

Role of chain length on the surface chemistry of dienes studied by scanning tunneling microscopy

D. Shachal, Y. Manassen, and E. Ter-Ovanesyan

Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel

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The scanning tunneling microscope has been used to observe sites selection of diene molecules on Si(111) 7×7 as a function of their chain length. The molecules 1,6-heptadiene and 1,7-octadiene can chemisorb on either of three geometries on the surface. The different relative affinity of the molecules to these sites is explained by matching between the molecules length and the surface sites. For 1,13-tetradecadiene, each end of the molecule reacts with a different half of the unit cell. [S0163-1829(97)05315-0]

The emergence of the scanning tunneling microscope (STM) has opened the opportunity to study the adsorption of molecules on well-defined surfaces with atomic resolution. In works that have been made to date on atomically resolved surfaces, small molecules with a single reacting group were studied.¹⁻⁶ In these kind of surface reactions, only the reactivity of the functional group with respect to the different binding sites on the surface is affecting the chemical reaction. However, for almost all surface chemical reactions existing in nature, from catalysis to cell recognition, much more complex molecules are involved. Their reaction is sensitive to the structure of the molecules and their matching to the binding sites. It is tempting to use the STM to address such questions. In this work, we try to confront this issue by studying bifunctional molecules reacting with two surface sites. The parameter being changed related to the molecular structure is the length of the aliphatic chain separating the two reacting groups. Since a reaction induces a change in the local density of states (LDOS) of the surface, an adsorbed bifunctional molecule will appear as a pair of reacted sites separated by a typical distance. As the atomic resolution of the surface is retained, the specific adsorption sites can be identified and insight is gained to the binding geometries and chemistry on the surface as a function of the molecule length. As a prototype, three different diene molecules were adsorbed on a Si(111) 7×7 surface.

The 7×7 reconstruction has been extensively studied and possesses chemical richness and diversity. The unit cell due to the surface stacking fault can be divided into two subunits, the faulted and unfaulted halves. The available reacted sites, the dangling bonds, are either adatoms that are located at the outermost layer or the rest atoms located at the second layer. Two types of adatoms exist, a center and a corner adatom. While a corner adatom has a single adjacent rest atom, each center adatom has two adjacent rest atoms (Fig. 1). This difference in number of available adjacent rest atoms gives rise to different chemistry for center and corner adatoms in reactions involving both adatoms and rest atoms. A variety of molecules react with the Si(111) 7×7 surface.⁸ In particular, ethylene adsorbs nondissociatively at room temperature. High-resolution electron energy-loss spectroscopy studies showed that the molecule is bi- σ bonded: the double bond breaks to form two Si-C bonds.⁹ Piancastelli *et al.*, using tunneling spectroscopy, proposed that ethylene is bonded to

a pair of adjacent Si adatom-rest atom.⁴

The carbon-carbon double bond is used as our reacting group at each end of the molecule. Three molecules were studied: 1,6-heptadiene and 1,7-octadiene were chosen to fit the distance between adjacent adatoms, 1,13-tetradecadiene was chosen to fit the distance between next-nearest-neighboring adatoms (Fig. 1). The floppy aliphatic chain, a saturated hydrocarbon having a closed shell, is not expected

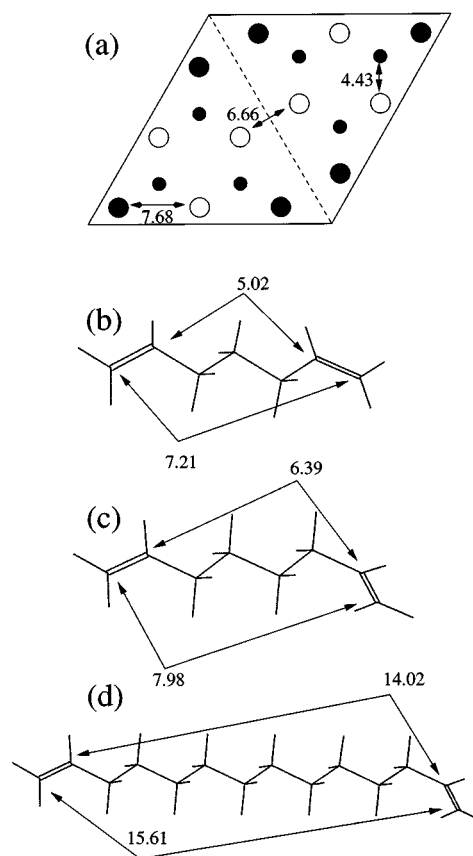


FIG. 1. (a) A unit cell of Si(111) 7×7 showing the different adsorption sites: center adatoms (open circles), corner adatoms (large solid circles), and rest atoms (small circles). (b) 1,6-heptadiene. (c) 1,7-octadiene. (d) 1,13-tetradecadiene. All distances are in Å. The distances between the two double bonds of the molecules were calculated by a force-field calculation software (Ref. 7).

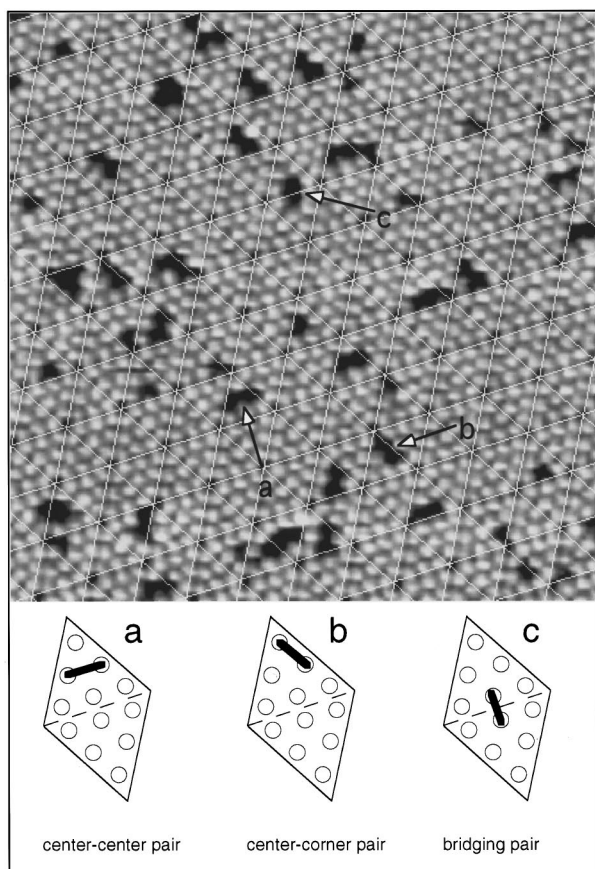


FIG. 2. Adsorbed molecules of 1,7-octadiene on Si(111) 7×7 (top). Lines intersecting the unit cells are drawn for clarity. The three different possible pairs of reacted adatoms are marked and shown schematically (bottom).

to react with the surface^{8,10} but provides the double bonds with some limited freedom for accommodation to the surface sites.

The experiments were carried out under UHV (base pressure 2×10^{-10} Torr). The *n*-type Si(111) wafer was out-gassed overnight and flashed to 1000 °C in order to remove the oxide layer. After an hour, either 1,6-heptadiene (Aldrich 99%), 1,7-octadiene (Fluka 97%), or 1,13-tetradecadiene (Aldrich 90%) were dosed through a leak valve from a gas manifold. Typically, imaging began 3 h after the flash. The images shown were taken at sample bias +2 V and tunneling current of 1 nA. Figure 2 is an image of a Si(111) 7×7 surface that has been exposed to 1,7-octadiene. The atomically resolved surface exhibits reacted sites that appear dark. In the experiments to be described, typically 10% of the adatoms have reacted. A closer look at 373 reacted adatoms reveals that 60% of them form isolated pairs of nearest-neighbor dark adatoms. The remaining are individual dark-reacted adatoms and very few islands composed of more than two reacted adatoms. In order to understand the meaning of this large number of isolated pairs, a simulation was conducted. It consisted of randomly picking adatoms on a 7×7 surface with a probability of 10% and counting the number of isolated pairs of nearest neighbors. The result, 15% implies that the high concentration of pairs found experimentally cannot be accounted for by a random distribution of defects or impurities and therefore is identified as

adsorbed reacted molecules. Adsorbate-adsorbate interactions may play a role at this high coverage. However, as seen from the images, most of the pairs are isolated and separated from neighboring reacted pairs by at least a unit cell. At these distances, the interaction between two saturated hydrocarbons is small compared to the adsorption energy of a chemically bonded molecule. Different pairs are seen in the image: the center-center adatom pair, the center-corner adatom pair, and a pair that will be referred as a bridging pair consisting of adjacent center adatoms from two different halves of the unit cell (bottom of Fig. 2). The different pairs can be oriented in three directions reflecting the threefold symmetry of the surface.

A detailed statistics of 224 isolated pairs reveals 174 pairs in the faulted half, 43 in the unfaulted half, and 7 bridging pairs. The higher reactivity of the faulted half was shown for other molecules^{4,11} and is explained by a higher density of states in the faulted half. There are 129 center-center and 45 center-corner pairs in the faulted half implying a ratio of about 3:1. A similar ratio (32:11) is found for the unfaulted pairs. The number of bridging pairs is not sufficient for qualitative analysis.

Figure 3 is an image of a surface exposed to 1,6-heptadiene. As for 1,7-octadiene, the chemisorbed molecules are seen as pairs of reacted adjacent adatoms. Statistics of 504 isolated pairs reveals 421 pairs in the faulted half, 73 pairs in the unfaulted half, and 10 bridging pairs. There are 368 center-center and 53 center-corner pairs in the faulted half, implying a ratio of about 7:1. In the following we will try to relate these different ratios to the chemistry of the molecules and the surface.

The different probability of finding either pairs may be attributed to three factors: First, the steric matching between the molecules and the surface sites giving rise to different adsorption energies. Second, a possible reactivity difference between center and corner adatoms. Third, the number of possible configurations for each pair. Although the images reveal only the reacted adatoms, it is assumed that as was found for ethylene, each double bond reacts with an adatom and an adjacent rest atom. One should consider the number of possible combinations of adatoms–rest atoms that can give rise to a center-center adatom pair and a center-corner adatom pair.

Since the only difference between the two molecules is an addition of a carbon atom to the chain, we believe that the factor affecting the different ratios for the two molecules is the relative adsorption energies of the molecules to the surface sites due to the steric matching. Three combinations of nearest-neighbor adatom–rest atom pairs can react with the two double bonds of each molecule as illustrated in Fig. 3. They differ in the distance separating the two adatom–rest atom pairs. In principle, for each of these combinations the molecule can assume four adsorption geometries because the primary carbons at the two ends of the molecule can react with either an adatom or a rest atom. A knowledge of the relative adsorption energies of the two molecules to the different sites may elucidate the experimental observations.

Imaging bifunctional molecules can be extended to even larger molecules, for example 1,13-tetradecadiene as seen in Fig. 4. The image reveals pairs of reacted adatoms separated by an unreacted adatom. The size of the long molecule im-

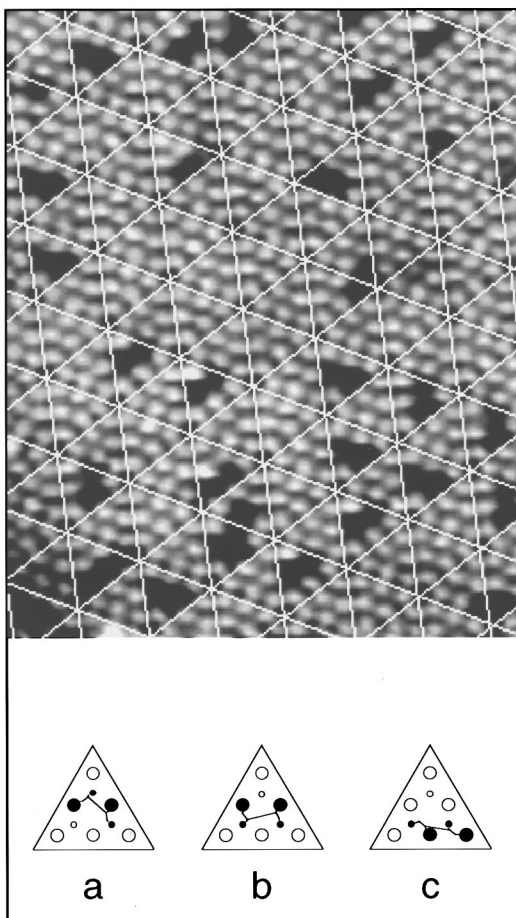


FIG. 3. Adsorbed molecules of 1,6-heptadiene on Si(111) 7×7 (top). Lines intersecting the unit cells are drawn for clarity (bottom). The possible combinations of adatom–rest atom pairs (solid circles) giving rise to bonding with the two double bonds of either 1,6-heptadiene or 1,7-octadiene, for two reacted center adatoms [(a),(b)] and for reacted center-corner adatoms. A line representing the aliphatic chain connects the two pairs of carbon atoms.

poses reaction with one end of the molecule situated in the faulted half and the other end in the unfaulted half of the 7×7 unit cell. Two possible combinations of adatoms are seen in the image. Statistics of 196 molecules reveals a preference (111 molecules) towards the next-nearest-neighbor center-center adatom pair. The fact that an adatom is clearly imaged between the two reacted adatoms, demonstrates that the change in the LDOS is due to the reaction with the two double bonds and not due to the aliphatic chain. This also supports the interpretation given for the two shorter molecules, identifying a pair of reacted nearest-neighbor adatoms with adsorption sites of each end of the molecule. Although the difference in reactivity between the two halves cannot be distinguished in the final product, based on the adsorption of the shorter diene molecules, one can assume that adsorption is likely to occur with one of the double bonds of the molecule first reacting with the more reactive faulted half followed by the second double bond reacting with the unfaulted half.

Several features are common for the diene molecules. The reacted sites appear as dark spots, which is common for other

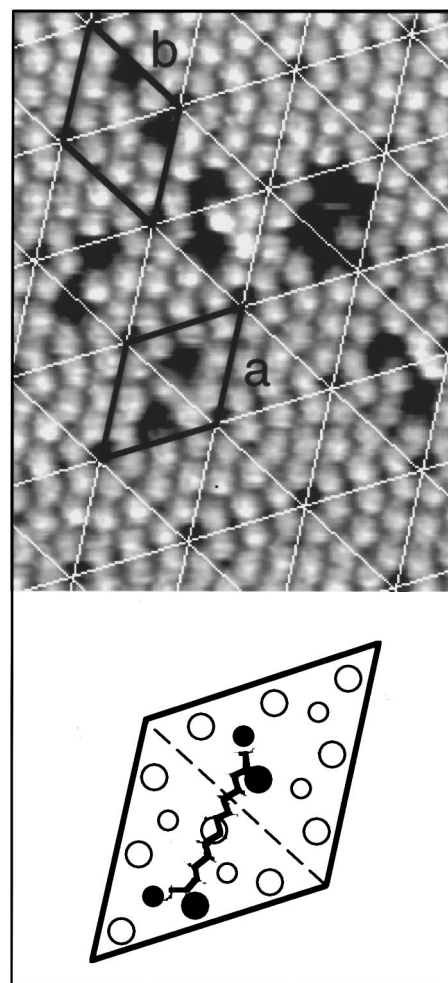


FIG. 4. Adsorbed molecules of 1,13-tetradecadiene on Si(111) 7×7 (top). Lines intersecting the unit cells are drawn for clarity. Two unit cells are outlined showing the two possible combinations of reacted adatoms: next-nearest center-center pair (a) and next-nearest center-corner pair (b). Schematic diagram representing molecule (a) in the image (bottom). The molecule and the unit cell are shown on the same scale. The reacted adatoms and rest atoms are solid filled symbols.

small molecules studied on Si(111) 7×7 : NH_3 (Ref. 1), H_2O (Ref. 3), and C_2H_2 (Ref. 4). This is attributed to a net reduction in local density of states. The origin of spots that do not correspond to the molecular length might be due to molecules that bind with only a single end and contaminants, most likely oxygen present in the gas manifold. The aliphatic skeleton is not seen in the images. The energy levels of a long aliphatic chain are much lower than the Fermi level of Si and therefore do not contribute to the tunneling current.

In summary, 1,6-heptadiene, 1,7-octadiene, and 1,13-tetradecadiene were imaged on a Si(111) 7×7 surface. The ends of the molecules, which are chemically bonded, are seen as dark protrusions on top of an atomically resolved surface. Adsorption geometries of individual molecules are assigned and scaled according to their interaction with the surface. This is the first time, to our knowledge that adsorption of such large molecules are studied with this level of detail. Future studies of other molecules may reveal other

structural related affects on the molecule-surface chemistry, for example, molecules with two different reacting groups to study the competition between the two groups or molecules with a bulky nonreacting group in the aliphatic chain to study the affect of steric hinderance.

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