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Photon and Electron Stimulated Surface Dynamics of Single Molecules

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1. Results from DOE Support

1.1. Summary

Over the 4 year grant period, DOE funds were used to partially support the research of 1 postdoctoral fellow and 2 graduate students as they built up and used an ultra-high vacuum, low and variable temperature, scanning tunneling microscopy (STM) system to study a variety of surface reactions on Pt(111). Three papers[1,2,3] were published which acknowledge support from the grant and 4 working manuscripts[4,5,6,7] remain in preparation for submission. The initial goal of the grant was to build up an entirely new low temperature STM and ultrahigh vacuum system to examine the electron and photon induced chemistry of single molecules at low surface temperatures where thermal diffusion would be quenched. This was an ambitious undertaking and given the project budget and the unavailability of commercial low temperature STM instruments in 1995, we built a specialized STM system in-house (details elaborated upon below in Sect. 1.2). As the performance of our home built STM was being iteratively improved, we first examined the photochemistry of CH_3Br on Pt(111) at 90 K using liquid nitrogen (LN_2) sample cooling.[1] Initially, we had planned to simply use CH_3Br photofragmentation as a relatively clean source of adsorbed Br atoms that could be imaged by STM. Surprisingly, at least to us, Br atoms were quite mobile even at 90 K and were only visible by STM when coalesced along Pt step edges or in Br islands structures. Br was observed to form both $\sqrt{3} \times \sqrt{3}$ and 3 x 3 island structures, the former of which we observed for the first time (later confirmed by LEED in our laboratory). More importantly, we discovered that the 193 nm photofragmentation of CH_3Br efficiently created monovacancies in the substrate at 90 K.[1] Apparently, hot Br atom photofragments abstracted single Pt atoms from the Pt(111) terraces leaving monovacancies behind. Given that kinetic and spectroscopic studies of alkyl radical species on metals often begin with radical generation from thermal or non-thermal dissociation of halogenated hydrocarbons,[8] it may be important to recognize that the presence of not only halogen fragments but also etched monovacancies or adatoms may influence the surface radical chemistry observed. To test if adatom and monovacancy pair generation generally occurs when halogen containing species dissociatively adsorb, we examined the chemistry of Br_2 and CH_3I on Pt(111).[4,5] The energy requirement to create an adatom/monovacancy pair on the Pt(111) terraces is estimated theoretically at 1.45 eV[9], whereas the nascent energy of adsorbing halogen atoms created by photofragmentation of CH_3Br is 1.7-2.1 eV, 1.5 eV for photofragmentation of CH_3I, and 1.1 eV for Br_2 dissociative adsorption. Neither of the latter processes generated monovacancies at low temperature. Nevertheless, when these surfaces were heated beyond ~400 K thermal etching of the surface began and vacancy islands, PtX_z compound, and Pt adatom islands could be visualized by STM. In summary, we found that at elevated temperatures there is considerable restructuring and reactive attack of the Pt surface by halogens but that for traditional, lower temperature studies of alkyl radicals prepared by thermal dissociative adsorption of alkyl iodides there is probably no problem with adsorbing I generating monovacancies on the surface.

Given our interest in using photon and electron stimulated chemistry of adsorbates to prepare hot atoms which could react with coadsorbed species, we examined the dynamics of the hot Br atoms formed by dissociative adsorption of Br_2.[3] Dosing Br_2 from a solid state electrochemical doser onto a Pt(111) surface held at 25 K led to dissociative adsorption whose outcome could be visualized by STM because thermal diffusion of the Br atoms was quenched at 25 K. We discovered that hot Br atoms form Br_2 dissociative adsorption ($<\Delta x_{Br-Br}> = 9.2 \pm 0.1$ Å) travel further than hot O atoms from O_2 dissociative adsorption ($<\Delta x_{O-O}> = 5.5$ Å) on Pt(111). This was an important result because hot atom motion from different dissociative adsorption systems had not been compared for the same metal substrate. We introduced a methodology to estimate an upper bound for the friction coefficient of hot atoms from dissociative adsorption (i.e. $\eta_{Br} \leq 2.2$ ps^{-1}). Our experimental results strengthened the theoretical case that corrugation of the adsorbate/substrate potential is the key issue in determining hot atom travel (and not so much nascent energy or mass). In addition, our Br_2 dissociative adsorption data as a function of coverage provided strong evidence for the transient existence of a weakly adsorbed and mobile Br_2 precursor to dissociative adsorption (via formation of Br atom islands at a temperature where thermal diffusion of Br atoms was quenched).

We also conducted experiments imaging individual molecules at low temperature.[6] Although we are able to take STM images at surface temperatures as low as 15 K, the expense of building our instrument limited the residual funds available for liquid helium cooling and consequently most of our experiments employed LN_2 cooling (despite the fact that LN_2 cooling creates more vibrational noise than LHe). Nevertheless, at this time, our STM system is quite competent at low temperature imaging and we propose to move away from halogen chemistry in the new proposal and attack questions concerning the catalytic activation and dissociation of several important, energy related, small molecules on metals.

There were no unexpended funds at the end of the project period.

STM Design and Performance

Figure 1(a) shows a cross sectional view through our multi-technique UHV chamber for low and variable temperature STM. The entire chamber is supported on an air-levitated Newport optical table. The ion pumped chamber's nominal base pressure of 1.3 x10^{-10} Torr drops into the high 10^{-11} Torr range when the sample is cooled using liquid cryogen. The sample manipulator consists of an x-y stage and a differentially pumped rotary platform through which an Oxford Instruments cryostat extends. Fig. 1(b) gives a schematic view of the key manipulator details that concern vibrational isolation and cooling of the sample. Sample cooling is accomplished through a copper braid connection to the cryostat and heating is by electron bombardment from a tungsten filament located behind the sample. A temperature range of 15 - 1350 K has been achieved for our Pt(111) samples. The home-built STM uses Besocke's inertial approach[10] and is styled after the scuttling "Beetle" instruments developed by Comsa[11] and Salmeron.[12] The STM is put in to operation after being lowered by its own manipulator onto the Mo ramp surrounding the sample. The STM movement and scanning is driven by electronics and software from RHK Technology. The STM can be operated at all sample temperatures up to at least 400 K (limited by potential thermal depolarization of its piezoelectric legs).

A key feature of the STM system is its relatively unusual ability to iteratively perform STM and other surface analysis spectroscopies without losing sample temperature control and hence control over the adsorbate coverage and surface condition. The surface analysis techniques available include Auger electron spectroscopy (AES) using a single pass cylindrical mirror analyzer, and thermal programmed desorption (TPD) and laser initiated time-of-flight (TOF) spectroscopy using a twice differentially pumped quadrupole mass spectrometer. In the new proposal, the electron transfer chemistry of adsorbates will be examined by STM on a local scale and pulsed laser triggered TOF spectroscopy will be used to examine the adsorbate dynamics of ensembles of molecules. Importantly, the STM can be used to examine the condition of the surface before and after the laser irradiation leading to a particular TOF spectrum. In this manner, single molecule resolved information (e.g. are only molecules near alkali metal promoters or steps desorbed or dissociated?) can be related to dynamical information gleaned from the study of molecular ensembles.
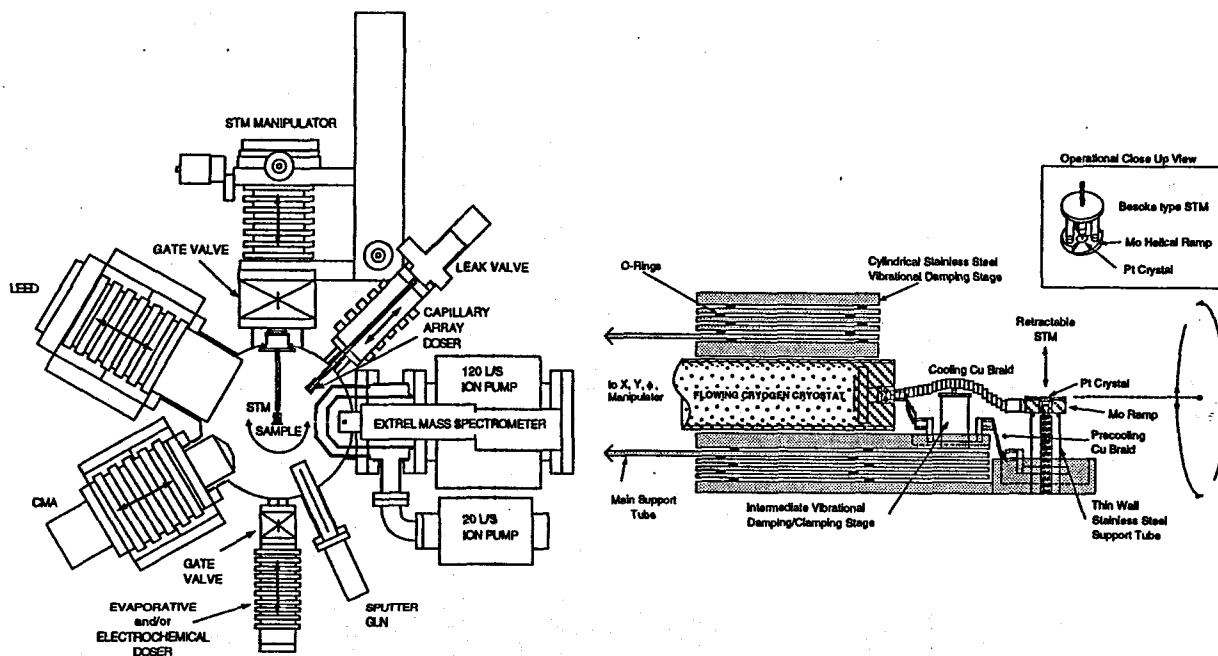

Fig. 1 (a) Cross-sectional view of the UHV system for scanning tunneling microscopy and surface photochemistry. An (x, y, φ) manipulator is used to position the sample towards different surface analysis/preparation stations. (b) Schematic view of the manipulator illustrating the key details relevant to sample cooling and vibrational isolation. Inset shows the STM in its operational position supported by the Mo ramp surrounding the 5 mm dia. sample.

Considerable effort was expended to achieve good STM performance at surface temperatures sufficiently low that thermal diffusion of adsorbates could be quenched. Our initial manipulator design utilized Comsa's idea that noise from a flowing cryogen cryostat could be adequately reduced by clamping the Cu braid to an intermediate heavy mass before coupling the braid to the sample, which itself was fixed to a heavy mass. Comsa accomplished this task using a long linear manipulator. We chose to implement his concept using a smaller manipulator that

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could rotate the sample as illustrated in Fig. 1(b). Our initial design had two stages of vibrational isolation for the sample using viton o-rings sandwiched between stainless steel floating cylinders. We later squeezed in 4 stages of vibrational isolation. Initially, our minimum sample temperature was limited to 35 K with liquid He cooling. We then added precooling "guard rings" which took some cooling from the radiation shield and distributed it to the lower third of the thin wall stainless steel tubes which supported the intermediate clamp of the Cu braid and the sample itself. With this last improvement we achieved sample temperatures of 15 K at 1.5 l/hour LHe flow rates. The crystal temperature was calibrated at low temperature by TPD of multilayers of rare gases. The low thermal drift and low vibration sensitivity intrinsic to the Besocke Beetle STM design coupled with our vibrationally isolated manipulator led to good overall STM performance. Below, are some examples of STM images that we've obtained.

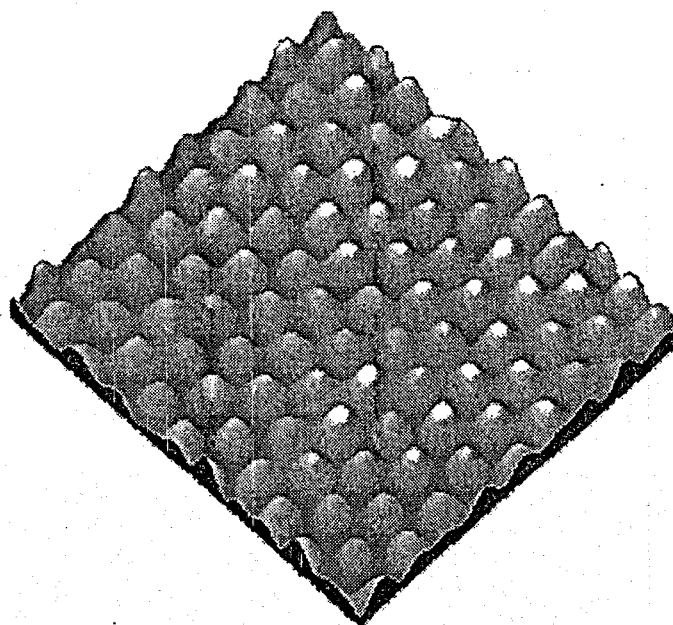**Examples of STM Images from Our Microscope**

Fig. 2 An atomically resolved image of a Pt(111) terrace for which the nearest neighbor spacing is 2.77 Å and the observed corrugation amplitude is 0.1 Å.
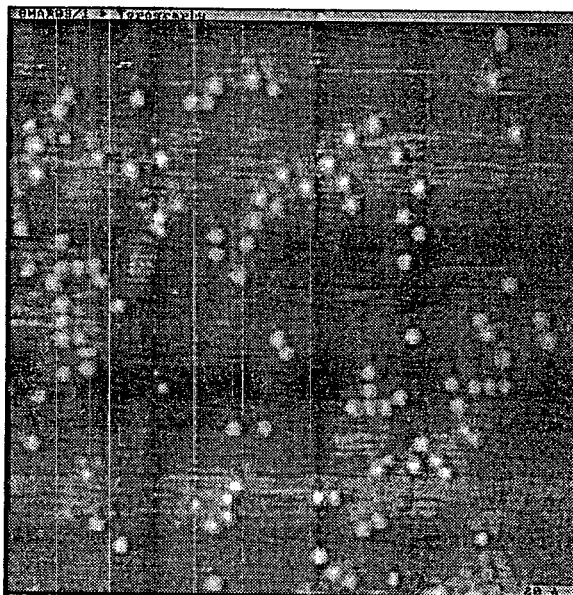
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Fig. 3 A 160 Å x 160 Å image of Br atoms on a 25 K Pt(111) surface following dissociative adsorption of Br$_2$ dosed by a solid state electrochemical cell. The Br coverage is θ_{Br} = 0.03 ML.[3]
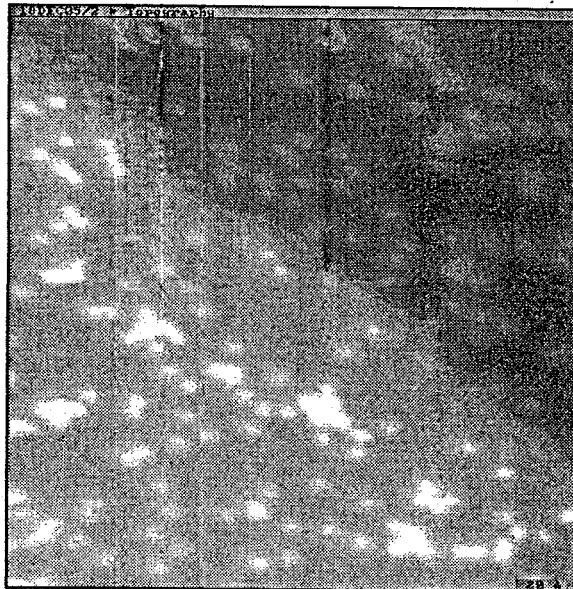

Fig. 4 A 160 x 160 Å image of CH$_3$Br molecules on a 36 K Pt(111) surface at θ_{CH3Br} = 0.08 ML. A step edge diagonally traverses the image.[6]
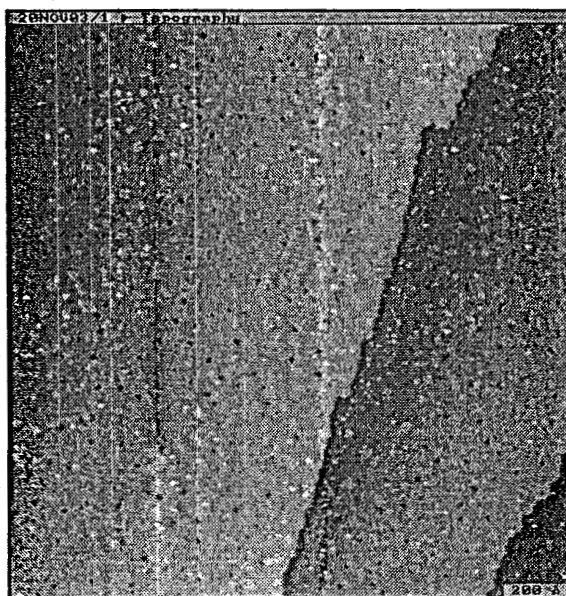
Fig. 5 A 640 Å x 640 Å image of a 0.25 ML Br covered Pt(111) surface after annealing for a minute at 500 K. Evidence of extensive mass transport across the surface can be seen. The black holes are vacancy islands, the larger white spots are Pt adatom islands and the grey islands are a PtBr$_x$ compound.[4]
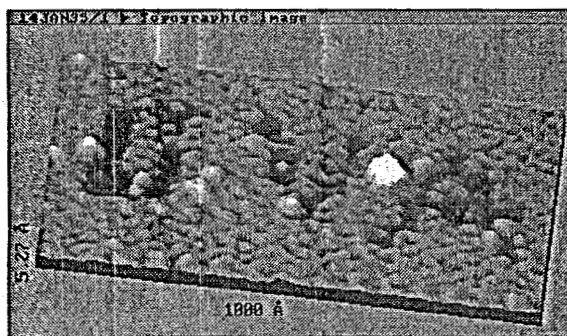

Fig. 6 An STM image of a CH$_3$Br covered Pt(111) surface at 90 K following electron induced nanolithography of "UVA" into the adsorbate layer. Earlier, STM tip electrons were used to dissociate the CH$_3$Br molecules at a substrate bias voltage of –2.5 eV. Imaging was done at a bias voltage of -19 mV and tunneling current of 1 nA.[7]

2. Bibliography

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