

Single Molecule Imaging and Vibrational Spectroscopy with a Chemically Modified Tip of a Scanning Tunneling Microscope

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The tip of a scanning tunneling microscope can be chemically modified by transferring a single molecule from the surface. Such a molecule-terminated tip yields enhanced resolution in topographical imaging of substrate atoms and molecular orbitals of molecules adsorbed on the surface. In addition, vibrational modes are detected in single molecule inelastic electron tunneling spectroscopy which are not observed with a bare tip. These new findings are revealed by transferring a carbon monoxide or an ethylene molecule to the tip and probing single carbon monoxide and oxygen molecules adsorbed on Ag(110) at 13 K.

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A general limitation encountered in scanning tunneling microscope (STM) is the lack of precise knowledge of the morphology and chemical composition of the tip. Despite this uncertainty, the STM has become a versatile tool for probing surface phenomena with unprecedented resolution and control. Nevertheless, a well-defined tip may enable new applications and expand the capabilities of the STM.

Modification of probe tips has previously been accomplished in the atomic force microscope (AFM) and the STM. Covalent bonding of a self-assembled monolayer to the cantilever tip in AFM made it possible to image functional groups by measuring the adhesive and friction forces between the tip and organic monolayer [1]. A nanotube can also be grown on the AFM tip, which enhances lateral resolution and enables clearer images of proteins and other large molecules [2]. Atom or molecule transfer between the STM tip and surface by applying a voltage pulse has been reported [3,4] and such transfer induced changes in the appearance and corrugation of STM images [4,5].

In this Letter, we demonstrate a reproducible method of preparing a tip *in situ* by transferring a single molecule from the substrate surface to the tip apex. A single carbon monoxide (CO) or ethylene (C₂H₄) molecule was reversibly transferred between the surface and the tip through controlled manipulation with tunneling electrons. With this molecule-terminated tip, atomically resolved surface corrugations were obtained and new vibrational modes were observed which were not achieved with a bare tip. While direct imaging of the substrate atoms allows determination of the adsorbate binding sites, the observation of previously missing vibrational modes expands the range of application and understanding of inelastic electron tunneling spectroscopy with the STM (STM-IETS) [6]. The tip functionalized with a single CO molecule (CO tip) or C₂H₄ molecule (C₂H₄ tip) was used to image and record the vibrational spectra of single CO and O₂ molecules adsorbed on Ag(110) at 13 K.

Experiments were carried out using a homemade, variable temperature STM [7] housed inside an ultrahigh vac-

uum chamber with a base pressure of 2×10^{-11} Torr. The Ag(110) sample and etched polycrystalline tungsten tips were cleaned by cycles of Ne ion sputtering and annealing cycles prior to use. The O₂ molecules were adsorbed on the sample at 45 K in order to ensure molecular chemisorption. The O₂ coverage was below 0.01 monolayer (ML). The sample and the STM were then cooled to 13 K for imaging, manipulation, and spectroscopy; experimental details have been described elsewhere [6–8]. Low coverages of CO and C₂H₄ molecules (<0.001 ML) were coadsorbed on the surface at 13 K. The molecules were found to be dispersed on the surface, thereby eliminating interactions between coadsorbed species.

Controlled vertical transfer of single molecules between the tip apex and the surface was possible by applying appropriate tunneling current and sample bias. The procedure for the formation of the C₂H₄ tip was similar to that of the CO tip [9] except for the sample bias. The bare metallic tip was positioned over a single C₂H₄ (or CO) molecule [10] with the junction set by 0.1 nA tunneling current and +70 mV sample bias voltage. While keeping the feedback loop on, the bias was flipped to -70 mV (to avoid tip crash) and then decreased to -140 mV (compared to an increase from +70 to +250 mV for CO). The tunneling current was then ramped from 0.1 to 10 nA to induce the transfer of the C₂H₄ (or CO) molecule to the tip. It was consistently possible for either the CO tip or the C₂H₄ tip to resolve surface atoms as illustrated in Figs. 1a and 1d. The spatial resolution of the C₂H₄ tip was less in the [1 $\bar{1}$ 0] direction than that of the CO tip, which is attributed to the elongated electronic structure of C₂H₄ as reflected in its STM images [10]. According to the near-edge x-ray absorption fine-structure measurement [11], the C₂H₄ molecule adsorbs on the Ag(110) surface through weak π bonding with the two CH₂ planes nearly parallel to the surface.

The molecule on the tip apex can be returned to the surface with spatial selectivity by applying a positive sample

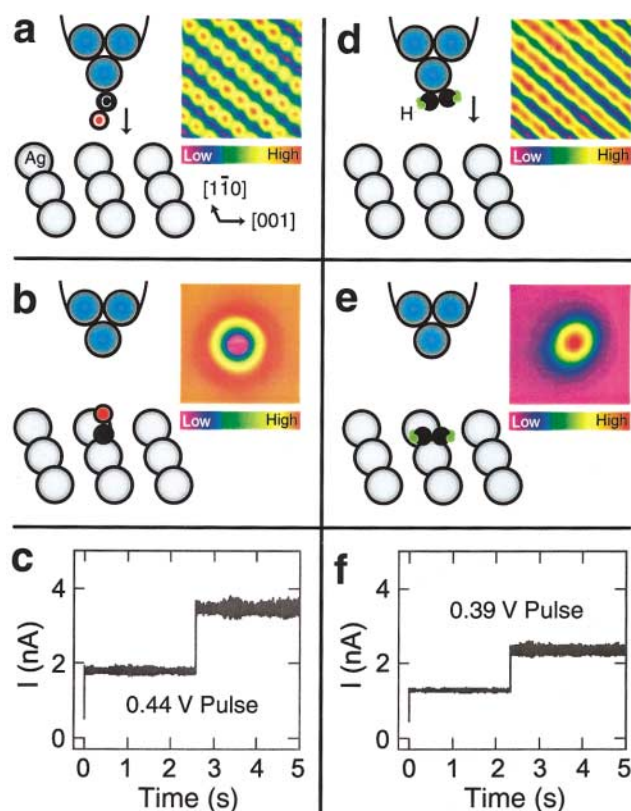


FIG. 1 (color). Schematic diagrams showing the transfer of a single molecule from the tip to the surface. The sizes of the circles are scaled to the atomic covalent radii of H, C, O, and Ag. The topographical images were obtained before [(a) and (d)] and after [(b) and (e)] molecular transfer. (a) The CO tip was positioned over a Ag atom followed by a +440 mV sample bias pulse. (b) The voltage pulse induced the detachment of CO from the tip and its bonding to the Ag atom. (c) Tunneling current during the +440 mV pulse showing the moment of transfer (step at ~ 2.65 s). (d) The C_2H_4 tip was positioned over a Ag atom followed by a +390 mV sample bias pulse. (e) The pulse induced the detachment of C_2H_4 from the tip and its bonding to the Ag atom. (f) Tunneling current during the +390 mV pulse showing the moment of transfer (step at ~ 2.34 s). Both CO and C_2H_4 molecules are bonded on atop sites, determined by imaging with the CO tip or the C_2H_4 tip. The images in (a), (b), (d), and (e), $20 \text{ \AA} \times 20 \text{ \AA}$, were taken at 70 mV sample bias and 1 nA tunneling current.

bias pulse. The molecule-terminated tip was positioned over a Ag atom. The feedback was then turned off and a sample bias pulse of +440 mV for CO (+390 mV for C_2H_4) [12] was applied. A rescan of the same area shows the CO (or C_2H_4) molecule was transferred from the tip to the Ag atom (Figs. 1b and 1e). It should be noted that Ag surface atoms were not resolved with bare metallic tips. The tunneling current during the bias pulse in Figs. 1c and 1f shows a sudden increase after 2 s which indicates the moment of transfer of the CO (or C_2H_4). Calculations [13] show that at a given tunneling current, a molecule-terminated tip should be closer to the surface than a bare tip. Thus the observed increase in the tunneling current can be understood when the molecule is transferred from

the tip to the surface while the feedback is turned off (tip height does not change). The enhanced spatial resolution is attributed to the spatially localized molecular orbital of CO (or C_2H_4) on the tip apex overlapping with the electronic states at the surface.

The chemically modified tips were used to image single CO and O_2 molecules, which revealed new features in the electronic structure of the adsorbates. Two types of chemisorbed O_2 species exist on Ag(110). The O_2 molecule can be bonded with the O-O axis oriented parallel to the surface and along the [001] direction, $O_2[001]$. This bonding geometry was determined from first principles calculations [14] and symmetry of the vibrational microscopy images [8]. The O-O axis has also been found to be oriented along the $[1\bar{1}0]$ direction, $O_2[1\bar{1}0]$. This bonding geometry was inferred from calculations [14] and the observation that the molecule was induced by tunneling electrons to dissociate into two O atoms along the $[1\bar{1}0]$ direction [15]. With a bare metallic tip, the CO is imaged as an inverted sombrero (a round depression with an elevated rim), as shown in Fig. 2a. For $O_2[1\bar{1}0]$, an oval-shaped depression is elongated along the $[1\bar{1}0]$ direction, the same direction as the O-O axis (Fig. 2e). The atomic scale of the surface atoms was not resolved in either image. In contrast, with the CO tip, CO imaged as a sharp protrusion at the center (over an underlying Ag atom) with four depressions around it (Fig. 2b). The topographical image of $O_2[1\bar{1}0]$ obtained with the CO tip exhibits a hexagonal shape with an internal structure (Fig. 2f). Two depressions can be seen inside the hexagon and are symmetrically located with respect to the $[1\bar{1}0]$ axis. With the C_2H_4 tip, less details were resolved for CO (Fig. 2c). The image is not much different from that of the bare metallic tip except for the asymmetry inside the central round-shaped depression. For $O_2[1\bar{1}0]$ imaged with the C_2H_4 tip, a hexagon-shaped depression without an internal structure was observed (Fig. 2g), in contrast to the richer image taken by the CO tip. The resolution of a C_2H_4 tip is intermediate between those of a bare tip and a CO tip.

Atomic resolution of substrate atoms with either the CO tip or the C_2H_4 tip allowed the determination of the adsorption site as atop and the fourfold hollow for CO and $O_2[1\bar{1}0]$ adsorption, respectively (Figs. 2d and 2h). No significant differences were observed between topographical images taken at positive and negative sample biases. It is possible that the molecule-terminated tips are not perfectly symmetric. For ~ 200 molecule-terminated tips we have made, the features in the single molecule images taken with them are slightly asymmetric while those obtained by the bare metallic tips are symmetric, as exemplified by Fig. 2. The asymmetry observed by the modified tips is not due to the adsorption geometry on the surface but the geometry of the molecule at the tip apex. This possibility is shown schematically as slightly tilted adsorption geometry for CO and C_2H_4 in Figs. 1a and 1d.

New vibrational modes were revealed in single molecule vibrational spectra recorded by STM-IETS for CO

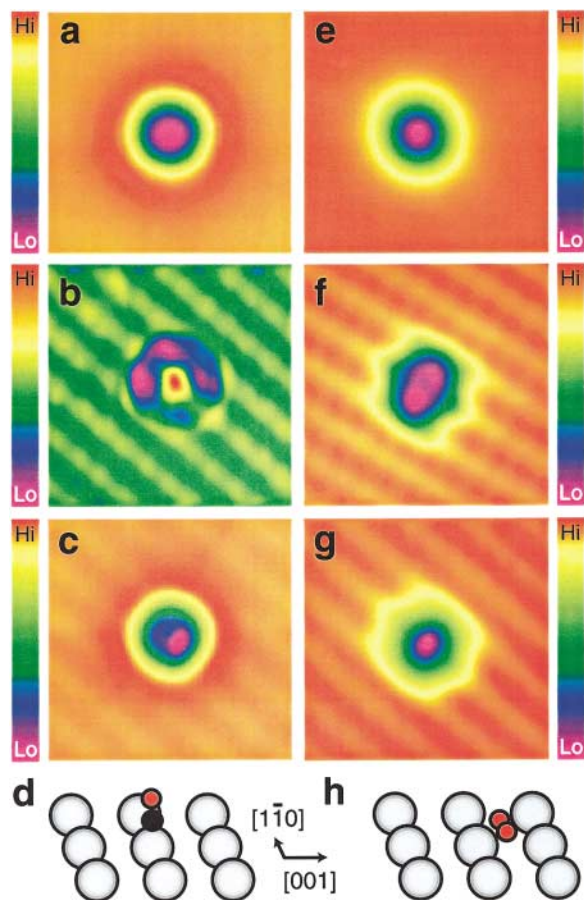


FIG. 2 (color). Topographical images of CO and $O_2[1\bar{1}0]$ molecules obtained with bare metallic and chemically modified tips. In the left column, the images are for a single CO molecule obtained with (a) bare metallic, (b) CO, and (c) C_2H_4 tips. The images in the right column are for a single $O_2[1\bar{1}0]$ molecule obtained with (e) bare metallic, (f) CO, and (g) C_2H_4 tips. All images, $25 \text{ \AA} \times 25 \text{ \AA}$, were taken at 70 mV sample bias and 1 nA tunneling current. Schematic diagrams of CO and $O_2[1\bar{1}0]$ adsorption on Ag(110) are shown in (d) and (h), respectively: red (O), black (C), and grey (Ag).

and $O_2[1\bar{1}0]$ with the CO tip and the C_2H_4 tip. Figure 3 presents d^2I/dV^2 spectra taken directly over the molecule (thin solid lines) and over the bare surface (dashed lines) with bare and modified tips. Contributions from the molecule on the tip were removed by subtracting the spectrum measured over the bare surface from that over an adsorbed molecule. The subtracted spectra (thick solid lines) reflect vibrational features of adsorbed molecules which were confirmed by the spectral shifts due to isotope substitution ($^{13}C^{18}O$ and $^{18}O_2$). The positions of the peaks and dips were determined by fitting the spectra to Gaussian functions with an uncertainty of 1–2 meV. With the CO tip, only the hindered rotation mode at 21 meV (19 meV at negative bias scan) [16] was observed over a CO molecule on Ag(110), as is the case for the bare metallic tip (Figs. 3a and 3b).

However, in addition to the hindered rotation mode at 20 meV, a new feature at 7 meV was observed over a CO

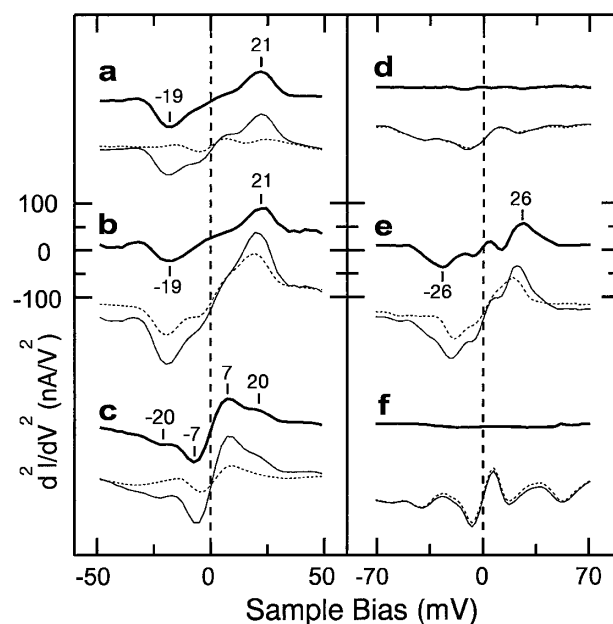


FIG. 3. Single molecule vibrational spectra obtained by STM-IETS for CO with (a) bare metallic, (b) CO, and (c) C_2H_4 tips and for $O_2[1\bar{1}0]$ with (d) bare metallic, (e) CO, and (f) C_2H_4 tips. The spectra taken over the clean Ag(110) surface (dashed lines) were subtracted from the corresponding spectra taken directly over the center of the molecular images (thin solid lines) to reveal spectra for single molecules adsorbed on the surface (thick solid lines). Dwell time of 300 ms per 2.5 mV step and 7 mV rms bias modulation at 200 Hz were used for recording the spectra. Tunneling gaps were set with 70 mV sample bias and 1 nA tunneling current. The line markers indicate the positions of the vibrational modes. Isotope shifts from $^{12}C^{16}O$ were ~ 0.9 and ~ 0.4 meV for hindered rotation and translation modes of $^{13}C^{18}O$, and ~ 1.7 meV for $^{18}O_2[1\bar{1}0]$ vibration from $^{16}O_2[1\bar{1}0]$. Higher resolution of 0.5 mV step and 5 mV rms modulation were used in spectra for determining the isotope shifts to within ~ 0.3 mV. The CO molecule on Ag(110) at 13 K is moved laterally when the bias is increased toward the C-O stretch energy, thus precluding its measurement. However, the CO molecule is stable at the tip apex and vibrational energies of ~ 18 and 268 meV were measured for the hindered rotation and the C-O stretch for a CO tip positioned over the clean Ag(110) surface.

molecule (Fig. 3c) with the C_2H_4 tip. This feature is assigned to the hindered translation mode of CO on Ag(110) [18]. In general, energies of the internal and external stretch vibrations of CO [19–21] are higher than that of the hindered rotational mode which in turn is higher than the hindered translation mode. For the case of the CO vibration recorded with the CO tip, the intensity of the hindered rotation before background subtraction [22] is larger than that of the subtracted one (Fig. 3b) by a factor of ~ 2 . This result indicates that the intensity is a simple algebraic sum of the contributions from the two CO molecules in the tip-CO/vacuum/OC-Ag tunnel junction.

No vibrational modes were found for $O_2[1\bar{1}0]$ with either the bare metallic tip or the C_2H_4 tip (Figs. 3d and 3f). However, a new mode at 26 meV was observed with the CO tip for $O_2[1\bar{1}0]$ (Fig. 3e). This feature can be due to either the hindered rotation of $O_2[1\bar{1}0]$ parallel to the

surface or an O₂-Ag stretch mode. This mode has not been reported in previous experimental and theoretical vibrational analysis of O₂ on Ag(110) [23]. The O-O stretch mode for O₂[1 $\bar{1}$ 0] was not observed with the CO tip.

Spatially resolved vibrational spectra and intensity mapping can provide unique information regarding the mechanism of inelastic electron tunneling. Simultaneous recording of the topographical and vibrational images was taken at biases corresponding to the energies of the observed modes. The observed symmetry in the topographical and vibrational intensity can reveal the vibrational modes and the electronic states of the tip, molecule, and substrate responsible for the observed images. For systems presented in this Letter, the vibrational intensities for all the modes exhibit a maximum at the center of the molecules. The vibrational images are found to be more spatially localized than the corresponding topographical images. Detailed interpretation of these data require theoretical analysis as well as the new modes and topographical features revealed by molecule-terminated tips.

The reversible, manipulated transfer of a diatomic or polyatomic molecule from the surface to the tip apex provides a greater control and understanding of the tip morphology and composition. In this Letter, such a chemically functionalized tip has been shown to increase the resolving power of the STM for imaging and vibrational spectroscopy. Furthermore, the molecule-terminated tip adds a new dimension in the study of catalytic reactions [25,26] especially when the release of the molecule is spatially controlled [9,26]. In addition to the expected increase in the use of chemically modified tips in scanning probe spectroscopy and microscopy, the new results present special challenges to theoretical calculations.

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- [1] C. D. Frisbie *et al.*, *Science* **265**, 2071 (1994).
 [2] J. H. Hafner, C. L. Cheung, and C. M. Lieber, *Nature (London)* **398**, 761 (1999).
 [3] D. M. Eigler, C. P. Lutz, and W. E. Rudge, *Nature (London)* **352**, 600 (1991); P. S. Weiss and D. M. Eigler, *Phys. Rev. Lett.* **71**, 3139 (1993).
 [4] L. Bartels, G. Meyer, and K.-H. Rieder, *Appl. Phys. Lett.* **71**, 213 (1997); *Surf. Sci.* **432**, L621 (1999).
 [5] J. C. Dunphy *et al.*, *Ultramicroscopy* **42-44**, 490 (1992); B. J. McIntyre *et al.*, *J. Vac. Sci. Technol. B* **12**, 1715 (1994).
 [6] B. C. Stipe, M. A. Rezaei, and W. Ho, *Science* **280**, 1732 (1998).
 [7] The STM is a variation of the one described in B. C. Stipe, M. A. Rezaei, and W. Ho, *Rev. Sci. Instrum.* **70**, 137 (1999); L. J. Lauhon and W. Ho, *Rev. Sci. Instrum.* **72**, 216 (2001).
 [8] J. R. Hahn, H. J. Lee, and W. Ho, *Phys. Rev. Lett.* **85**, 1914 (2000).
 [9] H. J. Lee and W. Ho, *Science* **286**, 1719 (1999).
 [10] A single C₂H₄ molecule on Ag(110) appears as an oval-shaped protrusion elongated along the [001] direction (Fig. 1e), compared to an inverted sombrero (a round depression with a protruding rim) for CO (Fig. 1b) in the topographical image taken by a bare metallic tip. Based on atomically resolved images taken with a CO tip or a C₂H₄ tip, C₂H₄ and CO [9] are bonded on atop sites.
 [11] J. L. Solomon and R. J. Madix, *J. Chem. Phys.* **93**, 8379 (1990).
 [12] Threshold voltage for molecule transfer from the tip apex to the surface depends on the tip condition. The lowest values were +440 and +390 mV at 1 nA tunneling current for CO and C₂H₄, respectively. Occasionally higher voltages up to +800 mV were required for both molecular transfers.
 [13] M.-L. Bocquet, J. Cerdà, and P. Sautet, *Phys. Rev. B* **59**, 15437 (1999).
 [14] P. A. Gravil, D. M. Bird, and J. A. White, *Phys. Rev. Lett.* **77**, 3933 (1996).
 [15] J. R. Hahn and W. Ho (to be published).
 [16] The asymmetry in the vibrational energy at positive and negative biases may be due to different interactions between the adsorbate and substrate under different bias polarities [17].
 [17] L. J. Lauhon and W. Ho, *Phys. Rev. B* **60**, R8525 (1999).
 [18] The energy of this mode is similar to those of the hindered translation of CO on Pd(110) (8.6 meV) [19], Ni(110) (7.5 meV) [20], and Cu(110) (4.9 and 3.1 meV) [21].
 [19] H. Kato, M. Kawai, and J. Yoshinobu, *Phys. Rev. Lett.* **82**, 1899 (1999).
 [20] M. F. Bertino and G. Witte, *Surf. Sci.* **385**, L984 (1997).
 [21] J. Ahner, D. Mocuta, R. D. Ramsier, and J. T. Yates, Jr., *Phys. Rev. Lett.* **79**, 1889 (1997).
 [22] The hindered rotational mode was also observed at -19 and +17 mV in the STM-IETS spectrum taken with a CO tip positioned over clean Ag(110), suggesting that the bare metallic tip is terminated with Ag atoms prior to transferring a CO to the tip. The C-O stretch vibration at 268 mV was also measured with the CO tip positioned over clean Ag(110). Physical contacts made with the surface during *in situ* tip sharpening may lead to the attachment of Ag atoms to the tip.
 [23] Two vibrational modes, the O-O stretch (80 meV) and the symmetric Ag-O₂ stretch (30 meV) have been observed for chemisorbed O₂ on Ag(110) by electron energy loss spectroscopy [24]. However, molecular orientation was not specified. In the STM-IETS study of O₂ (oriented along the [001] direction), O₂[001], the O-O stretch (82 meV) and the antisymmetric Ag-O₂ stretch (38 meV) were reported with the bare metallic tip [8].
 [24] B. A. Sexton and R. J. Madix, *Chem. Phys. Lett.* **76**, 294 (1980).
 [25] B. J. McIntyre, M. Salmeron, and G. A. Somorjai, *Science* **265**, 1415 (1994).
 [26] J. R. Hahn and W. Ho, *Phys. Rev. Lett.* **87**, 166102 (2001).