hemispherical and planer grids, and t is the time-of-flight of the desorbing particles from the crystal to the detector.[6,8] The TOF-ESDIAD apparatus, described previously,[6−9] allows for the separation of ESDIAD patterns corresponding to different time-of-flight windows. It is therefore possible to separate the ESDIAD patterns of desorbing species having different masses,[6,8,9] such as D^+ and H^+.

The Cu(110) sample was cleaned by cycles of argon-ion bombardment followed by annealing to 800 K. The cleanliness of the Cu surface was examined by Auger electron spectroscopy (AES) before and after the desorption experiment, and the crystal contained no detectable impurities.

The ESDIAD apparatus was also used as a low energy electron diffraction (LEED) apparatus to determine the azimuthal orientation of the Cu(110) crystal in laboratory coordinates and to perform digital LEED measurements for observing the ordered structure of the adsorbate overlayer.

Temperature-programmed desorption (TPD) was carried out using a UTI 100C quadrupole mass spectrometer with digital data acquisition during the electronically controlled temperature scan at $dT/dt = 2$ K/s.

3. Results

3.1. TPD and LEED Studies of 4-Picoline on Cu(110). A mass spectrometer was employed to determine the thermal desorption kinetics for the 4-picoline on Cu(110). Figure 2 presents a series of TPD spectra (monitored with the parent ion, $C_6H_7N^+$, $m/e = 93$ amu) of 4-picoline following the adsorption from various exposures of the 4-picoline on the Cu(110) surface at 80 K. At a 4-picoline exposure of 1.4×10^{14} molecules/cm^2, the 4-picoline desorbed as a single feature, with a peak (α_1) maximum at 372 K, as shown in Figure 2a. As the 4-picoline exposure was increased, the 4-picoline desorption peak continuously shifted to lower temperatures (Figure 2, spectra b−d). At a 4-picoline exposure of 6.5×10^{14} molecules/cm^2, an additional broad peak (α_2) appeared on the low-temperature edge ($T = 200$ K). With further exposure, the TPD spectrum exhibited additional desorption peaks, such as α_3 and α_4. At an exposure of 1.7×10^{15} molecules/cm^2, the TPD spectrum exhibited a relatively sharp peak (β) at a temperature of 170 K, which is due to second-layer or multilayer desorption. This peak continues to develop at higher 4-picoline exposures.

TPD spectra in the submonolayer regime between exposures of 1.4×10^{14} and 6.5×10^{14} molecules/cm^2 were simulated by a numerical method on the basis of the Polanyi−Wigner equation. From the optimal fit, the following values are obtained: $\nu^0 = 3 \times 10^{12}$ s^{-1}; $E^0_{des} = 0.98$ eV; and $E_{int} = 0.17$ eV/monolayer, which are similar to the pyridine/Cu(110) system ($E^0_{des} = 0.97$ eV; and $E_{int} = 0.16$ eV/monolayer).[12] The appearance of the low-temperature peaks, α_2, α_3, and α_4 cannot

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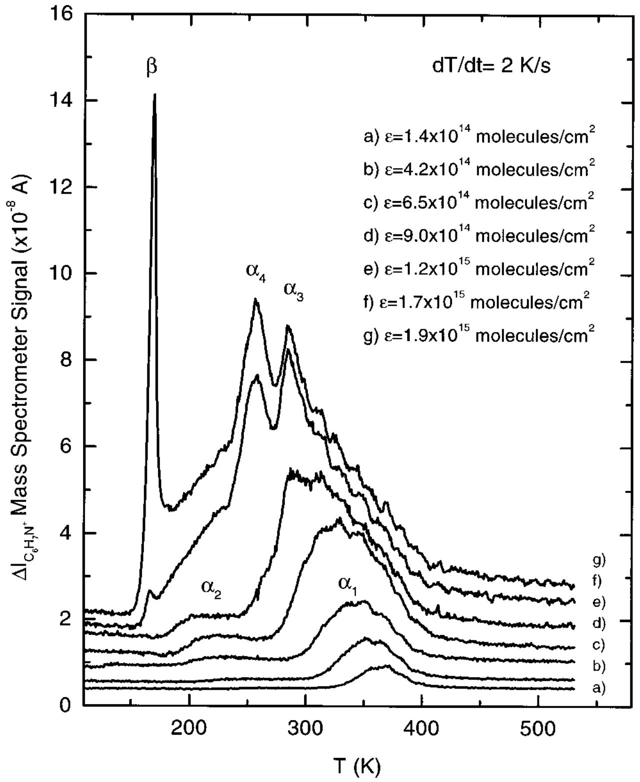

Figure 2. Thermal desorption spectra (taken at *m*/*e* = 93 amu) were obtained at different exposures. Heating rate = 2 K/s. Exposure: (a) 1.4 × 10^{14} molecules/cm^2; (b) 4.2 × 10^{14} molecules/cm^2; (c) 6.5 × 10^{14} molecules/cm^2; (d) 9.0 × 10^{14} molecules/cm^2; and (e) 1.2 × 10^{15} molecules/cm^2; (f) 1.7 × 10^{15} molecules/cm^2; (g) 1.9 × 10^{15} molecules/cm^2.

be explained by an increase of the repulsive adsorbate−adsorbate interaction deduced from the behavior of the α_1 state.

The LEED pattern for the 4-picoline overlayer shown in Figure 3a was recorded at an electron beam energy of 73 eV. The LEED pattern was obtained by a high exposure on Cu(110) at 80 K followed by heating of the surface to 160 K to remove the β-state. A poorly defined LEED pattern for low coverage was also observed. At high coverage, a LEED pattern clearly appeared and developed two equivalent domains, $\begin{pmatrix} 1 & -1 \\ 1 & 3 \end{pmatrix}$ and $\begin{pmatrix} 1 & 1 \\ 1 & -3 \end{pmatrix}$, as shown in Figure 3b. The unit cell shown in Figure 3b has one 4-picoline molecule per unit cell, indicating a coverage of 0.25 ML.

3.2. ESDIAD Study of 4-Picoline on Cu(110). As shown in Figure 1, the 4-picoline-methyl-d_3 isotopomer was employed to separate the ESDIAD patterns for D$^+$ and H$^+$ originating from different positions in the chemisorbed molecule. Our observations indicate that isotopic exchange between the deuterium atoms of the methyl group and the hydrogen atoms of the aromatic ring does not occur in the electron excitation process; therefore, the H$^+$ ESDIAD pattern corresponds to C−H bonds in the aromatic ring pattern, and the D$^+$ pattern originates from the methyl group. It is of significance that only the outward-directed C−H or C−D bonds yield ion beams, and that higher mass fragment ions (like CD_3^+) are not produced at measurable levels.

3.2.1. ESDIAD Pattern of H$^+$ Ions of 4-Picoline-methyl-*d*$_3$ at Low and High Coverage. 4-Picoline-methyl-d_3 was adsorbed on the Cu(110) surface at 80 K using several different exposures. The H$^+$-ESDIAD patterns of 4-picoline-methyl-d_3 were taken immediately after exposure. These ESDIAD patterns did not change by heating to just below the desorption temperature. Two different patterns were observed in the whole exposure range as shown in Figure 4. At an exposure of 1.3 × 10^{13} molecules/cm^2, a two-beam pattern of H$^+$ ion was observed which is aligned parallel to the ⟨001⟩ azimuth (Figure 4a). Upon increasing the exposure to 4.8 × 10^{14} molecules/cm^2, the H$^+$-ESDIAD pattern gradually changes into a four-beam pattern which develops from the two-beam pattern as shown in Figure 4b (and more clearly in Figure 9). The four-beam pattern of H$^+$ ion did not further change to a different pattern with increasing exposure.

3.2.2. ESDIAD Pattern of D$^+$ Ions of 4-Picoline-methyl-*d*$_3$ at Low and High Coverage. A 4-picoline-methyl-d_3 molecule has three deuterium atoms in the methyl group, which can be detected by ESDIAD, if the molecule were adsorbed in an upright configuration.[13] The methyl group of 4-picoline has an extremely low internal rotation barrier, 0.5860 meV in the gas phase.[14] The thermal energy at 80 K (7 meV) is enough therefore to activate the internal rotational motion of the methyl group. Therefore, we interpret the D$^+$-ESDIAD pattern as originating from the rotating CD_3 groups.

Figure 5 shows the D$^+$ ESDIAD patterns of 4-picoline-methyl-d_3 on Cu(110) at two different exposures. At an exposure of 1.3 × 10^{13} molecules/cm^2 (θ = 0.01 ML), the observed D$^+$ pattern resembled a pair of kidney shapes (Figure 5a). At an exposure of 4.8 × 10^{14} molecules/cm^2 (θ = 0.22 ML), the ESDIAD pattern of the methyl group does not change (Figure 5b). This is the exposure where the ESDIAD pattern of H$^+$ ions originating from the aromatic ring of 4-picoline changes from a two-beam pattern to a four-beam pattern. The D$^+$ ESDIAD pattern of the methyl group did not change in the whole coverage range studied (exposure = 1.3 × 10^{13} to 1.5 × 10^{15} molecules/cm^2).

3.2.3. Measurement of the Ejection Angle of the H$^+$ Ion in the Aromatic Ring Plane of Adsorbed 4-Picoline on the Cu Surface. The ESDIAD technique allows us to make an accurate determination of ion emission directions.[15,16] The maximum polar angle measurable without distortion of the ESDIAD image is limited by the detection solid angle of the microchannel plate. This restriction is experimentally overcome by applying a positive bias to the crystal which causes bending of the ion trajectories toward the macroscopic normal of the crystal, producing compression of the ESDIAD pattern. Two different methods were used to determine the true H$^+$ ejection direction in this work. For one angular measurement, a single rotation of the crystal will bring an off-normal H$^+$ beam to the axis of the analyzer system. The rotation angle measured was shown to be independent of the crystal bias. For a second type of angular measurement, the H$^+$ emission angle must be determined as a function of crystal bias, and then extrapolated to zero bias.[16] To define the orientation of molecule and the ejection direction of desorbing ions a set of three angles (α, β, γ) is used as shown in Figure 6. The angle, α, is defined as the angle of the molecular symmetry axis from the crystal surface

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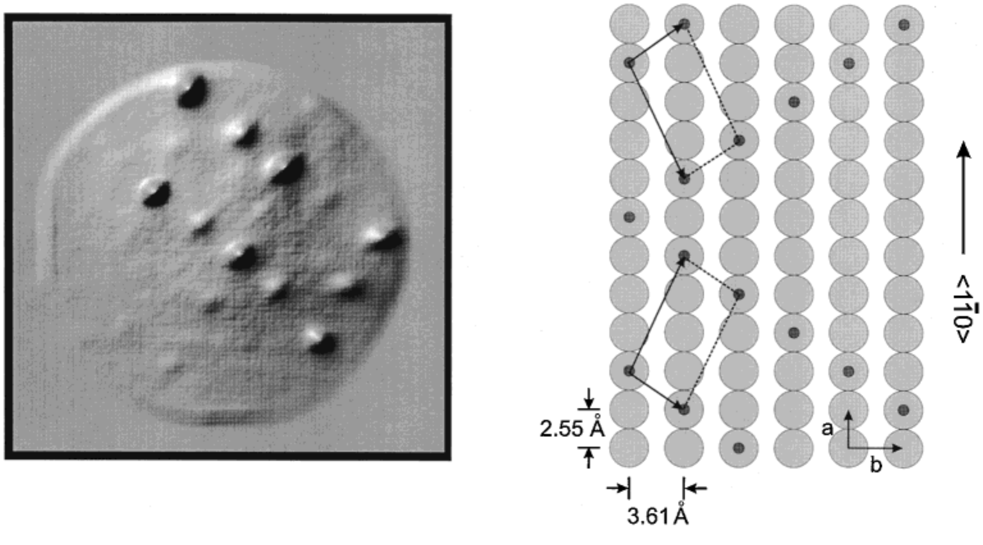
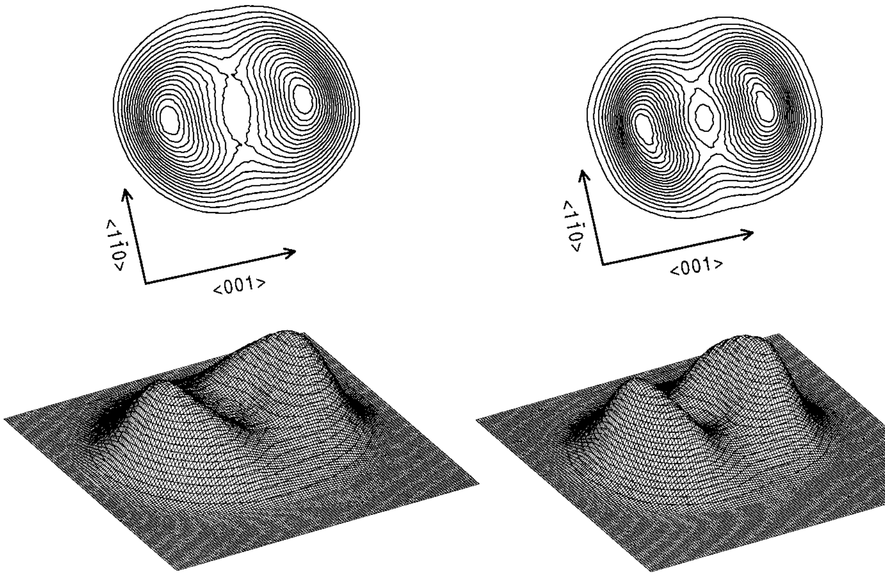


a) LEED Pattern ($I_e/A=10^{-7}$ A/cm^2, $V_e=73$ eV)

b) 4-Picoline $\begin{pmatrix}1, & 1\\ 1, & -3\end{pmatrix}$ and $\begin{pmatrix}1, & -1\\ 1, & 3\end{pmatrix}$ Super Structure ($\theta_{4\text{-Picoline}} \geqq 1/4$)

Figure 3. LEED Pattern of adsorbed 4-picoline on Cu(110) at saturation coverage.



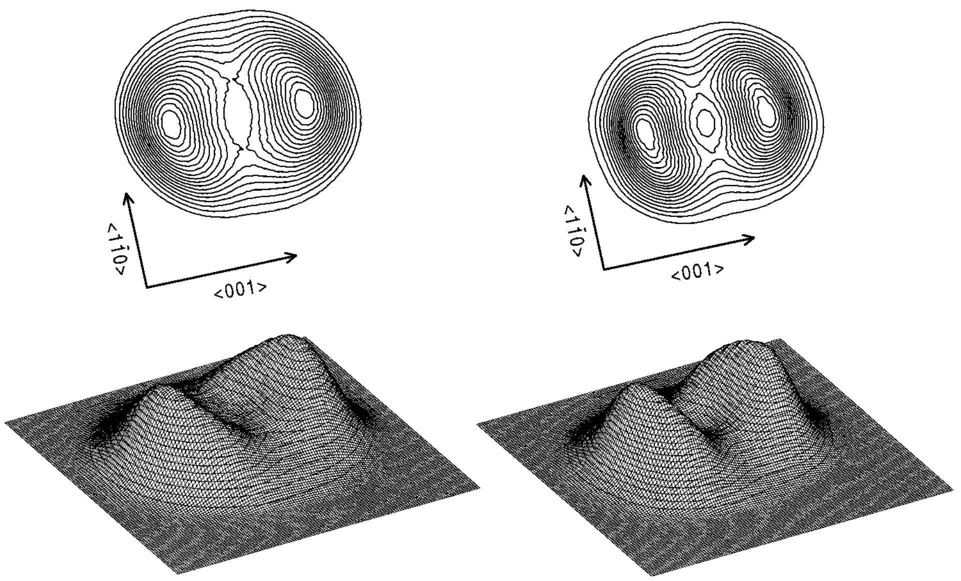
a) Low exposure ($\Theta = 0.01$ ML)

b) High exposure ($\Theta = 0.22$ ML)

Figure 4. ESDIAD pattern of H^+ ion from the aromatic ring of 4-picoline-methyl-d_3 at 80 K: (a) exposure = 1.3×10^{13} molecules/cm^2 ($\theta = 0.07$ ML); (b) exposure = 4.8×10^{14} molecules/cm^2 ($\theta = 0.22$ ML).

normal, i.e., the tilt angle. The angle β defines a rotation angle of the molecular symmetry plane about the molecular symmetry axis with respect to the plane defined by surface normal and the molecular symmetry axis i.e., the twist angle. The angle γ is an azimuthal angle of the molecular symmetry axis with respect to the $\langle 001 \rangle$ azimuth.

The emission angle of desorbing ions with respect to the surface normal along the $\langle 001 \rangle$ azimuth was measured by the rotation of crystal axis as shown in Figure 7. Initially, the crystal surface normal is set parallel to the ESDIAD detector normal, and then the crystal is rotated until the two split H^+ beams are centrally positioned. This means that the bond direction of ejecting ions is perpendicular to the ESDIAD detector. The angle of the H^+ ions ejection in the $\langle 001 \rangle$ azimuth from the normal at low and high exposures was 27 (±5)° from this measurement. This measurement therefore indicates that the molecular axis of 4-picoline is tilted by $\alpha = 33$ (±5)° from the normal along the $\langle 001 \rangle$ azimuth and that the outward-oriented 3- and 5-C−H bonds are being imaged for molecules tilted in opposite directions to each other. The H^+ beam splitting observed at a coverage ($\theta = 0.22$ ML) in Figure 4b was measured by extrapolation to zero crystal bias in Figure 8. Angles measured with respect to the $\langle 001 \rangle$ azimuth are shown in Figure 8 and the zero bias angle was estimated by the extrapolation of the crystal bias to the zero field condition using the method of Gao et al.[16] To determine the angle between the H^+-beams and the $\langle 001 \rangle$ azimuth of the ESDIAD patterns at different crystal biases, the ESDIAD patterns were cut along the $\langle 1\bar{1}0 \rangle$ azimuthal



a) Low exposure (θ = 0.01 ML) b) High exposure (θ = 0.22 ML)

Figure 5. ESDIAD pattern of D^+ ion from the methyl group of 4-picoline-methyl-d_3 at 80 K: (a) exposure = 1.3×10^{13} molecules/cm^2 ($\theta = 0.07$ ML); (b) exposure = 4.8×10^{14} molecules/cm^2 ($\theta = 0.22$ ML).

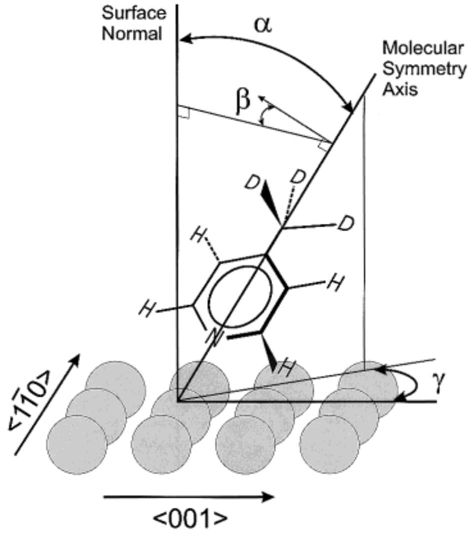


Figure 6. Definition of three angles describing the orientation of the adsorbed molecule.

direction and fitted by two Gaussian functions. The behavior of the measured H^+ ion ejection angle fits well within the calculated region for an H^+ energy range between $E_0 = 0.9$ eV and $E_0 = 1.4$ eV as obtained from an ion optics computer simulation. The field-free ion ejection angle from the ⟨001⟩ azimuth ranges from 24° to 29° (at zero bias) over the 0.9−1.4 eV H^+ energy range according to the simulation results. The best fit for our data involves a H^+ initial kinetic energy, $E_0 = 1.2$ eV, and a zero bias ion ejection angle = 27 (±3)° from the ⟨001⟩ azimuth. The initial kinetic energy of the H^+ ion (E_0) can also be estimated experimentally by TOF measurements. The value measured is 1.4 (±0.2) eV, in good agreement with the ion optical calculation of Figure 8.

The final state effects of image potential and reneutralization can influence the zero field ion desorption angle by distorting the ion trajectories and the angular distributions. Several theoretical papers have addressed the influence of the image force and the reneutralization effects on ion angular distribution measurements.[17−19] The attractive image potential increases the measured polar angle of the ion escaping from the surface while the reneutralization acts in an opposite sense to the image field to decrease the measured polar angle. These two effects tend to cancel each other, especially for small polar desorption angles. Madey et al. have carried out theoretical studies in which both

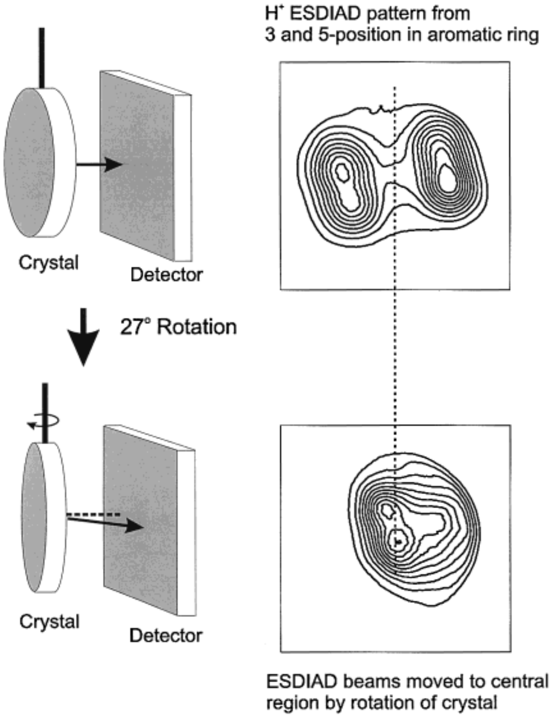


Figure 7. Determination of the ejection angle of the H^+ ion from the 3- or 5-positions on the aromatic ring of the 4-picoline-methyl-d_3 molecule toward the ⟨001⟩ direction with the respect to the surface normal. Measurements made by rotation of the crystal axis.

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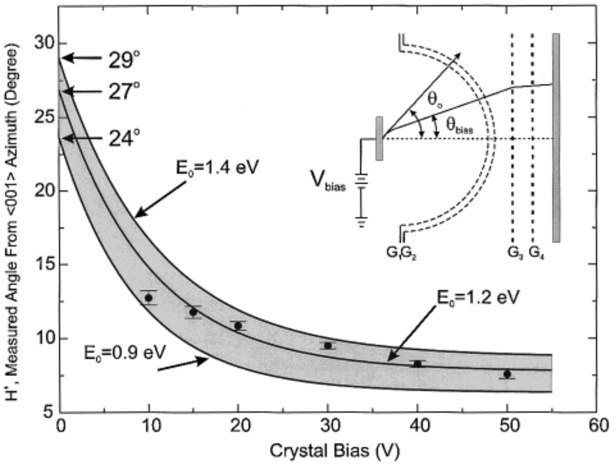

Figure 8. Determination of the ejection angle of the H^+ ions (in the split beam pattern) along the $\langle 1\bar{1}0\rangle$ azimuth by extrapolation of the emission angle of the H^+ ion at the various crystal biases to the zero bias condition. The angles at different crystal bias were determined from the distance between two peaks on a line-cut though the H^+ ESDIAD pattern in the $\langle 1\bar{1}0\rangle$ azimuthal direction. The experimental angle $\beta = 27$ (± 3)° was found at zero bias, by means of the extrapolation.

image potential and reneutralization effects are taken into account in order to obtain the true ion emission angle at zero bias voltage.[17,18] Using their methods, the ion ejection angle as derived from the ion optical extrapolation in Figure 8, was corrected to a twist angle of $\beta = 29$ (± 3)°.

3.2.4. Coverage Dependency of the H^+ ESDIAD Pattern Change from Two-Beam to Four-Beam. A series of experiments was performed to study the exposure dependency of the H^+ ESDIAD patterns from the aromatic ring of the 4-picoline-methyl-d_3 molecule at various coverages. The evolution of the two-beam H^+ ESDIAD pattern to the four-beam pattern was monitored by plotting the ratio of the half-width of the H^+ ESDIAD pattern in the $\langle 1\bar{1}0\rangle$ azimuthal direction to the half-width of ESDIAD pattern in the $\langle 001\rangle$ azimuthal direction. The half-width of the H^+ ESDIAD patterns was determined by a Gaussian fitting of the line-cut curves of the H^+ ESDIAD pattern in both directions. The beam splitting process occurs gradually over a wide coverage range suggesting that long-range interactions are responsible for the effect, as shown in Figure 9.

3.2.5. Simulation of D^+ ESDIAD Pattern for Ring Plane Tilting Model. The splitting of the two-beam H^+ ESDIAD pattern into four beams as the coverage is increased (Figures 4, 9) may be interpreted in two different ways: (1) by a change in the azimuth γ of the molecular axis toward the $\langle 1\bar{1}0\rangle$ direction; or (2) by a twisting of the aromatic ring about the molecular axis. To test the two models, a simulation of the D^+ ESDIAD pattern from the CD_3 group was performed for various azimuth angles, γ. This statistical simulation consists of about 10^5 D^+ desorption events which are created by a computer program in the following steps: At first, a random event for a desorbing ion is created by a random number generator program. The distribution of created events has a maximum along a circle of the rotating C−D chemical bond. Second, the event frame is tilted by a certain angle (by simulation) with respect to the crystal normal. Third, to consider the reneutralization effect, the D^+ neutralization probability is calculated at the emission angle of the event using the equation proposed by Madey et al.[20] The calculated probability is used to determine statistically whether the event is neutralized or not. Finally, if not neutralized by the surface, the event is recorded in the detector coordinate and then a new event corresponding to a different CD_3 rotational angle is created. About 10^5 such events are repeatedly created for the simulation.

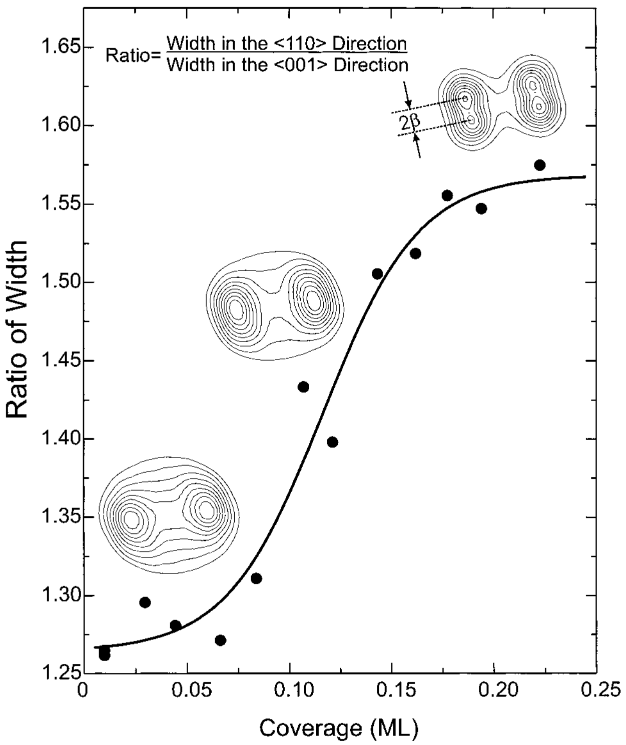

Figure 9. Coverage dependency of the change of the H^+ ESDIAD pattern from the aromatic ring plane of 4-picoline-methyl-d_3, as ring plane twisting occurs.

Simulated ESDIAD patterns for various molecular symmetry axis azimuthal angles are shown in Figure 10, where α is the symmetry axis tilting angle of the CD_3 group along the $\langle 001\rangle$ azimuth, and γ is the azimuthal angle compared to the $\langle 001\rangle$ azimuth. The angle α was determined previously to be 33°. In the simulation, α was kept constant at 33° while γ was changed. The result of the simulation shows that even a small azimuthal angle ($\gamma = 15°$) causes a perceptible change of the D^+ ESDIAD pattern causing the kidney shaped D^+ patterns to coalesce at their extremities. By comparing the modeled D^+ patterns to the experimental patterns shown in Figure 5, a maximum azimuthal angle of $\gamma = \pm 15°$ is found to be possible. Because of the insensitivity of this measurement to γ, we assume for discussion that γ is $0 \pm 15°$ in this paper.

4. Discussion

4.1. Adsorption Site and Geometry of the 4-Picoline/Cu(110) System. Figure 11 shows the adsorption geometry of 4-picoline on the Cu(110) surface at 80 K. On the basis of photoelectron diffraction (PHD) studies of the pyridine[21] and

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(20) The ion survival probability was calculated by the following equation.[17]

$$p(\theta) = \exp\left[-\frac{A}{av_0}\int_0^\infty\left(\beta\cos^2\theta + \frac{1-\beta}{1+\delta\xi}\right)^{-1/2} e^{-\xi}\,d\xi\right]$$

Here, $\beta = 1 - |V_I|/E_0$, $v_0 = (2E_0/m)^{1/2}$, and $\delta = (az_0)^{-1}$. The parameters are selected to be consistent with the experimental results. We use the following values of parameters: $|V_I|/E_0 = 0.25$, $E_0 = 1.2$ eV, $A/a = 5 \times 10^4$ m/s (corresponding to $a/b = 0$), $z_0 \cong 5.8$ Å, and $a = 3$ Å^{-1}.

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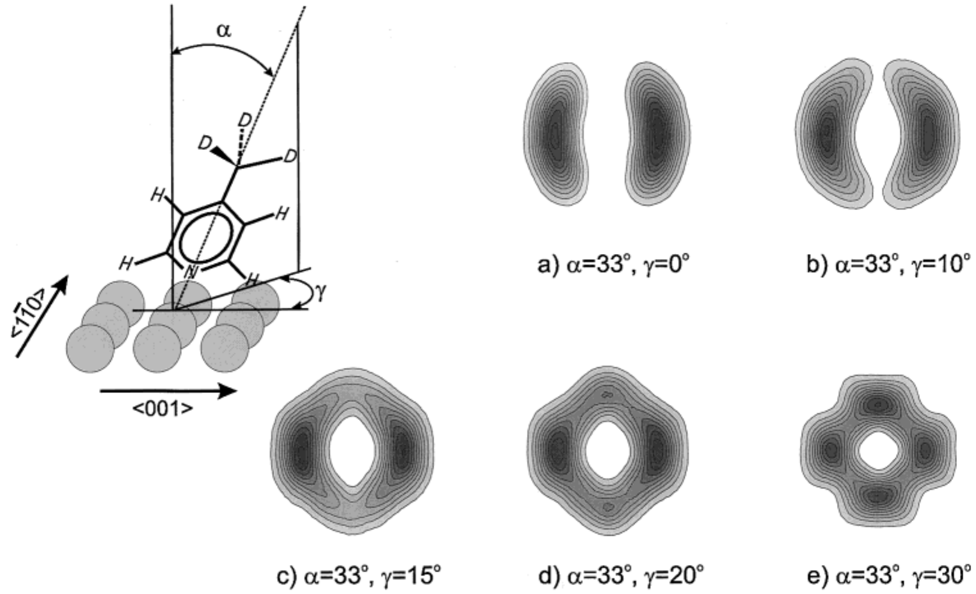
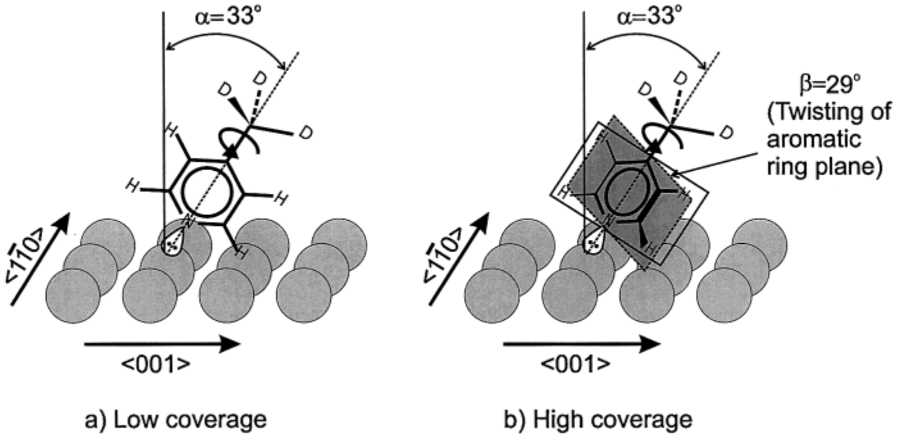


Figure 10. Simulated ESDIAD patterns of D^+ ions from rotating methyl groups of 4-picoline-methyl-d_3 at various azimuthal angles, γ: (a) $\alpha = 33°$, $\gamma = 0°$; (b) $\alpha = 33°$, $\gamma = 10°$; (c) $\alpha = 33°$, $\gamma = 15°$; (d) $\alpha = 33°$, $\gamma = 20°$; (e) $\alpha = 33°$, $\gamma = 30°$, where α is the tilting angle from the surface normal, and γ is azimuthal angle with respect to the ⟨001⟩ azimuthal direction. On the basis of a comparison with experimental data in Figure 5, we estimate that γ is less than 15°.



a) Low coverage

b) High coverage

Figure 11. Adsorption geometries of the 4-picoline on the Cu(110) at 80 K: (a) low coverage; (b) high coverage.

2-picoline[22] molecules which were found to adsorb on atop Cu atom sites, we assume that 4-picoline is also adsorbed on atop sites. At low coverages, the molecular axis of 4-picoline is tilted 33 (±5)° in the ⟨001⟩ azimuth from the crystal surface normal and the aromatic ring plane is parallel to the ⟨001⟩ azimuth (Figure 11a) as determined by the H^+ ESDIAD pattern ($\alpha = 33°$, $\beta = 0°$, and $\gamma = 0°$). The 29° splitting of the H^+ ESDIAD pattern at higher coverages results from the twisting of the aromatic ring plane about the tilted molecular axis. The four H^+ beams originate from twist angles in two directions that originate from adsorbate molecules, possibly in different adsorbate domains being sampled on the surface, and one of these tilted and twisted molecules is shown in Figure 11b ($\alpha = 33°$, $\beta = 29°$, and $\gamma = 0°$).

There are three interesting questions related to the observed geometry for 4-picoline on the Cu(110) surface: (1) what is the cause of the tilting of molecular axis in the ⟨001⟩ direction not in the $\langle 1\bar{1}0\rangle$ direction; (2) what causes the twisting of the aromatic ring plane at high coverage; (3) why is the ring plane oriented closely parallel to the ⟨001⟩ azimuth? Detailed answers to these questions may come from modeling of the forces between 4-picoline molecules arranged in structures of increasing coverage.

4.1.1. Molecular Axis Tilting. The 4-picoline molecule has a highly polarizable methyl group at the 4-position and a high permanent dipole moment (2.7 D).[23] In a theoretical study of the pyridine/Cu(110) system,[24] the chemisorption bond of pyridine on copper involves a very small transfer of electron density from the metal into the π-antibonding orbital of pyridine (π-back-bonding) in addition to N atom lone pair electron donation directly to the metal surface. The chemisorption of 4-picoline on Cu(110) will also involve a similar donor−acceptor mechanism of bonding via the N atom as is found for pyridine. The positive-outward dipole can interact with the metal

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surface by a permanent dipole−image dipole interaction. The 33° tilting of the molecular axis of 4-picoline at low coverage may therefore be caused by this electrostatic interaction between the molecular dipole and the metal surface. For comparison, pyridine (dipole moment = 2.2 D) is untilted at low coverages on Cu(110).[25] We are not able to explain the preferential ring tilting for 4-picoline in the ⟨001⟩ direction.

A 33° tilt of the molecular axis of 4-picoline along the ⟨001⟩ azimuth from the crystal surface normal has been measured. This corresponds to a spacing between the H atom at the 2- or 6-position on the aromatic ring and the nearest Cu atom of 1.9 Å. This distance is shorter than the sum of the H and Cu van der Waals radii ($r_{\mathrm{rdw}}^{\mathrm{H}} + r_{\mathrm{rdw}}^{\mathrm{Cu}} = 2.6$ Å),[26] but longer than a Cu−H chemical bond length (1.68 Å).[27]

There are three possible consequences to this tilting angle causing the close interaction of the 2- or 6-C−H bond with the surface: (1) C−H bond dissociation; (2) C−H bond angle distortion away from its radial direction from the center of the aromatic ring; (3) hydrogen bond-type interaction between the H atom and the neighbor Cu atom. Options 1 and 2 are unlikely because of the energetic consequences of these options which are not observed in comparing the desorption activation energy at zero coverage for tilted 4-picoline ($E_{\mathrm{des}}^{0} = 0.98$ eV) and for untilted pyridine ($E_{\mathrm{des}}^{0} = 0.97$ eV). We are therefore left with option 3 involving a "hydrogen bond" type interaction between the 2- or 6-H atoms and the Cu surface. Such interactions, involving C−H bond softening, have been observed by vibrational spectroscopy for alkanes adsorbed on metal surfaces.[28,29]

4.1.2. Twisting of the Molecular Plane at High Coverage. The molecular axis tilting causes a more favorable configuration in the adsorbed 4-picoline on the Cu(110) surface to interact with neighbor adsorbed molecules at high coverage. As shown in Figure 9, twisting increases with increasing coverage. The low coverage where this twisting occurs may indicate that 4-picoline molecules cluster together in islands as the long ordered rows are formed. The twisting causes the aromatic rings to nest together in a parallel configuration in these molecular rows.

4.1.3. Ring Plane Orientation Parallel to the ⟨001⟩ Azimuth at Low Coverage. At low coverage, both pyridine and 4-picoline exhibit a ring plane orientation which is parallel to the ⟨001⟩ direction, and our TOF-ESDIAD results show that thermally activated molecular rotation of the ring plane does not occur below 300 K for either molecule. The stabilization energy in this configuration may be related to H−Cu bonding between the 2- or 6-H atoms and the neighbor Cu atoms located in the ⟨001⟩ azimuth from the chemisorption site.

4.2. Comparison of the 4-Picoline/Cu(110) System to the Pyridine/Cu(110) System. It is of interest to compare the results for 4-picoline/Cu(110) to pyridine/Cu(110), because two significant differences are observed in the adsorption structures.

(1) The molecular axis of pyridine is normal to the Cu(110) surface over the entire coverage range whereas 4-picoline exhibits an inclined molecular axis [33 (±5)°] in the ⟨001⟩ azimuthal direction over the entire coverage range.

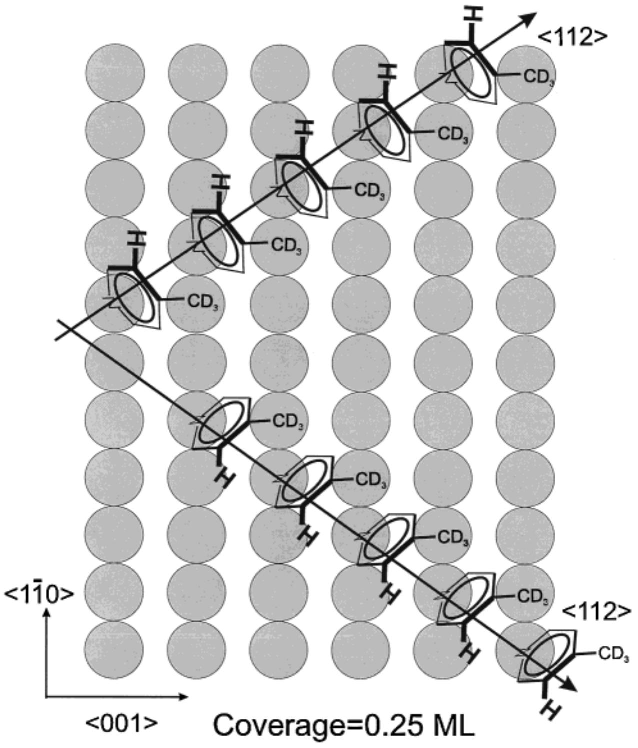

Figure 12. Adsorption structure of 4-picoline on Cu(110) at 0.25 ML coverage.

(2) The adsorbed pyridine on the Cu(110) forms a chain structure of pyridine ring arranged in a chainlike chevron pattern at full coverage the chains being aligned along the ⟨1$\bar{1}$0⟩ azimuth. In contrast, the molecular chain of 4-picoline on the Cu(110) surface is aligned in the ⟨112⟩ azimuth at saturation coverage. The 4-picoline molecules twist by 29° into parallel rings, where pyridine twists by 25° to form antiparallel ring configurations at high coverages.

It is likely that the larger dipole moment of 4-picoline, compared to pyridine, governs the different conformational behavior of the two closely related molecules. Thus, the titled 4-picoline molecule experiences different intermolecular forces as the coverage increases compared to pyridine, which is not tilted at any coverage due to its smaller dipole moment. These forces cause 4-picoline to form ⟨112⟩ oriented chains and to twist into conformations with parallel ring plane, whereas pyridine, in the ⟨1$\bar{1}$0⟩ oriented chains, chooses to twist oppositely forming antiparallel rings as the coverage builds up. Understanding the details of these forces awaits theoretical calculation of the intermolecular interactions. A schematic picture of the configuration of 4-picoline at a coverage of 0.25 ML on Cu(110) is shown in Figure 12.

5. Summary

The following results have been obtained for the interaction of 4-picoline with the Cu(110) surface.

(1) TOF-ESDIAD has been used the first time to image different structural regions of a chemisorbed molecule which has been separately labeled with H and D atoms. The combination of these measurements allows one to triangulate the structure of the adsorbed molecules, leading to a detailed

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conformational analysis of the local molecular structure on the adsorption site. This application is termed ESD-MT (electron stimulated desorption-molecular triangulation).

(2) The activation energy for desorption of 4-picoline from Cu(110) closely resembles that of pyridine (0.98 vs 0.97 eV) at zero coverage. In both cases repulsive interadsorbate interactions of the order of 0.17 eV/monolayer are observed, and a similar progression of TPD spectra is found for both molecules as coverage is increased.

(3) At the lowest coverage, the molecular axis of 4-picoline is tilted by 33 (±5)° degrees in the ⟨001⟩ azimuthal direction, with the molecular plane of the aromatic ring remaining parallel to the ⟨001⟩ azimuth. This tilting is thought to be a consequence of the interaction of the adsorbate dipole with its image in the metal substrate.

(4) It is found that the CD_3 group on 4-picoline-d_3 is rotating nearly freely at 80 K, and that the C−D bond direction may be imaged by ESDIAD for CD_3 rotor angles which project the C−D bonds at small angles with respect to the normal to the surface. These favorable projections occur when the C−D bond is oriented near to the ring plane, parallel to the ⟨001⟩ azimuth.

(5) At high coverage, intermolecular interactions between 4-picoline molecules cause the aromatic plane to twist 29° as two equivalent domains involving rows of 4-picoline molecules are formed. The rows run in the ⟨112⟩ direction across the surface. In these rows, the aromatic ring planes for neighboring molecules are parallel.

(6) The different long-range structure and conformation found for 4-picoline and for pyridine adsorbed on Cu(110) may be due to the propensity for 4-picoline to tilt because of its larger dipole moment, whereas pyridine does not tilt. Such molecular tilting at low coverage may govern the forces that control conformational developments as the coverage increases.

(7) The measurement of the twisting and tilting of large adsorbed organic molecules, arranged in ordered patterns on single-crystal substrates, provide new insights into the factors governing the structure of self-assembled monolayers.[30]

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