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# A low temperature scanning tunneling microscope designed for imaging molecular adsorbates

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**Abstract**

We report on the development of a low temperature scanning tunneling microscope (STM) used for imaging molecular adsorbates. The microscope operates near 85 K and features in situ tip and sample exchange. Cooling is accomplished via a clamping mechanism that provides a direct mechanical link between a liquid nitrogen dewar and the STM stage. During imaging, the clamping mechanism is released, and the STM stage is isolated from vibrations using a dual spring suspension system that incorporates magnetic eddy current damping. Additional isolation is provided by uncoupling the liquid nitrogen dewar from the vacuum chamber. We have used this STM to image benzene and carbon monoxide coadsorbed on the Pd (1 1 1) surface. The resulting acquired images show both the ordered arrangement and internal structure of the benzene molecules. Depending on the dosing conditions, three different ordered overlayer structures were formed, only one of which has been previously reported. Future plans include using the low temperature imaging capability of the STM to observe molecular binding sites, orientation, and tilt, as well as dynamical processes on the surface, such as chemical reactions. 

*Keywords:* Scanning tunneling microscope; Ultra high vacuum; Liquid nitrogen cooling; Benzene; Carbon monoxide; Palladium; Pd(111)

## 1. Introduction

Proximal probe techniques, such as scanning tunneling microscopy (STM), enable researchers to probe surface details that may elude other analysis methods. Since the first successful demonstration of STM, [1] many interesting structural and electronic surface properties on a variety of systems ranging from biological to chemical to physical have been elucidated. Each STM image represents a snapshot of the surface configuration during the time of image acquisition. While these images are useful for observing static information, dynamic information from a surface process, such as a chemical reaction, may be more difficult to determine. Often, several STM images are linked together to form a movie of the surface. While each image is still a snapshot, by viewing images sequentially, surface changes are more readily identified. In order for a movie to be a useful analysis tool, a limited number of changes must occur between each image in the movie. Therefore, it is desirable that the image acquisition time be comparable to the rate of the surface process. At room temperature, many chemical reactions proceed at rates greater than can be normally imaged. To alleviate this problem, either the image acquisition time needs to be greatly reduced, which may include changes to the entire data acquisition system, or the speed of the reaction needs to be slowed, which can be accomplished by operating at low temperatures.

Ultra high vacuum (UHV) low temperature STM's can be grouped into two general categories according to the cooling system employed, either active or passive. Active cooling is characterized by the sample being mechanically connected to the cooling during image acquisition [2–13]. Although a direct connection to the cooling system may result in a lower sample temperature, the risk of introducing mechanical vibrations from the cooling system is increased. Passive cooling is characterized by pressing the sample stage against a

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cold reservoir, but then removing any connections to the reservoir during imaging [14–17]. By removing any direct cooling connections, the sample is mechanically uncoupled from any vibrations that may exist in the cooling system. As a consequence of not having a direct cooling connection, passive cooling results in an inherently less stable sample temperature than active cooling.

Our low temperature STM falls into the passive cooling category and is cooled through a rigid mechanical connection between the STM stage and a liquid nitrogen ($LN_2$) dewar. Once the desired temperature is reached, the connection is released, and image acquisition begins. In this paper, we report on the design and implementation of our UHV low temperature STM. We also present images acquired with our low temperature STM on the system of chemisorbed benzene and carbon monoxide (CO) coadsorbed on the Pd (111) surface at 85 K.

## 2. Surface Analysis System

Our surface analysis system consists of two adjacent vacuum chambers, each with base pressure $8 \times 10$ [11] torr, separated by a gate valve. The analysis chamber is pumped by both turbomolecular and ion pumps and contains both low energy electron diffraction (LEED) optics and a cylindrical mirror analyzer for Auger electron spectroscopy (AES). These tools are used to provide information about the structure and chemical composition of the sample and adsorbate overlayer. In the analysis chamber, samples are mounted onto a manipulator that contains an integral $LN_2$ reservoir which is used to facilitate low temperature adsorption studies. The manipulator also is used to properly orient the samples for cleaning, AES, and LEED. Samples are cleaned by argon ion bombardment followed by annealing using electron beam bombardment with a barium oxide cathode as the electron source. A mass spectrometer mounted in this chamber is used to monitor gas dosing conditions.

Attached to the analysis chamber is a turbomolecular-pumped load lock system that uses a magnetically coupled linear transfer arm to allow the entry of both samples and tips into the vacuum system. Samples are moved from the transfer arm onto the manipulator using a wobble stick. Once prepared, samples and tips are transferred from the manipulator to the STM chamber via another magnetically coupled linear transfer arm. Vertically oriented samples and tips are transported on cylindrical stubs, [18] as in an earlier instrument [19]. The transfer arms, the manipulator, and the STM stage all have holes to accept the sample stubs. In the analysis chamber, the stubs are grasped with commercially available forks mounted on wobble sticks [18]. The adjoining chamber contains the $LN_2$ dewar and the low temperature STM.

## 3. Low temperature STM

A cross section of the complete low temperature STM system is shown in Fig. 1. An integral component of the entire system is a clamping mechanism [20] that serves a two-fold purpose. First, it is the key link in the thermal conduction path between the $LN_2$ dewar and the STM stage. Second, it also fixes the position of the STM stage during tip and sample exchange. The clamping mechanism is housed in the bottom end of the radiation shield and is actuated via a retractable rotary feedthrough. Closing the clamping mechanism on the copper conduction rods creates a mechanical link between the STM stage and the $LN_2$ dewar.

A detailed drawing of the clamping mechanism is shown in Fig. 2. The clamping mechanism consists of a pair of pivoting jaws, a movable cam, and an actuating

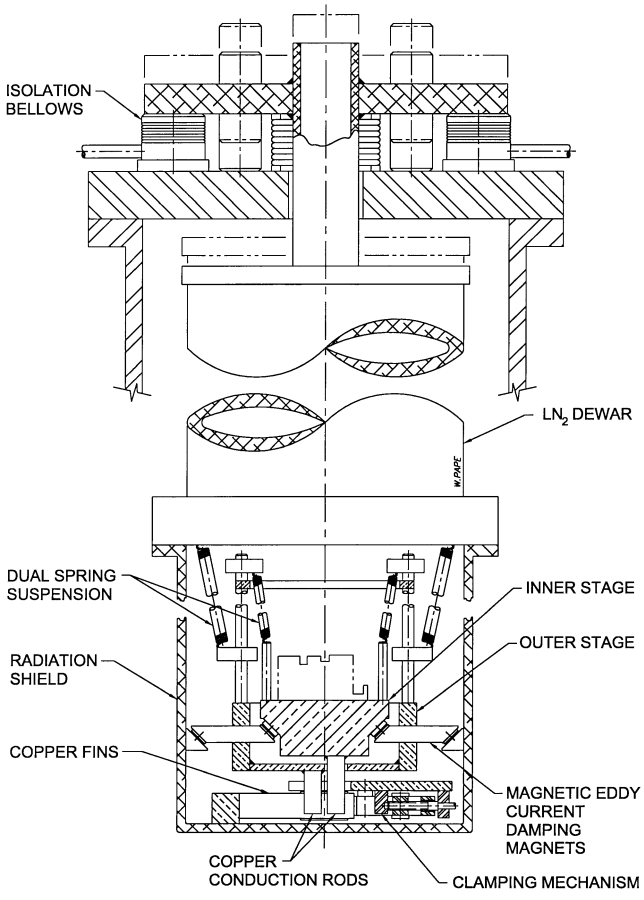


Fig. 1. A cross sectional view of the low temperature STM showing the arrangement of the STM stage, clamping mechanism, radiation shield, and $LN_2$ dewar. When actuated, the clamping mechanism provides a mechanical link between the $LN_2$ dewar and the STM stage. The $LN_2$ dewar can be uncoupled from the vacuum chamber by inflating the isolation bellows.

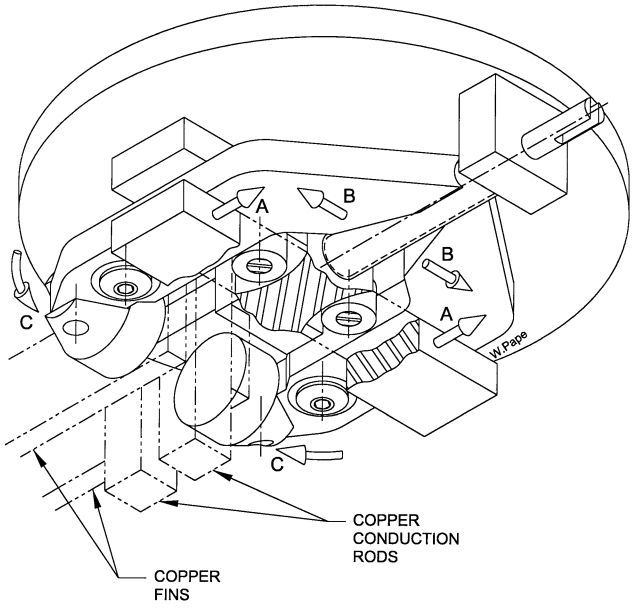


Fig. 2. The clamping mechanism, shown here with the bottom plate removed for clarity, is located in the bottom of the radiation shield. Turning the actuating screw causes a cam to move (A) which in turn causes the jaws to open at one end (B) and close at the opposite end (C). Pivoting pads on the jaws ensure good thermal contact between the copper fins and the copper conduction rods.

screw. As the actuating screw is turned, the cam is forced against the back of the jaws causing them to open. Since the jaws pivot, forcing the back of the jaws to open causes the front of the jaws to close. The jaws close on two flexible copper fins that press against two copper conduction rods. Pads on the end of the jaws ensure uniform force over a large area of the copper fins. An indium gasket is used in the connection between the copper fins and the radiation shield to improve thermal conduction. Turning the actuating screw in the opposite direction causes the cam to move towards the front of the jaws. As the cam moves forward, a compression spring positioned between the copper fins opens the jaws creating separation between the copper fins and the copper conduction rods.

Another component integral to the entire cooling system is the radiation shield that is constructed from a cylindrical aluminum tube (dimensions 4.6'' OD × 10'' length × 0.1875'' wall thickness) with a closed bottom and an open top. The top of the shield attaches directly to the bottom copper plate of the $LN_2$ dewar, and the shield completely surrounds the STM. An indium gasket is used between the copper dewar and the aluminum shield to ensure a good thermal connection. Thermal conduction through the shield is so great that the clamping mechanism reaches 77 K even though it is housed in the bottom end of the shield. Two aluminum sliding doors, which cover the sample and clamp access holes in the side of the shield, are actuated with a wobble stick.

Two separate copper pieces, an inner disk and an outer ring comprise the STM stage. Projecting from the bottom of each stage is a 0.25'' square copper conduction rod that terminates between the jaws of the clamping mechanism as shown in Fig. 2. When the clamp is actuated, a heat path is completed between the stages and the $LN_2$ dewar, passing through the copper conduction rods, the copper fins, and the aluminum radiation shield. By actuating the clamping mechanism with a retractable feedthrough, the cooling process is quicker and a lower temperature is attained because any conductive heat path between the stages and the vacuum chamber is eliminated. Also, the ability to retract the feedthrough after releasing the stages provides isolation from any mechanical vibrations that may be transmitted by the feedthrough.

An important consideration for any STM is mechanical vibration isolation, which is often achieved through spring suspension. A unique feature of our low temperature STM is that vibration isolation is not only accomplished through spring suspension, but also by isolating the $LN_2$ dewar from the vacuum chamber. As shown in Fig. 1, the STM stage is a two piece design with the outer stage suspended from springs connected to the $LN_2$ dewar and the inner stage suspended from springs attached to support posts mounted to the outer stage. By utilizing a dual spring suspension system, the effective length of each spring is increased without increasing the distance between the stage and the $LN_2$ dewar. Magnetic eddy current damping is used both between the inner and outer stages and between the outer stage and radiation shield. The $LN_2$ dewar, along with the radiation shield and the entire STM, is isolated from the vacuum chamber by inflating a set of three bellows located on the air side of the vacuum flange. All the components of the vibration isolation system, the dual spring stage, the magnetic eddy current damping, and the isolated $LN_2$ dewar, work in concert to minimize the transmission of mechanical vibrations to the STM.

A drawing of the STM stage is shown in Fig. 3. The STM has a single piezoelectric tube scanner [21] with dimensions of 0.125'' OD × 0.625'' length × 0.02'' wall thickness. As a consequence of the cooling design, the entire stage, including the scanner, nearly reaches liquid nitrogen temperature ($\sim$85 K). In this temperature regime, the scan range of the instrument is 0.75 μm in the Z direction and 2.25 μm in the X and Y directions. Tips are held in a small trough attached to the end of the tube scanner and are secured in the trough via a machine screw.[19] A wobble stick with a 0.06'' diameter wire attached to the end is used to move tips into and out of the trough and to manipulate the securing screw, providing in situ tip transfer. STM tips are fabricated by AC electrochemical etching of 0.01'' diameter tungsten wire in 1M KOH solution and then cleaned

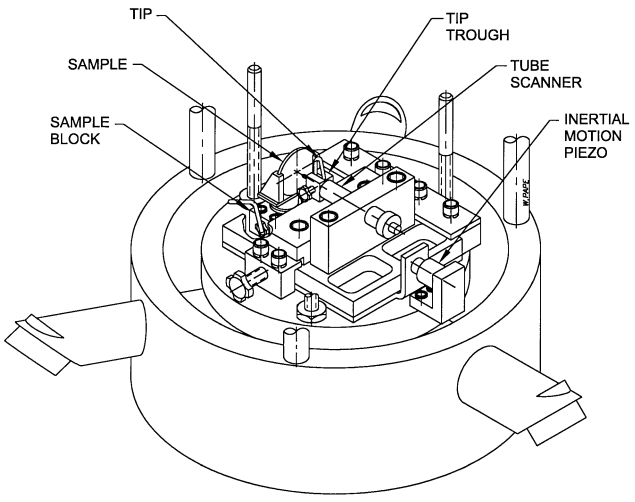


Fig. 3. The STM is constructed from a single tube scanner, featuring in situ tip exchange, mounted to an inertial sliding mechanism that provides motion in both the X and Z directions. Samples, tips, and securing screws are all manipulated with a wobble stick. The dual spring suspension system and the radiation shield are omitted for clarity.

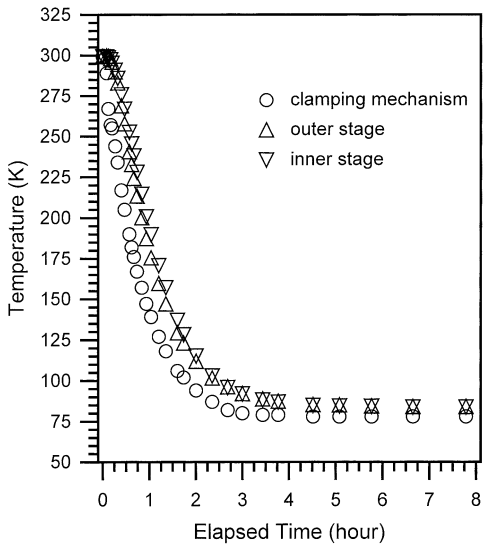


Fig. 4. Plot of temperature of various elements of the STM as a function of elapsed time during the cooling process. The entire system can be cooled from room temperature to $LN_2$ temperature in four hours. Temperatures are monitored by permanently mounted thermocouples. Maintaining the system at low temperatures for the duration of an experiment minimizes thermal cycling.

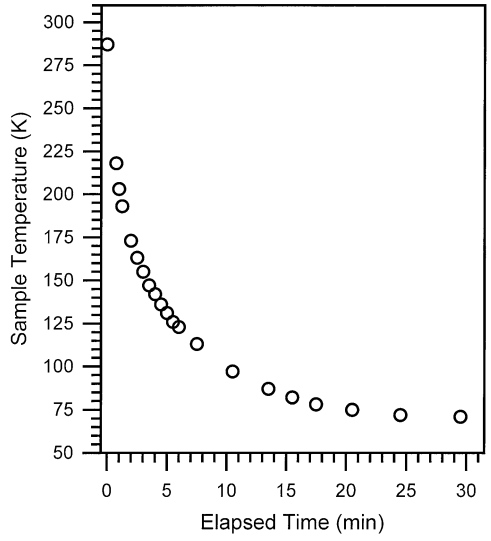


Fig. 5. Plot of sample temperature versus elapsed time for a room temperature sample placed onto the cold STM stage. The sample reaches low operating temperature in twenty minutes. Since it is not possible to directly attach a thermocouple to the sample, a temperature calibration between the sample and inner stage was completed prior to conducting the experiments.

in UHV by thermal desorption using the same electron beam source used for sample annealing. Cylindrical sample stubs are placed in a copper block that is electrically isolated from the inner stage by sapphire washers. Sapphire washers are chosen for this application because they exhibit high thermal conductivity at low temperatures. Another securing screw in the block, also actuated by the wobble stick, secures the sample stub in position.

The scanning piezoelectric element is mounted to an inertial sliding mechanism [22] that provides coarse motion in both the X and Z directions. The inertial sliding mechanism consists of a lower plate that rests on the inner stage and is connected to a piezoelectric tube (dimensions 0.25" OD × 0.375" length × 0.02" wall thickness) and an upper plate which is free to slide on the lower plate. Inertial walking is accomplished by driving the lower plate with a modified square wave. Typical parameters for the driving signal are 800 volts peak to peak at 160 Hz. The low temperature performance of the walker is approximately 150 nm per step, which translates to a speed of $\sim$1.5 mm per minute.

Cooling the entire system from room temperature takes four hours, as shown in Fig. 4. Once cooled, the 2.5 l $LN_2$ dewar maintains temperature for about fourteen hours, alleviating any need to refill the dewar during an experiment. When a room temperature sample is introduced onto a cold STM stage, the sample cools to its final temperature in approximately twenty minutes, as shown in Fig. 5. All temperature measurements are performed using type K thermocouples. Permanently mounted thermocouples monitor the temperatures of the clamping mechanism and the inner and outer stages. Since it is not practical to have a thermocouple mounted directly onto the movable sample holder, a calibration between the sample and inner stage temperatures was performed by temporarily mounting a thermocouple directly onto a sample holder. All thermocouple and electrical leads are thermally heat sunk to the $LN_2$ dewar before being attached to their respective electrical feedthroughs.

To prepare a sample for low temperature imaging, the door covering the sample access hole in the radiation shield is slid partially shut using the wobble stick. Next, the clamping mechanism is released, the actuating arm is withdrawn, and the door covering the clamp access hole is closed. At this point, the $LN_2$ dewar is uncoupled from the vacuum chamber by inflating the set of three bellows which effectively isolates the $LN_2$ dewar, and everything attached to the $LN_2$ dewar including the STM stage, from the vacuum chamber. An optical microscope is positioned to view the coarse tip approach through the sample access hole. Final tip approach and imaging are performed using commercial electronics [23]. While it is possible to image immediately after the approach, the instrument becomes more thermally stable by waiting approximately 30 minutes before imaging. Once the clamping mechanism is released and the sample access hole in the radiation shield is closed, the temperature of the sample rises at a rate of $\sim 1$ K per hour.

## 4. Experimental results

To test the performance of the STM, we desired to use a well known adsorbate structure that readily formed on Pd (111). The coadsorption of benzene and CO was a prime candidate because the system has been extensively studied [24,25]. We prepared our Pd (111) samples with repeated cycles of argon ion bombardment (3 μA sample current at 1 kV accelerating potential) followed by annealing at 950 °C, until AES was not able to detect a sulfur peak. Another cleaning cycle was performed after AES, and the sample was briefly annealed one final time before dosing. All gas dosing for this system was done at room temperature. The CO gas line was flushed, and several freeze, pump, thaw cycles were completed on the benzene to prepare for the dosing procedure. Gases were admitted through sapphire-sealed leak valves, and the coadsorbate structure was viewed by LEED during the dosing process. Once the dosing parameters for a particular coadsorbate structure were determined, samples destined for STM imaging were not exposed to the electron beams for LEED or AES before imaging.

By altering the dosing conditions of the CO and benzene, we determined that three different adsorbate structures could be formed. We observed the previously studied $3 \times 3$ structure, [24,25] as well as two new structures, a $(2\sqrt{3} \times 2\sqrt{3})R°30$ structure and a three domain rectangular structure. Fig. 6 is a low temperature STM image of the $(2\sqrt{3} \times 2\sqrt{3})R°30$ structure. The arrangement and structure of the benzene molecules is evident in the image. Both the $(2\sqrt{3} \times 2\sqrt{3})R°30$ structure and the $3 \times 3$ structure are made by initially dosing the Pd(111) surface with CO and then dosing CO and benzene together. The total benzene dose determines whether the $(2\sqrt{3} \times 2\sqrt{3})R°30$ structure or the $3 \times 3$ structure is formed on the CO covered surface. As benzene is adsorbed onto the CO covered surface, a $(2\sqrt{3} \times 2\sqrt{3})R°30$ pattern is initially observed with LEED, followed by coexistence of the $(2\sqrt{3} \times 2\sqrt{3})R°30$ pattern and the $3 \times 3$ pattern. As the surface is exposed to more benzene, the $(2\sqrt{3} \times 2\sqrt{3})R°30$ pattern begins to fade, and eventually only a sharp $3 \times 3$ pattern remains. A more detailed STM study of this phase transition will be published elsewhere [26].

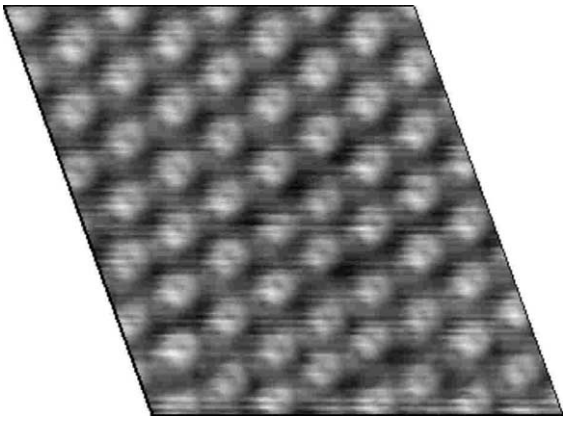

Fig. 6. A 75 Å × 75 Å STM image of the $(2\sqrt{3} \times 2\sqrt{3})R°30$ structure of CO and benzene coadsorbed on Pd (111). The ordered arrangement and internal ring-like structure of the benzene molecules is clearly evident in the image. The image was acquired at 95 K with imaging parameters of 0.7 nA tunneling current and 0.1 V sample bias. This structure is formed by initially dosing CO on a clean Pd (111) surface, followed by dosing CO and benzene together. The image has been corrected for thermal drift.

The three domain rectangular structure is made by initially dosing the Pd(111) surface with benzene and then dosing benzene and CO together. Fig. 7 is a low temperature STM image of the three domain rectangular structure. Three separate ordered domains can clearly be identified in the image.

## 5. Conclusion

We have described the development of our low temperature STM. The imaging capability has been demonstrated by displaying images showing molecular detail of an adsorbate system of CO and benzene on Pd (111). We observed two previously unpublished structures of this system, a $(2\sqrt{3} \times 2\sqrt{3})R°30$ structure and a three domain rectangular structure. We thank W. Pape for the instrument drawings. We acknowledge funding support from the National Science Foundation (CHE-95-20366, CHE-0111671) and the Campus Laboratory Collaboration Program of the University of California Office of the President. Acknowledgement is also made to the donors of the Petrollium Research Fund,

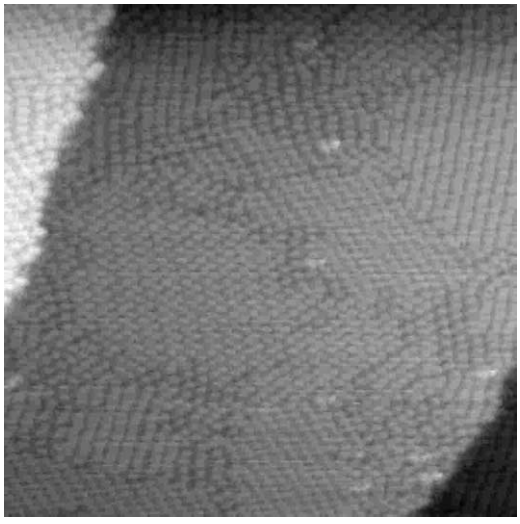

Fig. 7. A 250 Å × 250 Å STM image of the three domain rectangular structure of CO and benzene coadsorbed on Pd (111). The benzene molecules are tightly arranged within each domain, while the domain boundaries display disorder. The image was acquired at 100 K with imaging parameters of 0.5 nA tunneling current and 0.1 V sample bias. This structure is formed by initially dosing benzene on a clean Pd (111) surface, followed by dosing benzene and CO together.

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