

A. Research Scope and Objectives

This project seeks to understand the mechanisms of elementary chemical reactions on solid surfaces, with implications for heterogeneous catalysis, corrosion, pollution control, atmospheric chemistry, and materials synthesis. The emphasis of our study is placed on an atomic scale understanding by probing the fundamental motions of individual molecules such as vibration, rotation, diffusion, conformational change, and nuclear motions leading to bond dissociation and formation. The pathways of energy flow during a chemical transformation are investigated by considering the excitation sources (photons, tunneling electrons, and heat or phonons), electronic and nuclear relaxation mechanisms and rates, and charge and energy transfers. We seek to understand chemistry at the spatial limit by analyzing, manipulating, and reacting atoms and molecules one by one.

B. Description of Research Effort

Variable, low temperature (8 K – 350 K) scanning tunneling microscopes (STM) operating under ultrahigh vacuum conditions (2×10^{-11} Torr) are used as the main tool to probe surface chemistry with atomic resolution. Inelastic electron tunneling spectroscopy (IETS) with the STM (STM-IETS) was first demonstrated in our group in 1998, which allowed us to reach the limit of sensitivity of vibrational spectroscopy, that of a single bond. Thus, chemically sensitive analysis at the sub-Ångström level is now possible with the STM. In addition, by analyzing changes in the tunneling current as a function of time (with the feedback turned off), motions in a single molecule are revealed, including rotation, vibration, conformational change, and diffusion. These molecular noises are uniquely probed by the STM and reflect the fundamental motions within a molecule. All the spectroscopic properties, including STM-IETS, are contained in the I-V and its derivative curves. Samples consist of single crystal metals (Pt, Ag, Cu, Ni, Au) and semiconductors (Si) with well-characterized surfaces prepared by surface science techniques.

A tunable femtosecond Ti:sapphire laser (30 fs, 78 MHz repetition rate, 760-840 nm and its second and third harmonics) is used to irradiate the tunnel junction in order to couple optical energy into the single molecule in the junction. In addition, individual molecules are excited by the tunneling current by controlling the junction voltage.

Spectroscopy and microscopy are used to probe individual molecules on metal and semiconductor surfaces. The study of chemical reactions involving single metal atoms deposited on surfaces and the extension to aggregates of metal atoms provide a starting point for understanding bimetallic catalysis. Since STM-IETS is a chemically sensitive local probe with atomic resolution, effects of steps, defects, and neighboring atoms and molecules can be investigated. Such structural discontinuities are important and could dominate surface chemistry. Tunneling electrons are used to record vibrational spectra, to induce and view rotational motions and structural changes, to dissociate bonds, to manipulate atoms and molecules, and to form new bonds. We have demonstrated that STM is an all-purpose tool,

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ideally suited to probe and manipulate atoms and molecules one at a time. The combination of femtosecond laser and STM provides a unique opportunity to probe time resolved phenomena with sub-Ångström resolution.

C. Experimental Arrangement

The low-temperature STM (LT-STM) is completely homemade, which includes the scanner, electronics, and software; it took two graduate students (Mohammad Rezaei and Barry Stipe) more than three years (1992-1996) to design, build, and debug the LT-STM. A schematic of the overall apparatus is shown in Fig. 1. The STM system has three main attributes; it is simple, versatile, and stable. Temperature has been varied over the range 8 K - 350 K, which makes it feasible to carry out thermally activated processes such as surface diffusion and molecular rotation. Both the tip and the sample can be changed in situ; a carousel contains 8 samples and 24 tips. Sample and tip can be sputtered and annealed. The same area of the surface can be imaged before and after photon irradiation, gas dosing, and metal evaporation, allowing the tracking of individual molecules.

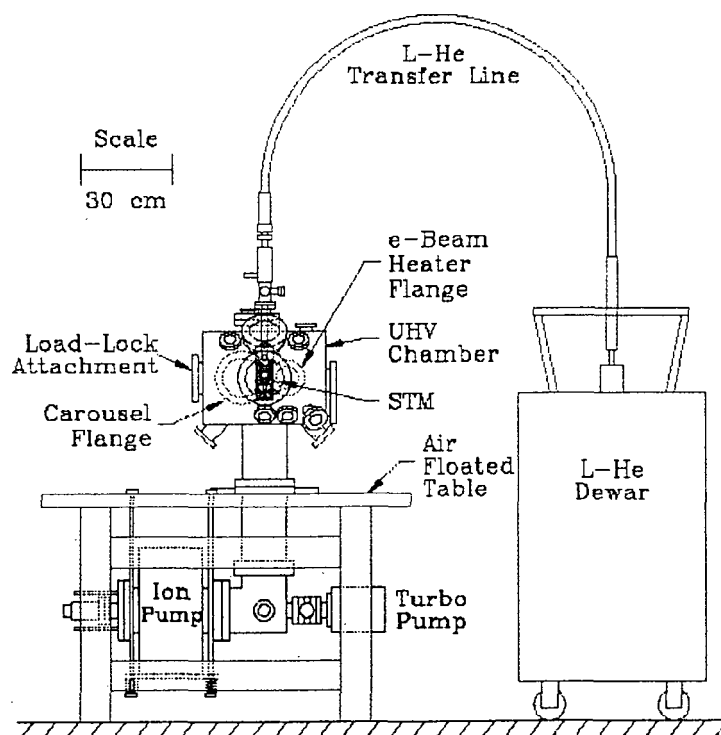


Fig. 1: *Overview of the variable-temperature UHV-STM system.* The STM is cooled by a continuous flow liquid He/N₂ cryostat. The first stage of vibrational isolation is accomplished by bolting the UHV chamber to an optical table equipped with pneumatic legs. The position of the proposed load-lock attachment is shown. (Taken from Publication #6.)

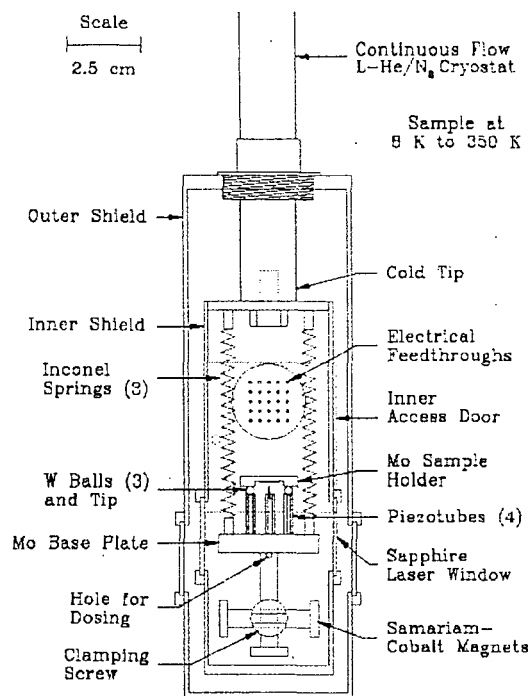


Fig. 2: *The home-made, variable-temperature scanning tunneling microscope.* The STM and the sample hang from three springs which provide the second stage of vibrational isolation. The design allows for in situ dosing and laser irradiation of the sample as well as the exchange of sample and tips. (Taken from Publication #6.)

A cross section view of the LT-STM is shown in Fig. 2. The measured drift in the tunneling current is $\sim 0.25\%$ per minute which corresponds to a drift in the tip-sample spacing of $0.001 \text{ \AA}/\text{min}$. For experiments at 8 K, temperature typically remains stable to better than 10 mK during a day of experiments. Cryogen use is 1.2 l/hr at 8 K and decreases at higher operating temperatures. The inner shield is close to 4 K while the outer shield is about 30 K. Because of the cryopumping of the shields, the pressure should be much lower than the rest of the vacuum chamber of 2×10^{-11} Torr since the sample and tip can remain clean for days. The atomic cleanliness and the stability of the sample and tip are necessary to perform inelastic electron tunneling spectroscopy (STM-IETS). A detailed description of the apparatus has been published in the Review of Scientific Instruments (Publication # 6).

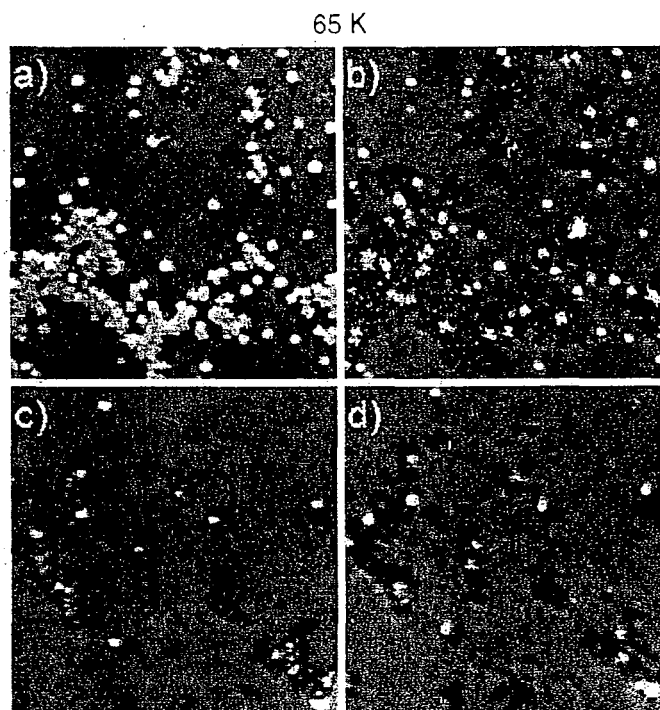
D. Summary of Scientific Achievements

(i) Single Molecule Dissociation on Metal Surfaces: Photons, Electrons, Heat

The first experiments that we performed were with only the inner shield which allowed us to reach 30 K. The experiments proved that the STM that we have constructed was very stable and the sample was very accessible for photon irradiation and gas dosing. The capability of the LT-STM to provide atomically resolved information on the reactants and products in surface photochemistry was demonstrated for O_2 on Pt(111) at 65 K (Publication #1). Most notably, it was possible to visually determine the distances traveled by the photofragments (atomic oxygen), as shown in Fig. 3. An important conclusion reached was that the distances traveled were comparable between dissociation induced by tunneling electrons and photon irradiation. These nonthermally induced processes were compared to thermally induced dissociation. In all three methods of excitation, the dissociation of O_2 produced two O atoms which were found within two lattice constants of the original molecule and one to three lattice constants apart. These

results provide a visual understanding of the dissipation of ~ 1 eV/atom of energy during the transition of adsorbed O_2 to O.

Photoinduced Dissociation



Dosed at 85 K and cooled to 50 K

Fig. 3: *A real space view of surface photochemistry.* Photoinduced dissociation and conversion of O_2 on Pt(111): (a) STM image of the Pt(111) surface dosed with O_2 at 65 K and irradiated with a HeCd laser (325 nm, 45 mW, 3 mm spot size) for 200 s. Clustering of molecules on bridge sites (labeled K) as well as impurities (I) can be seen. Image size is $180 \text{ \AA} \times 180 \text{ \AA}$. (b) Same area after irradiation for an additional 1400 s, leaving oxygen atoms (labeled o) and only a small number of bridge site molecules (B). (c) Surface at 50 K after dosing at 85 K. Oxygen molecules are found on both bridge sites (labeled B) and fcc sites (F). Image size is $140 \text{ \AA} \times 140 \text{ \AA}$. (d) Same area after irradiation for 100 s. FCC site molecules have dissociated; hcp (h) site oxygen atoms appear brighter than fcc (f) atoms. Two fcc site molecules have converted to bridge sites (labeled B). (Taken from Publication #1.)

(ii) Atomic Switch and Single Molecule Chemistry on Semiconductor Surfaces

The LT-STM was then used to investigate semiconductor surfaces and their reactivity. The reversible displacement of a single atom of Si on the Si(111)- 7×7 surface (*an atomic switch*) was accidentally observed at 50-150 K (Publication #2). The displacement was found to be site specific, with strong preference for center Si adatoms in the faulted half of the unit cell, thus revealing the different energetics of the surface atoms. It was possible to monitor each displacement event, as shown in Fig. 4, and obtain a quantitative understanding of the mechanism.

The use of the LT-STM to carry out single molecule dissociation and single atom displacement was reviewed (Publication #3). The dissociation of a single molecule was extended to adsorbed H_2S and D_2S on Si(111)- 7×7 surface, as shown in Fig. 5 (Publication #4). Direct comparison was made to the photodissociation of the same system and provided fundamental insights into the chemistry achieved by electron versus photon irradiation. The different chemical reactivity of the Si surface atoms and the sample temperature also dictated H_2S and D_2S

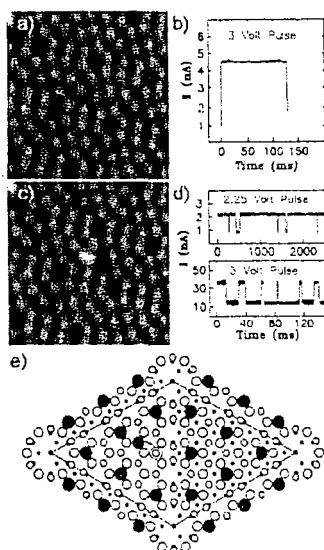


Fig. 4: *A reversible atomic switch on Si.* (a) STM image of the Si(111)-(7x7) surface at 52 K. (b) Tunneling current during a 3 V sample bias pulse applied directly above the centersite adatom in the middle of (a). (c) Rescan shows the adatom in one of the two equivalent metastable T_4 sites. (d) Current recorded at 2.25 and 3 V sample bias over a center adatom in the faulted half of a unit cell at 121 K. Each transition of current level represents a reversible hopping, away (high to low current) and return (low to high current), of the selected center adatom. This singel atom motion continues as long as the voltage is applied. (e) Dimer-Adatom-Stacking-fault (DAS) model for the surface showing the site occupied by the adatom before and after transfer in the faulted half of the unit cell. (Taken from Publication #2.)

adsorption on Si(111)7x7 (Publication # 5). The adsorption and single molecule dissociation with tunneling electrons of D_2S on the Si(111)7x7, Fig. 5, and the Si(100)2x1, Fig. 6, surfaces were compared and contrasted (Publication # 7). Single molecule desorption by tunneling electrons on a semiconductor was demonstrated for NO on Si(111)7x7, as shown in Fig. 7 (Publication #8). Important insights were obtained for single molecule dissociation and desorption on metal versus semiconductor surfaces. These experiments on single atom manipulation, desorption, and dissociation demonstrate the versatility and control at the atomic scale with our LT-STM.

Local Dissociation: HS on Si(111)-7x7

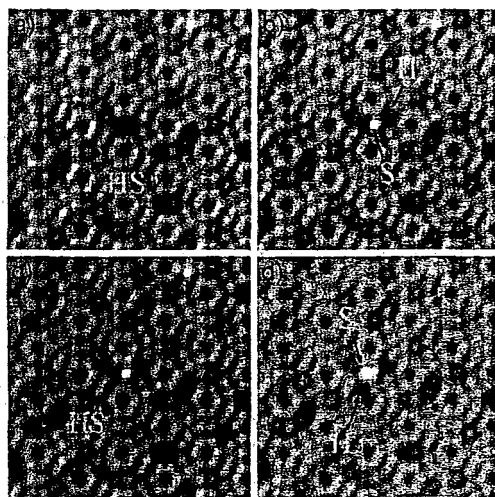


Fig. 5: *Localization of single molecule dissociation.* STM induced single molecule dissociation of HS on Si(111)7x7 at 200 K. (a) The tip is positioned over a HS molecule. (b) Image taken after a 2.5 V, 0.7 nA, 100 ms pulse; the HS molecule is dissociated into H and S, without affecting the neighboring HS. (c) The tip is moved over the second HS molecule. (d) After another 2.5 V, 0.7 nA, 100 ms pulse, the second HS molecule is dissociated. The images were scanned at 1 V sample bias and 0.1 nA tunneling current. (Taken from Publication #4.)

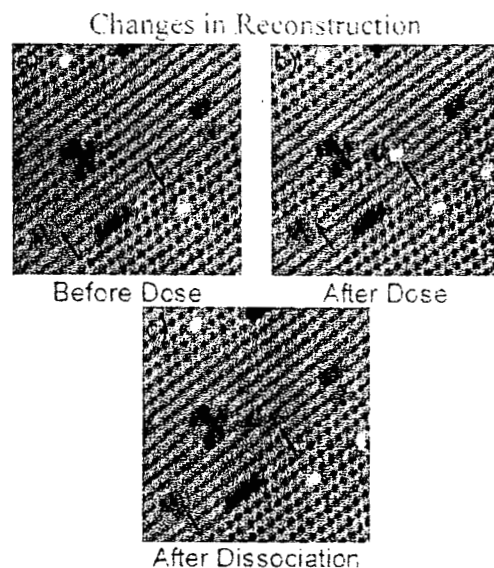


Fig. 6: *Effects of a single molecule on long range surface reconstruction.* Effect of D_2S adsorption and dissociation on the surface reconstruction of Si(100) at 150 K. (a) The clean surface. (b) Surface after a light dose. Note the change in the reconstruction from symmetric to asymmetric in the marked row. (c) The STM-induced dissociation of the adsorbate causes the reconstruction to revert to the symmetric configuration. The images were scanned with 1 V sample bias and 1 nA tunneling current. (Taken from Publication #7.)

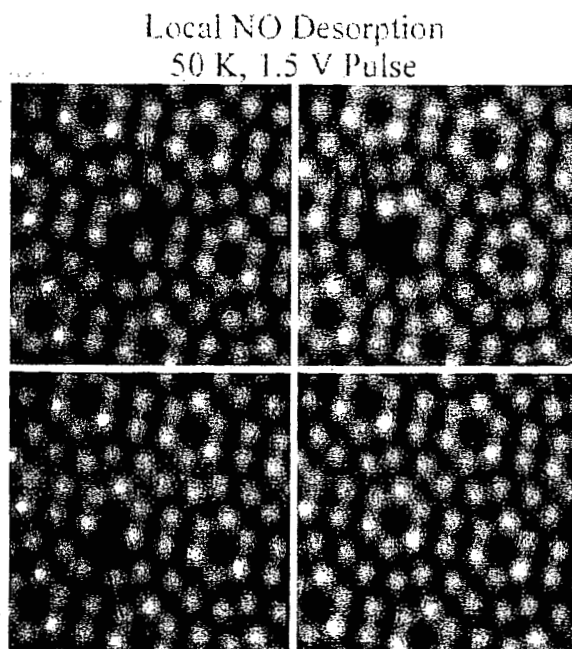


Fig. 7: *Selective breaking of single molecule-surface bond.* (Upper Left) Two NO adsorbates on Si(111)7x7 at 50 K. The tip is positioned on the molecule marked by red arrow and a voltage pulse is applied to move it to a new position next to the one marked by blue arrow. (Upper Right) The tip is positioned on the NO marked by the red arrow and a voltage pulse of 1.5 V and 0.3 nA is applied to desorb the molecule. (Lower Left) Only the targeted NO molecule is desorbed, demonstrating that the low voltage desorption is well controlled and local. The tip is positioned on the next molecule and a similar voltage pulse is applied. (Lower Right) The NO molecule is desorbed. The STM images were scanned at 0.7 V sample bias and 0.1 nA tunneling current. (Taken from Publication #8.)

(iii) The Birth of STM-IETS

Encouraged by these initial experiments which demonstrated the stability and versatility of the STM, we decided to attempt STM-IETS in June 1997. An outer shield was added to lower the temperature since the vibrational width would otherwise be too large. A decrease from 30 K to 8 K was achieved. In addition to the hardware modification, the software was constantly upgraded to allow the performance of experiments requiring new procedures. These flexibilities reflect the crucial advantages of a homemade system.

On January 16, 1998, we first successfully perform single molecule vibrational spectroscopy and microscopy with the STM. There were three experimental factors which made this possible with the homemade STM system: the stability of the hardware (scanner and electronics), the flexible and adaptable software (C under Window 3.1), and judicious choice of adsorbate-substrate system for first demonstration (Publication #6). STM-IETS transforms the STM into a chemically sensitive tool with atomic resolution and reaches the limit of sensitivity of vibrational spectroscopy, that of a single bond. A schematic diagram of the inelastic tunneling process is illustrated in Fig. 8. The first successful system was acetylene on Cu(100) at 8 K and the image and spectra for its three isotopes are shown in Fig. 9.

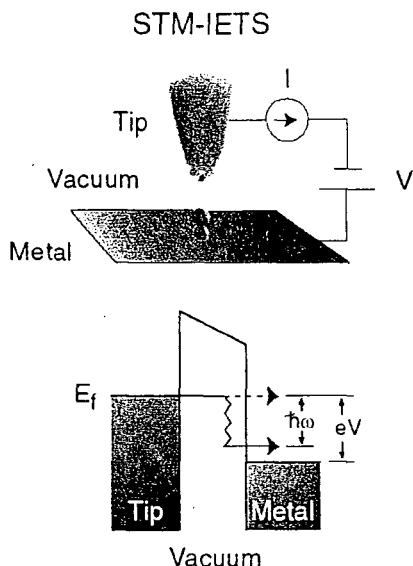


Fig. 8: *Concepts behind STM-IETS.* (Upper Panel) Schematic showing a single molecule in the STM junction. (Bottom Panel) Schematic showing the elastic and vibrationally inelastic tunneling process.

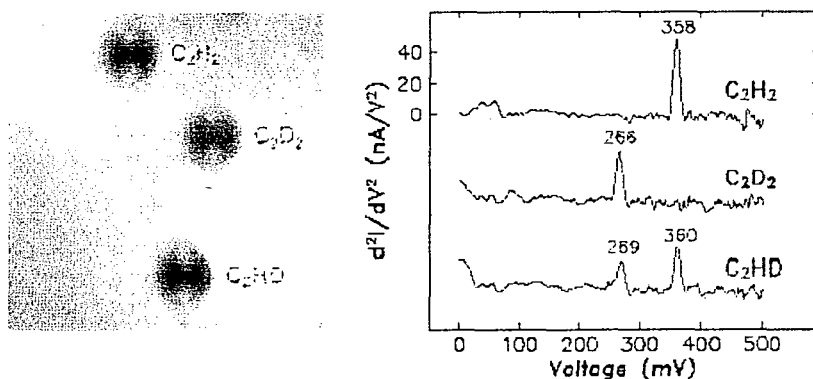


Fig. 9: *Vibrational fingerprinting of single molecules.* STM image, 56 Å x 56 Å, (Left Panel) and single-molecule vibrational spectra (Right Panel) of three acetylene isotopes on Cu(100) at 8 K. The imaged area was scanned at 50 mV

sample bias and 1 nA tunneling current. The vibrational spectra are the average of 16 scans of 2 min each, with the feedback turned off during each scan. Background spectrum over the bare surface has been subtracted. Each spectrum was taken with the tip directly over the center of the corresponding isotope. A rms modulation voltage of 5 mV at 200 Hz was used. (Taken from a review paper showing this figure from our work in: A. Yazdani and C.M. Lieber, "Up Close and Personal to Atoms", Nature **401**, 227-230 (1999).)

(iv) Chemical Synthesis One by One

Individual CO molecules were manipulated and bonded to single Fe atoms on Ag(110) at 13 K to form $\text{Fe}(\text{CO})$ and $\text{Fe}(\text{CO})_2$ molecules – an example of metal catalyzed reaction (Publication #9). The individual reactants and products were unambiguously identified by STM imaging and IETS. These experiments represent the first demonstration of the construction of molecules by forming one bond at time. This work was highlighted as News of the Week in Chemical & Engineering News and highlighted as a Search and Discovery in Physics Today.

The manipulation procedure used to accomplish the construction is illustrated in Fig. 10. A sequence of STM images showing the stepwise construction of molecules is shown in Fig. 11. STM-IETS played a crucial role in the definitive identification of the individual reactants and products, including the verification that bonds have actually been formed. As an example, spatially resolved STM-IETS was used to identify the side-lobe in the image of $\text{Fe}(\text{CO})$ corresponded to the location of the CO ligand (Publications #9 and #13). The C-O stretch intensity was found to be localized in the region of the lobe (Fig. 12). The versatile STM was used to manipulate and synthesize molecules, image reactants and products, and measure vibrational spectra. In effect, the STM has become a nano-laboratory, with capabilities for transforming and characterizing bonds with sub-Ångström resolution. This work demonstrates the concept of “Chemistry One by One”, the theme of this proposal.

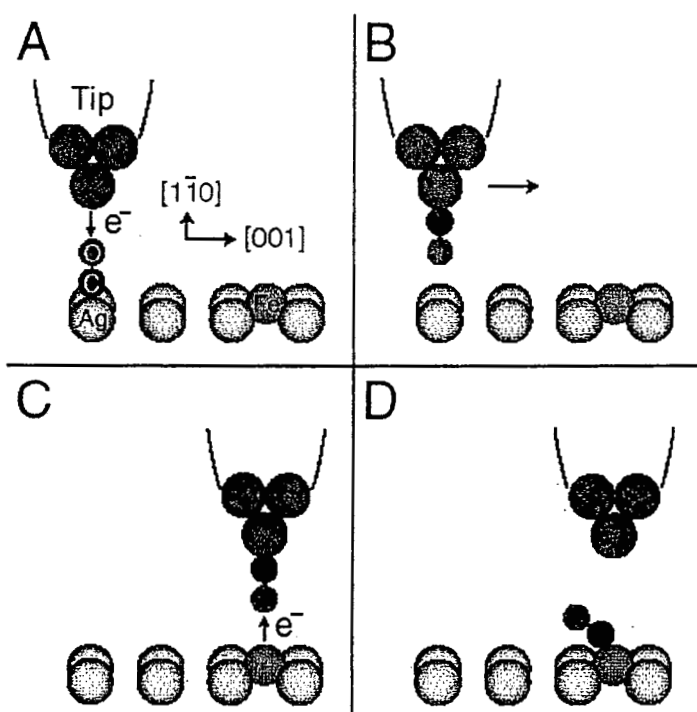


Fig. 10: *A nano-laboratory with Ångström dimensions.* Schematic showing the different steps in the formation of a single bond with the STM. The binding sites are determined by imaging the adsorbed species with a CO molecule on the tip (forming a “supersharper” tip). (A) The tip is positioned over a single CO molecule to induce the detachment of CO from Ag(110) at 13 K and its bonding to the tip. (B) The tip with the attached CO is translated and positioned over an Fe atom. (C) The bias voltage and the flow of electrons are reversed, inducing the transfer of CO from the tip to the Fe. (D) A single Fe-CO bond is formed. A second CO can be bonded to $\text{Fe}(\text{CO})$ to form $\text{Fe}(\text{CO})_2$ by repeating the

procedure. A maximum of three CO molecules can be bonded one by one to form $\text{Fe}(\text{CO})_3$. (Taken from Publication #9.)

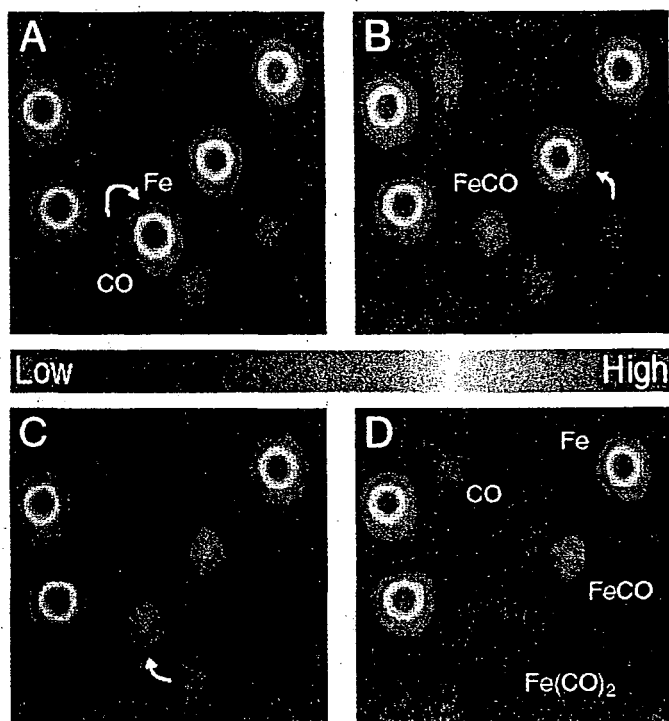


Fig. 11: *Real space view of the individual steps involved in the construction of single molecules.* A sequence of STM topographical images, $63 \text{ \AA} \times 63 \text{ \AA}$, recorded at 70 mV sample bias and 0.1 nA tunneling current. White arrows indicate the pair of adsorbed species involved in each bond formation step. (A) Five Fe atoms and five CO molecules are adsorbed in this area of the Ag(110) surface. (B) A CO molecule has been manipulated and bonded to an Fe atom to form Fe(CO). (C) Another Fe(CO) is formed by binding a second CO to a second Fe atom. (D) An additional CO has been bonded to Fe(CO) to form Fe(CO)₂. (Taken from Publication #9.)

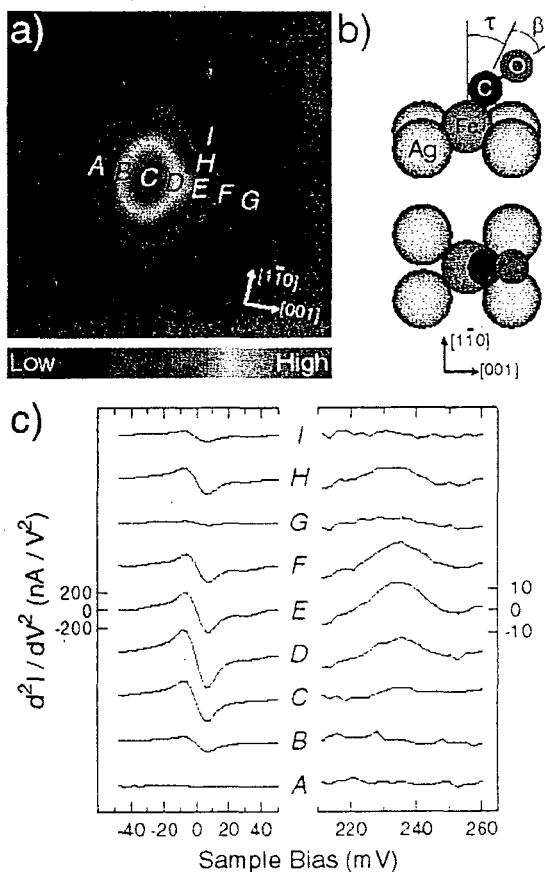


Fig. 12: *Chemical structure determination by spatially resolved STM-IETS.* (a) $25 \text{ \AA} \times 25 \text{ \AA}$ image of Fe(CO) recorded at 70 mV and 1 nA. Letters A through I denote the tip position for the corresponding vibrational spectra shown in (c). (b) The side view and top view of Fe(CO) showing the CO to be tilted by angle τ and bent by angle β . (c) Spatially resolved and background subtracted single-molecule vibrational spectra, showing that the C-O stretch intensity is localized in the region of the side lobe in the STM image. The asymmetry of the image and the spatially resolved vibrational spectra lead to the structure shown in (b). (Taken from Publications #9 and #13.)

The STM was also used to synthesize $\text{Cu}(\text{CO})$ and $\text{Cu}(\text{CO})_2$ in order to compare the reactivity of single Fe vs. Cu atoms (Publication #13). The reactants and products were characterized by STM imaging and IETS. In the case of Cu, a maximum number of two CO molecules can be bonded, compared to three for Fe. In addition, bonding geometries were found to be different for both mono- and di-carbonyls, as shown in Fig. 13. Although the tilt and bent angles need to be quantitatively determined from theoretical calculations, the qualitative differences in bonding between Fe and Cu atoms are visualized and spectroscopically asserted.

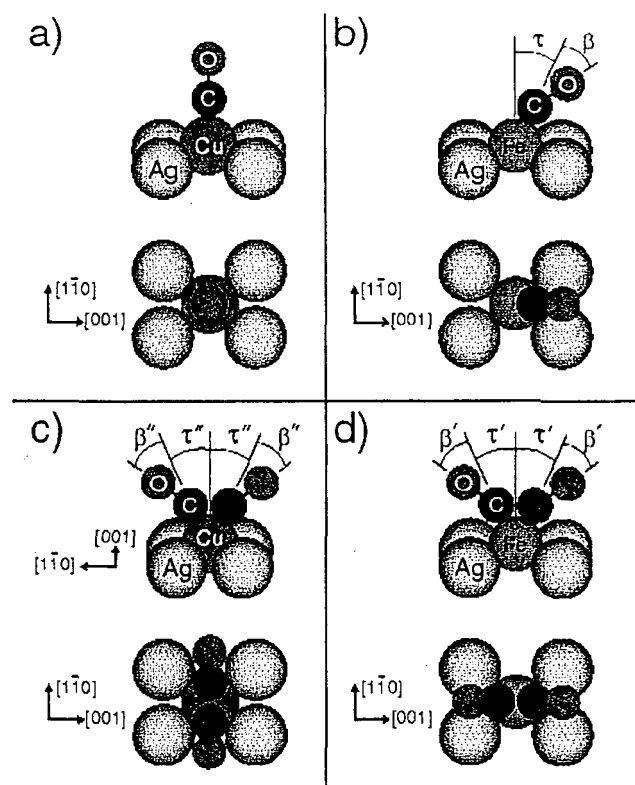


Fig. 13: *Isolated bi-metallic catalyst.* Schematic showing the contrast in bonding of one and two CO molecules to single Cu and Fe atoms on Ag(110) at 13 K, as determined from STM imaging and spatially resolved IETS intensity of the hindered rotation and the internal stretch mode of CO. These molecules were synthesized one by one by the technique shown in Fig. 10. The angles tau (τ , τ' , τ'') and beta (β , β' , β'') are qualitatively determined from experiment; the CO molecules are inclined in Fe(CO) and in both di-carbonyls. Note the plane of the di-carbonyls are 90° from each other in $\text{Cu}(\text{CO})_2$ and $\text{Fe}(\text{CO})_2$. (Taken from Publications #9 and #13.)

(v) Bond-Specific Chemistry

Tunneling electrons were used to selectively dissociate a bond within a single molecule. The two C-H (C-D) bonds in C_2H_2 (C_2D_2) were sequentially broken, and in C_2HD , the C-H bond is preferentially dissociated over the C-D bond. The STM works as a nano-laboratory for the dissociation and characterization of the reactants and products (Publication #10). The product ethynyl (CCH and CCD) is distinguished from acetylene and dicarbon (fully dehydrogenated) by its image, vibrational energy, and rotation rate, as shown in Fig. 14. The C-H (C-D) vibration in CCH (CCD) is 395 meV (313 meV) compared to 357 meV (265 meV) in C_2H_2 (C_2D_2). The rotational barrier for ethynyl is ~ 3 times lower than that of acetylene. The plane of the ethynyl is rotated 45° from that of the acetylene and its C-C bond axis is tilted from the surface plane. The identification and detailed characterization of the ethynyl intermediate, in addition to acetylene and dicarbon, provides an understanding into dehydrogenation reactions.

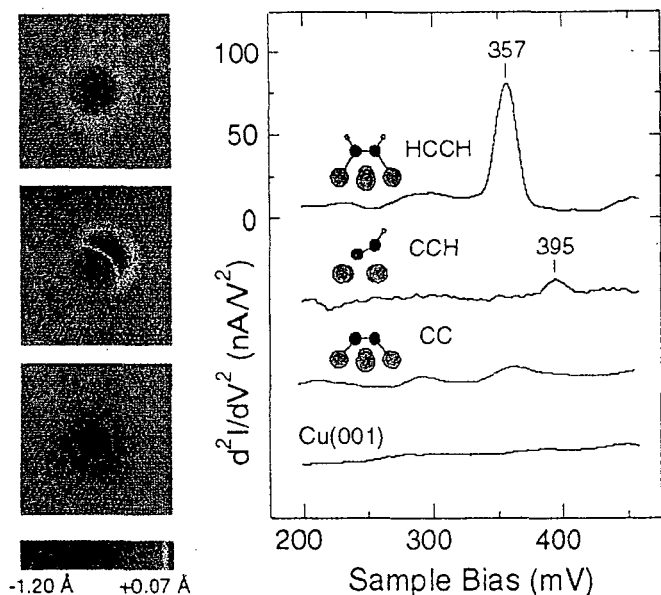


Fig. 14: **Multistep Unimolecular Reaction.** STM images of acetylene (C_2H_2 , C_2D_2), ethynyl (CCH, CCD), and dicarbon (CC), top to bottom in left column of figure. Only one of the four possible orientations of the ethynyl is captured in the STM image. The vibrational spectra of single C_2H_2 , CCH, and CC along with the clean part of Cu(001) are shown in the right panel. Spectra for C_2D_2 and CCD were obtained to show the isotopic shifts in the vibrational peaks, similarly for C_2HD . The C-H bond is preferentially dissociated over the C-D bond from studies of the three isotopes. (Taken from Publication #10.)

(vi) IETS Mechanism – Resonant Elastic and Inelastic Tunneling

In order to understand the mechanisms involved in STM-IETS, it is necessary to have the critical amount of data, thus the need to study different adsorbate-substrate systems. In addition, theoretical efforts are absolutely critical to provide the framework and to substantiate our understanding. To date, STM-IETS have been observed for over a dozen systems. The key issues on the vibrational peaks which have emerged from these studies over the last 2.5 years are: 1. the type of vibrational modes observed, 2. their intensity, 3. their lineshape, and 4. the spatial distribution of the vibrational intensity.

Significant advancement has been obtained in our understanding of the STM-IETS mechanisms as a result of an active collaboration with theorists at Chalmers University, Sweden (Drs. Mats Persson, Nicolas Lorente, Shiwu Gao, and Prof. Bengt Lundqvist). This collaboration has continued for the last 3 years and has become even more active at the present time.

Striking results have been observed for O_2 adsorbed on Ag(110) (Publication #14). IETS from this system revealed for the first time inelastic tunneling through an electronic resonance of the adsorbed O_2 . There are two notable consequences of this STM-IETS mechanism: 1. negative instead of the usual positive vibrational peaks at positive sample bias, and 2. the spatial distribution and its symmetry of the vibrational intensity of the observed modes match those of the molecular electronic resonance. In fact, two vibrational modes are observed, the O-O stretch and the antisymmetric O_2 -Ag stretch. A selection rule based on the symmetry consideration of the electronic resonance and the vibrational modes has been successfully developed; it is capable of explaining which modes are symmetry allowed. This selection rule not only provides an explanation for the O_2 /Ag(110) system but also for other adsorbate-substrate systems such as acetylene and CO on Cu(001). The $1\pi_g^\perp$ resonance of O_2 overlaps the Fermi level and is responsible for the resonant process in IETS. A nodal plane exists perpendicular to the O-O bond axis.

The O-O bond axis is parallel to the surface and its bonding site is determined from the atomically resolved STM image taken with a “supersharp” tip, i.e. with a CO molecule transferred to the tip. The striking difference in the images obtained with a bare and a CO-terminated tip is shown in Fig. 15. In addition to resolving the Ag atoms, features in the O₂ image can be attributed to the imaging of the $1\pi_g^\perp$ resonance. The spatial distribution and the symmetry of this resonance along with the two vibrational modes are displayed in Fig. 16. The intensities observed for the two vibrational modes (taken at positive or negative sample bias) are concentrated in two areas for this diatomic bond. All the results are consistent with resonant inelastic tunneling through the $1\pi_g^\perp$ resonance of O₂ on Ag(110).

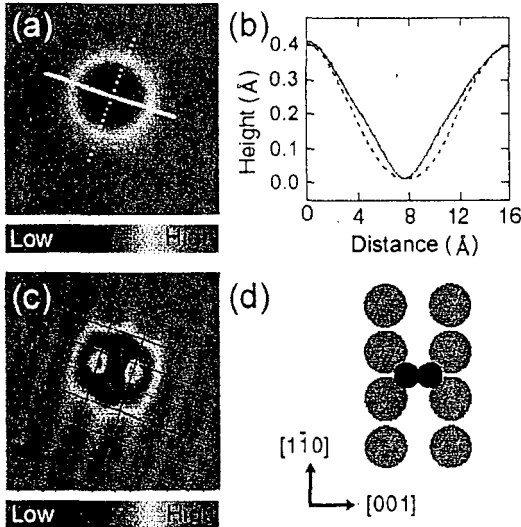


Fig. 15: *Atomically resolved imaging with a CO-terminated supersharp tip.* STM images of single O₂ molecule chemisorbed on Ag(110), 25 Å x 25 Å. The O₂ was dosed at 45 K and cooled down to 13 K for IETS. (a) Topographic image obtained with a bare tip at 70 mV bias and 1 nA tunneling current. (b) Cross sections of (a) taken along the [001] (solid line) and [1 $\bar{1}$ 0] (dashed line) directions. (c) Atomically resolved STM topographic image obtained with a CO-terminated tip at 70 mV bias and 1 nA tunneling current. Grid lines are drawn through the silver surface atoms. (d) Schematic of the adsorption site. The small black circles represent oxygen atoms and the large gray circles silver atoms. (Taken from Publication #14.)

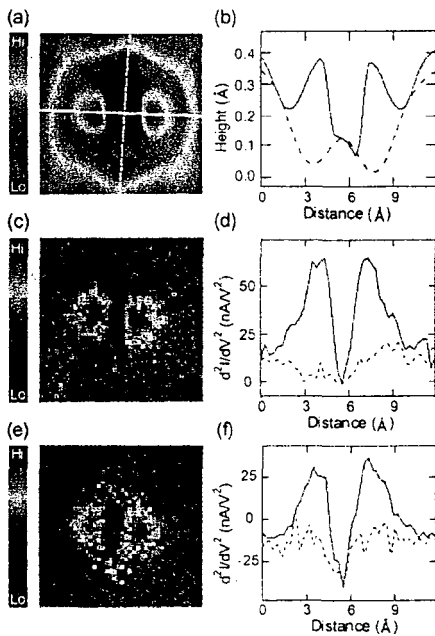


Fig. 16: *Symmetry in vibrational microscopy and resonant inelastic tunneling.* Comparison of the topographic image of O₂ and the spatial distribution of STM-IETS intensity for the two observed vibrational modes. (a) Topographic image, 12 Å x 12 Å, taken at 70 mV bias and 1 nA tunneling current with a CO-terminated tip. (b) Cross sections of (a) taken along the [001] (solid line) and the [1 $\bar{1}$ 0] (dashed line) directions. (c) Vibrational image obtained at -76.6 mV sample bias, corresponding to the O-O stretch vibration. (d) Cross sections of (c) taken along the two directions shown in (a). (e) Vibrational image obtained at -35.8 mV bias, corresponding to the antisymmetric O₂-Ag stretch. (f) Cross sections of (e) taken along the two directions shown in (a). (c) and (e) were obtained with a bare tip. The raw data, 12 Å x 12 Å area, are shown at a resolution of 0.3 Å/pixel. (Taken from Publication #14.)

(vii) Application of STM-IETS to Large Molecules

The extension of imaging and STM-IETS to large molecules can provide further understanding of the STM-IETS mechanism and broaden the application of this technique. We have chosen Cu(II) etioporphyrin-I mainly for four reasons. First, the molecule is known to adsorb with its plane parallel to the surface, thus exposing different parts of the molecule to the STM probe. Second, its Fe(II) analog is related to the Heme-group. Third, bonding of molecules such as CO and O₂ to the central atom is interesting from chemical and biological standpoint. Fourth, Cu(II) etioporphyrin-I holds the record over all other molecules for the maximum absorption of light, which is a favorable candidate for a combined probe by the laser and the STM.

The topographical image of Cu(II) etioporphyrin-I on Cu(001) and its IETS spectrum are shown in Fig. 17 (Publication #15). The methene bridge C-H stretch vibration at 359 meV is the only mode that was observed. The closeness of this energy to the C-H stretch observed for acetylene on Cu(001) strongly suggest the similarity in the bond character in these two molecules, i.e. the C has basically sp² hybridization. Vibrational imaging showed the occurrence of equivalent C-H intensity in four places, 90° apart, which is the proper symmetry for the molecule adsorbed parallel to the surface. The lack of observation of other vibrational modes provides a stringent test for theoretical calculations. The family of porphyrins (including the Heme-group) is a triumphant case for density functional theory calculations of its electronic structure which is an integral part of the STM-IETS calculation. The nature of the bonding of porphyrins to the surface is also of interest since the molecules are stable and remain bonded to the Cu(001) surface at room temperature.

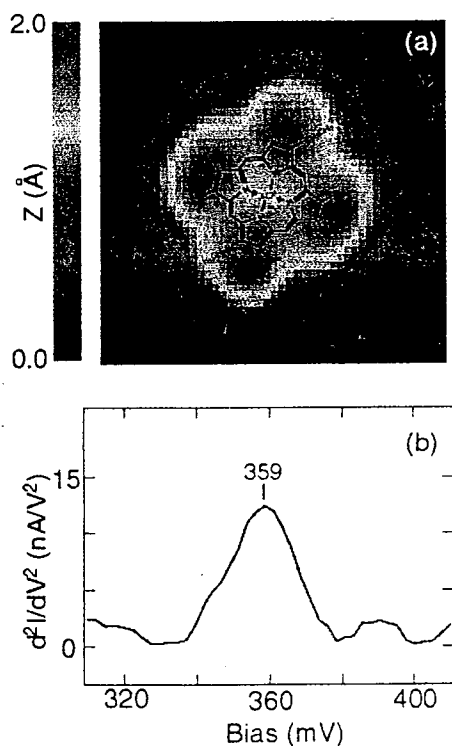


Fig. 17: *Large molecules – is STM-IETS possible?* (a) Topographical image, 27 Å x 27 Å, of Cu(II) etioporphyrin-I on Cu(001) at 11 K taken at 250 mV bias and 1 nA tunneling current. The bond lengths in the superimposed molecular structure are scaled according to their lengths in a free molecule. The * shows one of the four equivalent tip locations where the methene bridge C-H stretch has the maximum intensity. (b) Single molecule vibrational spectrum of Cu(II) etioporphyrin-I, showing the methene bridge C-H stretch at 359 meV. (Taken from Publication #15.)

(viii) Combining Femtosecond Laser with the STM

The possibility of probing ultrafast phenomena with Ångström resolution is an intriguing one. In principle, one way to implement this experimentally is to combine a femtosecond laser with an STM by irradiating the STM junction with a pair of femtosecond laser pulses temporally delayed from each other and monitor the response of the tunneling current. In practice, there are a number of challenges, including the proper choice of systems to study.

We have successfully combined a femtosecond laser with a low temperature STM. To demonstrate the feasibility of such experiments, we have studied time-resolved dynamics at Ag(110) and Cu(100) surfaces by collecting photoemitted electrons with the tip of a scanning tunneling microscope in ultrahigh vacuum. A pair of femtosecond laser pulses (the pump and the probe), with a variable time delay between them, was focused at the STM junction. A coherent electron population was impulsively generated (pumped) by 1.53 eV (810 nm) femtosecond laser pulses and its time evolution was probed by multiphoton photoemission with 1.53 eV pulses. Mode beating associated with coherent electron-phonon scattering was observed as shown in Fig. 18 (Publication #11). The beat frequencies, obtained from the Fourier transform, are attributed to those of the longitudinal phonon modes near bulk Brillouin zone boundaries. These experiments were carried out with the tip positioned 500 μm away from the sample surface at room temperature. We are currently working toward experiments with the tip positioned in the tunneling regime, i.e. $\sim 6\text{-}7$ Å away from the surface at low temperatures.

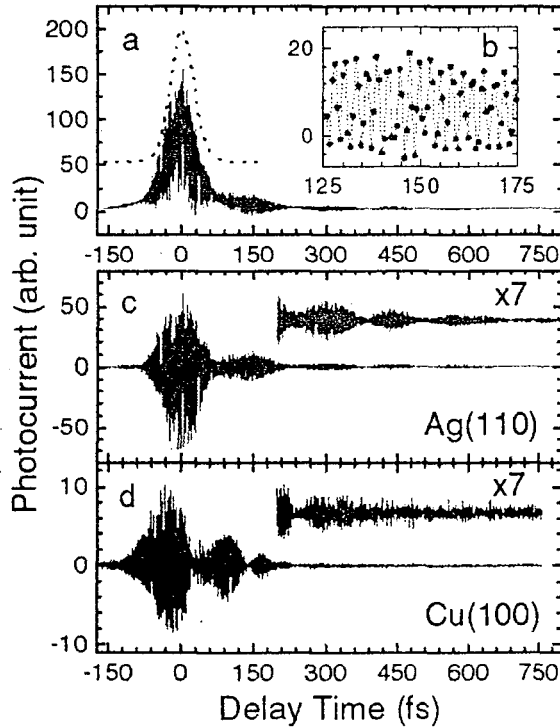


Fig. 18: *Femtosecond-STM*. (a) Time-resolved multiphoton photoemission from Ag(110) surface at 295 K. The pump and probe are 100 mW, s-polarized and 30 mW, p-polarized, respectively. The same laser beams were used to obtain the sum frequency generation signal from GaAs(110) in the sample position (dashed curve) for determining the zero delay between the pump and probe. Neither interference nor beating was observed in this signal. (b) An illustrative portion of the oscillatory part (c) from 125 fs to 175 fs time delay of the probe from the pump pulses. The dotted line is drawn to guide the eyes. (d) The corresponding oscillatory part from Cu(100) surface. The Fourier power spectra of the oscillatory signals reveal the origin of the beating to bulk longitudinal phonons modes. (Taken from Publication #11.)

(ix) Review Articles

Three review articles were written at different stages during the current grant period (Publications #3, #12, #16). Publication #3 discusses the discovery that the same mechanism operates in femtosecond surface photochemistry and STM induced chemistry. Publication #12 highlights the demonstration of STM-IETS and discusses some of its applications; it was written in commemoration of the opening of the Tsukuba Conference Center in Tsukuba, Japan in November 1999. In the most recent review, associated with an invited talk given by my student Lincoln Lauhon at the Faraday Discussions in England, more applications of STM-IETS are discussed, including the identification of reactants and products by vibrational fingerprinting.

List of Publications Acknowledging DOE Support (11/01/97 – 10/31/00)

- [1] B.C. Stipe, M.A. Rezaei, and W. Ho, "*Atomistic Studies of O₂ Dissociation on Pt(111) Induced by Photons, Electrons, and by Heating*", J. Chem. Phys. **107**, 6443-6447 (1997).
- [2] B.C. Stipe, M.A. Rezaei, and W. Ho, "*Site-Specific Displacement of Si Adatoms on Si(111)-(7×7)*", Phys. Rev. Lett. **79**, 4397-4400 (1997).
- [3] W. Ho, "*Inducing and Viewing Bond Selected Chemistry with Tunneling Electrons*", Acc. Chem. Res. **31**, 567-573 (1998).
- [4] M.A. Rezaei, B.C. Stipe, and W. Ho, "*Inducing and Imaging Single Molecule Dissociation on a Semiconductor Surface: H₂S and D₂S on Si(111)-7×7*", J. Chem. Phys. **109**, 6075-6078 (1998).
- [5] M.A. Rezaei, B.C. Stipe, and W. Ho, "*Atomically Resolved Determination of the Adsorption Sites as a Function of Temperature and Coverage: H₂S on Si(111)-(7×7)*", J. Phys. Chem. B **102**, 10941-10947 (1998).
- [6] B.C. Stipe, M.A. Rezaei, and W. Ho, "*A Variable-Temperature Scanning Tunneling Microscope Capable of Single-Molecule Vibrational Spectroscopy*", Rev. Sci. Instrum. **70**, 137-143 (1999).
- [7] M.A. Rezaei, B.C. Stipe, and W. Ho, "*Imaging the Atomically Resolved Dissociation of D₂S on Si(100) from 80 to 300 K*", J. Chem. Phys. **110**, 3548-3552 (1999).
- [8] M.A. Rezaei, B.C. Stipe, and W. Ho, "*Atomically Resolved Adsorption and Scanning Tunneling Microscope Induced Desorption on a Semiconductor: NO on Si(111)-(7×7)*", J. Chem. Phys. **110**, 4891-4896 (1999).
- [9] H.J. Lee and W. Ho, "*Single-Bond Formation and Characterization with a Scanning Tunneling Microscope*", Science **286**, 1719-1722 (1999).

- *** News of the Week, "STM: An All-In-One Tool", Chemical & Engineering News, p. 9-10, November 29, 1999, written by Mitch Jacoby.
- *** Search and Discovery, "Creating and Characterizing Individual Molecular Bonds with a Scanning Tunneling Microscope", Physics Today, p. 17-18, February 2000, written by Charles Day.
- [10] L.J. Lauhon and W. Ho, "Control and Characterization of a Multistep Unimolecular Reaction", Phys. Rev. Lett. **84**, 1527-1530 (2000).
- [11] Y.-M. Chang, L.J. Lauhon, and W. Ho, "Direct Observation of Coherent Electron Excitation and Electron-Phonon Scattering at Metal Surfaces", Phys. Rev. Lett., submitted (2000).
- [12] W. Ho, "Spectroscopy of Materials at the Spatial Limit", in Proceedings of Science Frontier Tsukuba 999 Conference, Tsukuba, Japan, November 17-19, 1999, pp. 321-329 (2000).
- [13] H.J. Lee and W. Ho, "Structural Determination by Single Molecule Vibrational Spectroscopy and Microscopy: Contrast Between Copper and Iron Carbonyls", Phys. Rev. B **61**, R16347-R16350 (2000).
- [14] J.R. Hahn and W. Ho, "Electronic Resonance and Symmetry in Single-Molecule Inelastic Electron Tunneling", Phys. Rev. Lett. **85**, 1914-1917 (2000).
- [15] T.M. Wallis, X. Chen, and W. Ho, "Single Molecule Vibrational Spectroscopy and Microscopy: Cu(II) Etioporphyrin-I on Cu(001)", J. Chem. Phys., Commun. **113**, 4837-4839 (2000).
- [16] L.J. Lauhon and W. Ho, "The Initiation and Characterization of Single Bimolecular Reactions with a STM", Faraday Discussions, September 2000, **117**, 249-255 (2000).
- [17] L.J. Lauhon and W. Ho, "The Effects of Temperature and Other Experimental Variables on Single-Molecule Vibrational Spectroscopy with the Scanning Tunneling Microscope", Rev. Sci. Instrum. **72**, 216-223 (2001).

ESTIMATE OF UNOBLIGATED BALANCES

There will be no unexpended funds allocated in the DOE budget for the period 11/01/97 – 10/31/00.