Selective Bond Breaking of Single Iodobenzene Molecules with a Scanning Tunneling Microscope Tip

Saw-Wai Hla\textsuperscript{1,2,*}, Gerhard Meyer\textsuperscript{1,3}, Karl-Heinz Rieder\textsuperscript{1}

\textsuperscript{1} Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany.
\textsuperscript{2} Department of Physics & Astronomy, Ohio University, Athens, OH 45701, USA.
\textsuperscript{3} IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikan, Switzerland.

Controlled step-by-step dissociation of single iodobenzene molecules has been performed at Cu(111) step-edges using tunneling electrons from a scanning tunneling microscope (STM) tip at 12 K. We show that the threshold tunneling electron energies to break a single bond inside a polyatomic molecule can be determined by using I-V spectroscopy of single molecules. Electron energies of 1.5±0.1 eV are necessary to break the $\sigma_{\text{C-I}}$ bond. This selective bond breaking procedure is possible due to the inherent bond energy differences inside the molecule. It requires electron energies of 3.1±0.1 eV or higher to further disrupt the $\pi$ ring.

* Corresponding Author: Saw-Wai Hla,

Department of Physics & Astronomy, Ohio University, Clippinger Laboratories, Athens, OH 45701, USA. Tel: 740-593-1727, Fax: 740-593-0433, Email: hla@helios.phy.ohiou.edu, web: www.phy.ohiou.edu/~hla
Due to the advances in molecular manipulation techniques with a scanning tunneling microscope (STM) tip, construction of single molecules from basic molecular building blocks is now a reality [1]. One of the research goals in this STM manipulation field is assembling of man-made designer molecules on an individual basis. During the molecular assembling process, selective bond breaking of molecules to cut off unnecessary parts may involve in basic block preparation [2]. In this way active sites can be created in the molecules, which will later join with other designated blocks to construct a new desired molecule or a nano-device.

It is already established that tunneling electrons can be used to break molecular bonds [1-5]. Based on the electron energy, the STM-tip induced molecule dissociation process can be separated into the field emission and inelastic tunneling regimes. High electron energies (roughly above 3 eV) are used in the field emission regime, where the tip acts as an electron emission gun. Early examples of this kind include dissociation of B$_{10}$H$_{14}$ and O$_2$ molecules on Si(111) with high STM biases (≥ 4V and ≥6V respectively) [3,4]. The dissociation involving inelastic tunneling process --in which lower STM biases are used-- was demonstrated in the case of oxygen molecule dissociation on Pt(111) [5]. Further step in this direction is controlled dissociation of polyatomic molecules. The polyatomic dissociation using tunneling electrons is more complex than that of diatomic species such as O$_2$. This is because polyatomic molecules can have a variety of bonds and hence, the tunneling process may involve more than one bond.

In the present work, we have chosen single iodobenzene (C$_6$H$_5$I) molecules adsorbed on Cu(111) step-edges to perform selective bond-breaking experiment. The iodobenzene is used in a century old aromatic ring coupling mechanism known as
Ullmann reaction where Cu acts as a catalyst [6,7]. With iodine atom attached to the benzene ring, three different types of bonds, C-C, C-H and C-I, are concerned. Their bond strength ratio in the gas-phase is approximately 3:2:1, respectively. The carbon π bonds have the highest strength and the single σC-I bond has the lowest strength inside the molecule [8]. It is known that the iodobenzene adsorbs on Cu(111) with its π ring lying parallel to the surface. The iodobenzene binds to the substrate with both iodine and π interactions [9,10].

The experiment was carried out with a homebuilt UHV low temperature STM at a base pressure of ∼4 x 10⁻¹¹ Torr and at the sample temperature of ∼12K. A polycrystalline W tip was used throughout the experiment. The Cu(111) sample was cleaned by repeated cycles of neon ion sputtering followed by annealing to 800 K. The Aldrich 99% iodobenzene was first purified by several freeze-pump-thaw cycles with liquid nitrogen and then a minute amount of iodobenzene was deposited onto the Cu(111) sample. The substrate temperature during deposition was kept at ∼40 K to avoid thermal dissociation of the molecules. Only isolated molecules located at the lower part of the substrate straight step-edges were chosen for the experiment to ensure uniform molecule/substrate binding conditions.

The STM images of iodobenzene on Cu(111) show an asymmetric shape with a larger protrusion at one side (Fig. 1). The calculated STM images of iodobenzene on Cu(111) [11] reveal that this larger part is the location of iodine atom inside the molecule.

To measure the threshold tip-induced C-I bond breaking energy, we first use the standard dissociation procedure [1,5]. During this experiment, the STM-tip is positioned above the molecule for 30 seconds and the tunneling electrons are injected into the
molecule (Fig. 1a). The corresponding tunneling current is monitored during this period and the abrupt changes of the tunneling current can be associated with the molecule dissociation event (Fig. 1d). We used 1.2 nA tunneling current in all the dissociation attempts. Initially, the voltage pulse supplied from the tip to the molecule was fixed at 0.5 V. Then the STM voltage was changed to a fixed 0.6 V and the procedure was repeated. We continued this procedure by increasing the bias for 0.1 V step at each subsequent experiment until the bias was reached to 2 V. The dissociation of the molecule was observed when biases higher than 1.4 V were used. Fig 1b and 1c show STM images acquired before and after the dissociation of a C₆H₅I molecule. The phenyl (C₆H₅) appears as larger protrusion (Fig. 1c) and shows a roughly triangular shape, in accordance with the previous observations [1].

After confirming the minimum tunneling electron energy for the C-I bond-breaking as 1.4 eV, we used a second approach to directly measure the threshold bond-breaking energy. In this procedure, the STM-tip was positioned above the molecule with a fixed height as before. However, instead of using a fixed STM bias, the voltage was ramped between 0.5 to 2 V and the corresponding tunneling current was recorded. This process is similar to the I-V spectroscopy measurement. During this experiment, the STM bias was steadily increased by 5 mV intervals with the ramp speed of 5 mV/s. The resulting I-V spectrum shows a sudden drop of current at around 1.5 V (Fig. 1e). The STM image after this experiment shows that the iodobenzene has been separated into iodine and phenyl. We ascribe the current drop as caused by the C-I bond-breaking event.

In an inelastic tunneling process the tunneling electron energy is transferred to the molecule and this can lead to bond breaking if the transferred energy is sufficient. Since
the probability of the energy transfer exponentially decreases with increasing bond-
strengths [12], breaking of the weakest bond inside the iodo benzene, C-I, is by several
order of magnitude favored over the two and three times stronger bonds of C-H and C-C.
Therefore by gradually increasing the tunneling electron energy, the C-I bond is first
broken when the energy transfer exceeds its dissociation barrier. As soon as the molecule
dissociates, the resultant phenyl and iodine atom are displaced from the original location
of the molecule under the tip. As a result, the intensity of tunneling current passing
through the phenyl and iodine is decreased. This greatly reduces the probability for
further dissociation of phenyl. We did not observe additional fragmentation of phenyls in
100 repeated dissociation experiments of single iodo benzene molecules.

Figure 2a shows an STM image recorded during a dissociation of an iodo benzene
molecule. First, the tip scanned the upper part of the image and is stopped above the
molecule (at the location indicated by a black circle). The STM feedback system was
then terminated and the tip-sample voltage was gradually increased from 0.5 to 2 V while
the corresponding tunneling current was recorded. Then the tip continued to scan the
lower part of the image where the separation of phenyl and iodine is clearly observed.

After the iodine abstraction from the iodo benzene, the resultant phenyl and iodine
atom are separated by several Å apart along the step. Data accumulated from 100
dissociation events show that the favor distance between the iodine and phenyl after the
dissociation as 2.5 \(a_0\) (\(a_0 = 2.55\) Å; Cu nearest neighbor atomic site distance) except for a
few 3.5 and 4.5\(a_0\) separations. The probabilities to find the specific separation distances
are plotted in Fig. 2b. The STM images reveal that both iodine and phenyl usually adsorb
at the Cu step edge after the dissociation: no adsorbed fragments on the terrace were
found. Because the drift in our STM system at 12 K is less than 1 Å/ hr, we are able to measure the relative displacements of phenyl and iodine with respect to their original locations before dissociation. The observed data shows that the iodine displaces twice as much distance as the phenyl.

We also measured the threshold voltage to dissociate phenyl at the Cu step-edge using the same procedure as above. For this purpose, the tip was stationed above the phenyl and then the STM bias was ramped from 0.2 to 4.8 V. As shown in the Fig. 3a, a sudden change of tunneling current occurs at 3.01 V that is associated with the fragmentation of phenyl as confirmed by STM imaging. This value is in good agreement with 2.9±0.1 V used for the STM-tip induced dissociation of benzene on Cu(110) [13]. The I-V curve of phenyl dissociation (Fig. 3a) includes additional features showing up as rapid fluctuations of the tunneling current between 1.9 to 3.1 V. Part of the curve (indicated by a rectangle box in Fig. 3a) is enlarged in Fig 3b. This behavior is attributed to changes of the position of the $\pi$ ring between the surface parallel and tilted geometry as illustrated in Fig. 3c. It is known that phenyl binds on the Cu(111) terrace with $\pi$ ring tilted ~ 43 degree from the surface plane [9]. This tilting is due to the binding of the free carbon atom of phenyl and a substrate Cu atom. At the Cu step-edge, such tilted geometry is initially not favored because the step Cu atoms are readily available for the binding of phenyl. However, when the phenyl is excited with the inelastic tunneling electrons under the STM-tip, such position changes can occur. Changes of molecule adsorption geometry due to inelastic excitation of tunneling electrons have also been observed in a number of experiments, such as molecule rotation [14,15].
Fig 4 illustrates a step-by-step dissociation sequence. An iodobenzene adsorbed at Cu(111) lower-step edge was dissociated into phenyl and iodine using the I-V spectroscopy dissociation scheme described above (Fig. 4a and b). In order to verify the identities of iodine and phenyl, we again used the tip-induced dissociation. First, the phenyl and iodine were further separated (Fig. 4b and 4c) by using lateral manipulation with the STM-tip to ensure injection of tunneling electrons only into a single fragment [1]. The tip-adsorbate attractive interactions are used in this relocation process. Then the I-V spectroscopy dissociation procedure was performed over each fragment. In this process, the STM bias was ramped from 0.5 to 6 V. The iodine should not be able to dissociate since it is a single atom. As expected, no fragmentation was observed on the feature assigned as the iodine atom even the tunneling voltage exceeds 6 V. The phenyl was dissociated when the bias reached to 3 V (Fig. 4c and 4d).

In summary, we report a relatively easy procedure to determine the threshold tunneling electron energy to selectively break molecular bonds within a poly-atomic molecule. The lesson of this experiment is that by choosing a proper molecule/substrate system, selective bond breaking can be performed using the STM-tip. By selecting various initial molecules, experimentalists will be able to produce different molecular fragments on an individual basis in a controlled manner for single molecule syntheses or various other STM experiments.

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References:

Figure Captions:

Figure 1. Selective bond breaking of single iodobenzene molecule at a Cu(111) step-edge. (a) Schematic illustration of the STM-tip induced bond breaking procedure. (b) An adsorbed iodobenzene molecule at lower part of a Cu(111) step-edge appears as an asymmetric shape with a larger bump at the right side which is contributed by the iodine atom of the molecule. (c) After breaking the C-I bond of the iodobenzene, both the resultant phenyl (larger protrusion with roughly a triangular shape) and iodine are adsorbed at the Cu step-edge. (d) The tunneling current signal recorded during this dissociation procedure shows an abrupt drop which is caused by the C-I bond breaking event. (e) Single molecule I-V spectroscopy curve of an iodobenzene showing the abrupt decrease in tunneling current at ~1.5 V caused by the C-I bond breaking event.

Figure 2. (Color) Fragment distribution. (a) A background subtracted STM image recorded before (upper part) and after (lower part) the dissociation process reveals the relative positions of iodobenzene, phenyl and iodine. The black circle over the molecule shows the tip position during electron injection to the molecule. (b) The distance between the phenyl and iodine after dissociation of 100 iodobenzene single molecules shows that about 80% of the fragments are 2.5 a₀ apart. (a₀ = Cu nearest neighbor atomic distance). Note: the phenyl appears larger after dissociation. (High to low intensity: red-blue-green)

Figure 3. Dissociation of phenyl. (a) An I-V spectroscopy curve of phenyl reveals dissociation of phenyl at 3.01 V threshold tunneling voltage. The current fluctuations
between 1.889 and 3.01 V (inset in (a) enlarged in (b)) are attributed to the changing of \( \pi \) ring positions between surface parallel and tilted geometry (c).

**Figure 4.** Step-by-step dissociation sequence. (a) An adsorbed iodobenzene at a lower part of Cu(111) step-edge. After breaking the C-I bond (b), the phenyl and iodine are further separated by using lateral manipulation with the STM-tip (c). The phenyl in (c) (indicated with an arrow) is then further fragmented by I-V spectroscopy dissociation scheme (d). The resultant fragments include protrusion and depression regions.
Fig. 1
Fig. 2
Fig. 3