Saturated Hydrocarbons on Silicon: Quantifying Desorption with Scanning Tunneling Microscopy and Quantum Theory

N. L. Yoder, N. P. Guisinger, and M. C. Hersam
Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, IL 60208-3108

R. Jorn, C.-C. Kaun, and T. Seideman
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113

Electron stimulated desorption of cyclopentene from the Si(100)-2x1 surface is studied experimentally with cryogenic UHV STM and theoretically with transport, electronic structure, and dynamical calculations. Unexpectedly for a saturated hydrocarbon on silicon, desorption is observed at bias magnitudes as low as 2.5 V, albeit the desorption yields are a factor of 500 to 1000 lower than previously reported for unsaturated molecules on silicon. The low threshold voltage for desorption can be attributed to hybridization of the molecule with the silicon surface, which results in low-lying ionic resonances within 2-3 eV of the Fermi level. These resonances are long-lived, spatially localized and displaced in equilibrium with respect to the neutral state, resulting, upon excitation, in symmetric (positive ion) or asymmetric (negative ion) motion of the silicon dimer atoms. This study highlights the importance of nuclear dynamics in silicon-based molecular electronics and suggests new guidelines for the control of such dynamics.

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The scanning tunneling microscope (STM) has progressed beyond basic imaging of surfaces to become a tool for manipulating single atoms and molecules. Examples include reversible vertical switching 1, lateral displacement 2-5, rotation 6, dissociation 5, and desorption 6-8. These new experimental techniques, combined with related theoretical studies 8-10, have enabled detailed understanding of fundamental physical processes at interfaces. In the emerging field of molecular electronics 11-14, significant experimental and theoretical effort has been invested into studying the electronic properties of single molecules, molecular nanostructures, and organic monolayers. A subfield of increasing interest is the integration of molecular electronic devices with conventional silicon microelectronic technology 17-20. A detailed understanding of both the electronic properties and the stability of organic molecules on semiconductors must be established, however, before reliable devices can be realized. On the one hand, it is relevant to develop general guidelines for molecules that will provide stable devices. In particular, it is widely believed that saturated organic/silicon systems offer stability with respect to current-induced failure of silicon-based molecular electronics 20. It is thus of both fundamental and practical importance to explore the extent to which this expectation holds true. On the other hand, it is desirable to explore systems that will provide dynamical function, such as current-driven molecular machines 3, switches or rectifiers 11. Previous work has illustrated the suitability of STM experiments, combined with structural and dynamical calculations, to address both questions 6, 7.

In this Letter, we study the desorption of cyclopentene from a silicon surface using the combination of STM measurements, electronic structure theory, quantum transport, and dynamical calculations. The efficiency of the desorption process is characterized by the yield, which is found to be a factor of 500–1000 lower than for benzene/Si(100) 8, 10 or chlorobenzene/Si(111) - 7x7 21. Measurements of the desorption yield for sample bias voltages from -5 V to +5 V show a clear turn-on behavior, with asymmetric threshold voltages. Yield measurements as a function of tunneling current strongly suggest that the desorption mechanism is a single electron process, resulting from transient excitation of a resonant state. Quantum transport theory, along with electronic structure and dynamical calculations give insight into the nature of the resonances and the associated nuclear dynamics.

Experiments were performed using a cryogenic, variable temperature ultra-high vacuum (UHV) STM 25 operating at 80 K, and heavily boron doped Si(100) substrates (ρ < 0.005 Ω-cm). Details of the experimental procedure for producing a submonolayer coverage of cyclopentene on the clean Si(100)-2x1 surface are given elsewhere 20. A quantitative measure of the desorption yield was obtained within a 3-step statistical approach. The surface is initially imaged at non-perturbative current conditions in order to induce desorption. Finally, the same area is scanned at elevated sample bias and/or tunneling current conditions in order to induce desorption. The yield (events/electron) is given by Y = N_D*(e/I*t), where N_D is the number of desorption events, I is the tunneling current, and t is the time.
FIG. 1: (color online). Desorption yield as a function of the sample bias between -5 V and 5 V (I = 2 nA). (inset) STM images of cyclopentene on Si(100)-2x1 before and after desorption. The desorption of cyclopentene usually leaves behind a clean silicon dimer (blue circles), but occasionally results in an apparent depression in place of the molecule (a red circle). For the purposes of this study, we have treated both cases as a desorption event.

current, e is the electronic charge, and t is the total time the tip spent over a molecule. Overcounting of the electrons (since the current continues to flow after desorption occurs) is corrected using first-order kinetics [27].

The electronic transport was computed ab initio within a non-equilibrium Green’s function approach [28], using a density functional theory (DFT) Hamiltonian expanded in a real-space basis with atomic cores defined by pseudopotentials. This formulation allows for proper description of the electronic properties through the use of an extended (open boundary) representation of both the tip and the substrate, extending to infinity in the vertical direction and, for the surface, including periodic boundary conditions in the lateral directions. The electronic structure calculations were carried out using DFT with the B3LYP functional and both 6-31G* and 6-311G** basis sets within Q-Chem [29].

The adsorption of cyclopentene on silicon substrates has been studied experimentally [30, 31] and computationally [32], and has been explained by a [2 + 2] cycloaddition reaction between the C=C bond of the cyclopentene and a silicon dimer, resulting in the formation of two covalent Si-C bonds. In STM images, cyclopentene molecules appear as protrusions centered on the silicon dimer row, as shown in Fig. 1 (inset). The desorption yield given in Fig. 1 shows that desorption occurs over a wide range of negative and positive bias voltages, and is strongly voltage-dependent, with the yield increasing exponentially after a threshold voltage is reached. A yield of 1x10^{-12} is the practical lower-limit for desorption measurements and is thus used to define the threshold voltage. We find asymmetric behavior, with a threshold voltage of -2.5 V at negative, and 3.5 V at positive sample bias. The dramatic sensitivity of the desorption yield to the sample bias rules out the possibility of an electric field-induced desorption (often difficult to distinguish from other mechanisms in STM experiments), suggesting an electronic mechanism. Measurements of the desorption rate (determined as the ratio of the desorption yield and the tunneling current) versus the tunneling current found very weak dependence of the rate on the current in the 0.1–2 nA range at -5 V sample bias. This approximately linear dependence rules out the possibility of a “vibrational heating” multiple-electron process, indicating that the desorption of cyclopentene occurs via a single-electron resonant process.

Several previous desorption studies [8, 10, 24] of organic molecules on silicon report threshold voltages (1-3 V) similar to those reported here, and describe the desorption mechanism in terms of a charge carrier resonance tunneling event. The presence of π-character in organic molecules bound to silicon gives rise to low-lying ionic resonances within a few eV of the Fermi level. Scattering via these resonances transiently promotes the molecule to an ionic potential energy surface on which the nuclei evolve subject to a finite lifetime. Provided that the equilibrium configurations of the resonance and neutral states differ appreciably, the molecule will attempt to relax while in the charged state, resulting in dynamics on the ionic surface [30]. As a result, subsequent to the resonance tunneling event, the molecule can be placed in an excited configuration on the neutral surface, resulting in further dynamics such as bond breaking and desorption.

Cyclopentene is believed to be stable toward such resonance processes since it does not retain π-orbital character upon chemisorption to the clean Si(100)-2x1 surface, and is therefore expected to lack resonances sufficiently close to the Fermi level to trigger desorption. The observation of desorption at both bias polarities over a wide range of sample biases and tunneling currents suggests the existence of a new avenue for resonance-mediated dynamics, which is of fundamental interest and may also be of technological relevance to the search for stable constructs. The desorption yield of cyclopentene from Si(100), ranging from 2x10^{-12} to 1x10^{-8} events/electron, is between 500 and 1000 times smaller than the reported yields for benzene on Si(100)-2x1 [8] or chlorobenzene on Si(111)-7x7 [24], suggesting significant differences in the desorption dynamics following resonant excitation.

To understand the desorption mechanism and explore its generality and implications, we applied a combination of ab-initio transport, structural, and dynamical calcula-
To complete our analysis of the resonance states and understand the low desorption yield observed, we computed the lifetimes of the ionic resonances. In the case of isolated resonances, relevant here, these can be extracted from fitting the PDOS to a Lorentzian form. The obtained lifetimes of the HOMO and LUMO are 94 fs and 257 fs, respectively. These long lifetimes allow for significant evolution of the vibrational modes in the ionic state and hence substantial transfer of electronic energy into vibrational excitation in the course of the tunneling event, enabling desorption. At the same time, the long lifetime implies that only a small fraction of the current is mediated via the resonance features. Expressing the desorption rate as an (energy integrated) product of a desorption probability per resonance event multiplied by the rate of electron transport through the resonance, one finds that the narrow features translate into low reaction rates, consistent with our observations.

In order to investigate the nature of the nuclear motion following the charge transfer event, we proceeded with a DFT study of the reaction dynamics within a cyclopentene-SiH12 model. Previous work has shown that, for the electronically localized case of a small organic molecule on Si(100), a cluster of this size suffices to capture the physics while being computationally accessible. Interestingly, as shown in Fig. 3, both ionic equilibrium geometries are markedly displaced with...
FIG. 3: (color online). Optimized equilibrium geometries of cyclopentene on a Si$_9$H$_{12}$ cluster: (a) neutral molecule geometry, (b) positive ion geometry, and (c) negative ion geometry.

with our observation that the desorption yields for cyclopentene are a factor of 500–1000 smaller than those reported for benzene.

In summary, the combination of cryogenic ultra-high vacuum STM measurements, with ab-initio transport, electronic structure, and dynamical calculations illustrate the possibility of desorbing fully saturated organic molecules from Si(100) at modest sample biases and provide a detailed picture of the desorption mechanism. Desorption occurs via resonance attachment of a hole/electron to the HOMO/LUMO of the substrate-adsorbate system. A key to the feasibility of such desorption events is strong hybridization of the molecule with the silicon substrate, which gives rise to new orbitals that are energetically remote from, and bear no resemblance to the orbitals of the isolated molecule. Such previously unexplored desorption pathways carry interesting implications both to the development of guidelines for the construction of stable (current-immune) silicon-based molecular electronics, and to the prospect of designing current-driven molecular devices.

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* Electronic address: m-hersam@northwestern.edu
† Electronic address: t-seideman@northwestern.edu

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