Inducing Desorption of Organic Molecules with a Scanning Tunneling Microscope: Theory and Experiments

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A scanning-tunneling microscope has been used to induce efficient local desorption of benzene from Si(100) at low currents (<100 pA), sample biases (∼−2.4 V) and temperatures (22 K). A theoretical model based upon first principles electronic structure calculations and quantum mechanical wave packet dynamics describes this process as occurring via transient ionization of a π state of the adsorbed molecule. This model accounts for the unexpected efficiency and sharp threshold of the yield.

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The development of the scanning tunneling microscope (STM) has made possible not only visualization but also manipulation of individual adsorbates [1]. Intensive research in this area has been motivated by the desire to better understand adsorbate-substrate interactions, surface dynamics, and the potential of local tip-induced modifications to fabricate nanoscale devices and induce novel molecular-scale chemical reactions. Earlier research focused on manipulation of atoms and diatomic molecules [1–4] but the exciting avenue of inducing single-molecule reactions in complex, multidimensional systems is now beginning to be explored [5]. Organic molecules, whose properties can be systematically tailored via the use of appropriate functional group substitutions, offer a rich variety of opportunities for both fundamental and technological studies. In particular, organic molecules covalently attached to silicon surfaces have attracted considerable recent interest, due to the potential of combining the wide range of functionality of organics with silicon technology for applications ranging from molecular electronics to biosensors [6].

A related problem of fundamental and practical interest is the prospect of using the STM environment as a laboratory for study of desorption induced by electronic transitions (DIET), proposed in Ref. [7]. The conventional means of studying this problem, i.e., photon stimulated, substrate-mediated desorption from metal surfaces, precludes quantitative theoretical modeling due to the difficulty of constructing excited state potential energy surfaces and coupling elements for adsorbate/metal complexes and to competition with vibrational relaxation. Hence theoretical work so far has focused on simple models [8]. By allowing DIET to be performed on nonmetallic surfaces, in a manner that avoids excited electronic states and competing processes, the STM environment introduces the possibility of modeling DIET quantitatively and comparing with comparably quantitative experimental data. It thus opens the way to the study of chemically interesting systems.

In this work we present a combined experimental and theoretical study of tip-induced breaking of covalent Si-C bonds in a prototypical organic/semiconductor system, benzene on a Si(100) surface. We observe this system to undergo enhanced desorption via resonance-mediated electron tunneling from the surface to the tip. The efficiency of the STM-induced desorption is up to 5 orders of magnitude greater than that found for the resonance-mediated desorption of CO from Cu(111) [3]. Our theory rationalizes the observations, provides a complete picture of the desorption dynamics, and points to a general qualitative description of analogous processes in organic adsorbates/Si systems.

The benzene/Si(100) system has a well-characterized chemical bonding configuration [9,10]. At substrate temperatures below 200 K benzene adsorbs onto Si(100) in only one configuration, the so-called "butterfly" structure, appearing in STM images as bright featureless protrusions centered on a Si dimer (Fig. 1). Experimentally, when

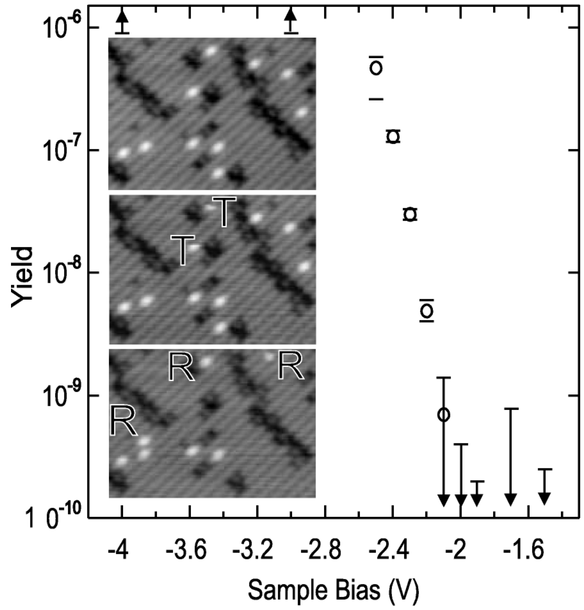

FIG. 1. Desorption yield for benzene/Si(100) as a function of sample bias at 22 K. Inset shows succesive STM images (42 pA, −2.3 V, 150 Å × 110 Å, 300 nm/s). Examples of molecules desorbing during the scan are marked "*T*" while readsorbed molecules are labeled "*R*".

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scanned at voltages above a threshold, local tip-induced bond breaking of covalent Si-C bonds is observed, as demonstrated by the three consecutive STM images shown in Fig. 1. It is apparent that six of the molecules have been dislodged while four others have remained unaffected. About 80% of the time, a displacement event is accompanied by an abrupt truncation of the molecule derived protrusion (denoted by T), indicating that the tip-induced bond-breaking interaction is localized over approximately the same lateral scale as the image of the benzene molecule. Some of the dislodged molecules are displaced laterally and readsorb in the single dimer configuration (denoted by R), while others leave the surface. No evidence of C-H or C-C bond breaking is observed.

Desorption yields (probabilities per electron) have been measured by counting the fraction of molecules that are dislodged after being scanned at a selected bias. This fraction is used to extract a yield using the measured area of a single adsorbate (0.5 nm^2) and the known tunneling current passing through the tip. The bias dependence of the yield at a substrate temperature of 22 K is shown in Fig. 1. In between -1.6 and -2.7 V there is a sharp threshold over which the yield rises an order of magnitude per 0.1 V change in sample bias. Variable temperature studies up to 293 K show that the yield does not increase with increasing temperature as expected for thermally activated bond-breaking mechanisms, suggesting dissociation via an electronic excitation [11].

An approximately linear dependence of the yield on current has been observed, indicating that the bond breaking is a single-electron driven process [4,8]. The observed threshold in the probability vs voltage curve coincides approximately with the binding energy of an adsorbate derived π state observed in photoemission studies of benzene/Si(100) [9]. These experimental observations suggest that the bond breaking involves resonant electronic excitation of this state.

To rationalize the substantial desorption yield and the sharp bias dependence, we proceed to compute the desorption dynamics from first principles. For lifetimes of practical interest the total desorption yield can be *approximated* as the product of an excitation probability per electron and a desorption probability per resonance event (this being the limit of an accurate expression, derived in [12]). The former function, equivalently considered a hole scattering probability, exhibits a step-function-like dependence on the bias voltage, V_b whose steepness is determined by the resonance lifetime. This factor gives rise to the sharp V_b dependence observed in Fig. 1. The latter function, denoted $P_{\mathrm{des}}(\tau)$ below, contains all the details of the desorption dynamics.

To determine these dynamics we proceed by calculating *ab initio* potential energy surfaces for the neutral and the ionic states. To that end we first characterize the key stationary state configurations on both surfaces (Fig. 2). Detailed inspection of the ionic and neutral structures shows that ionization is accompanied by significant displacement of the equilibrium configuration, predominantly in a collective ring-bending mode, while the C_{2v} symmetry of the neutral state equilibrium is conserved. We find, moreover, that desorption in the neutral state takes place along a C_{2v} pathway and is strongly dominated by two modes; motion of the center-of-mass from the surface and bending motion of the ring. Two unitless orthogonal coordinates are constructed, one of which (Z) has the physical significance of a desorption mode and the other (X) of a ring-bending mode. First principles potential energy surfaces, computed in terms of these coordinates, are shown in Figs. 2.

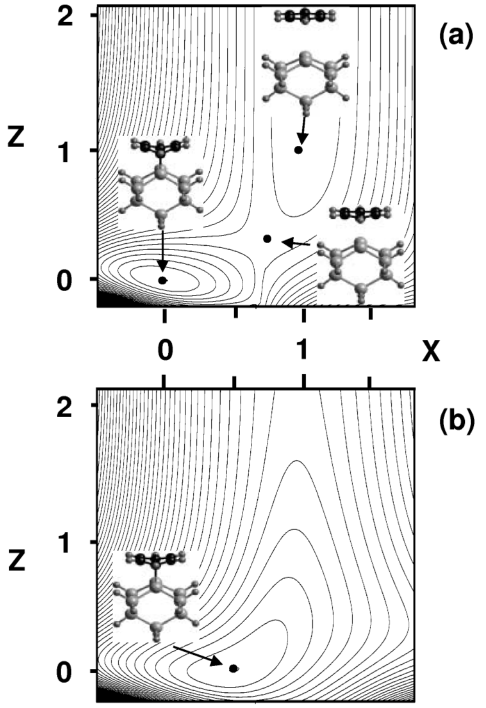

FIG. 2. Calculated potential energy surfaces vs the dimensionless coordinates X and Z: (a) neutral state; (b) ionic state. Black dots indicate the location of stationary points and the contour curves are spaced 0.2 eV apart. Optimized structures and energies are obtained from full-dimensional first principles calculations employing the hybrid Hartree-Fock/density functional theory approach of Becke (B3LYP) [13] and a 6-31G^{**} atomic centered basis set. A $\mathrm{Si}_9\mathrm{H}_{12}$-$\mathrm{C}_6\mathrm{H}_6$ cluster and its corresponding cation are used to model the ground and ionic states, respectively. For similar Si-cluster model studies, see Refs. [10,14]. Comparison of the cluster model results with full surface slab calculations and details of our method of constructing an orthogonal coordinate system for the potential surfaces calculation are given in Ref. [12]. We note that the STM electric field is quite small in the present study, below 0.3 V/Å, and is not accounted for in the calculation.

Figure 2 clarifies the desorption mechanism and suggests a qualitative rationale of its remarkable efficiency. Upon STM-induced ionization the system is displaced with respect to the stable equilibrium configuration of the ionic state, primarily along the ring-bending (X) mode (Fig. 2b). It is accelerated toward the ionic state equilibrium while continuously relaxing to the neutral state. Upon neutralization the wave packet carries vibrational energy which is initially localized in the ring-bending mode. Efficient mode coupling, apparent in Fig. 2a, is responsible for rapid transfer of the energy into the desorption mode, leading to desorption.

This qualitative picture is quantified in Figs. 3 and 4. We first examine the evolution of the wave packet in the neutral state subsequent to instantaneous neutralization at different times after the ionization event. Figure 3 shows the expectation values of X and Z in the time evolving neutral state wave packet after a residence time of 25 fs in the ionic state. Upon neutralization, the wave packet center is displaced with respect to the stable equilibrium and accelerates towards negative X. The desorption process is initiated by large amplitude vibration in the ring-bending mode, Fig. 3. Transfer of energy into Z is rapid and for ca. 500 fs the vibrational excitation shuttles periodically between the two modes. At the end of ≈750 fs, the desorption is complete and ca. 11% of the probability density reached the asymptotic region; the rest will subsequently vibrationally relax. The inset in Fig. 3 shows a snapshot of the wave packet at 750 fs, illustrating highly vibrationally mixed motion in the chemisorption well, some probability density in the physisorption site, and a portion of the wave packet propagating along the exit valley.

Figure 4 contrasts this behavior with the desorption dynamics that follows 10 and 40 fs residence times in the ionic state. In the former case, the wave packet center relaxes onto a low energy region of the neutral state, only low-amplitude vibrational motion ensues and the desorption probability vanishes to within the accuracy of the calculation. In the latter case, the center of the wave packet travels a substantial distance along the ring mode during the residence time and relaxes onto a highly repulsive region of the neutral surface; see Fig. 2a. There ensues large amplitude motion in the ring-bending mode, and rapid mixing of the two modes. By the end of 200 fs propagation on the neutral surface, a major portion of the wave packet has surmounted the transition state and the ring mode undergoes highly excited vibrational motion across the exit valley.

The propagation procedure yields residence-time-dependent desorption probabilities, $P_{\mathrm{des}}(\tau_R)$ [12], in terms of which the physical desorption probability, $P_{\mathrm{des}}(\tau)$, is approximated within the lifetime averaging procedure of Gadzuk [15]. Both $P_{\mathrm{des}}(\tau_R)$ and $P_{\mathrm{des}}(\tau)$ are displayed in Fig. 5. It is due to the nature of the equilibrium displacement of the neutral and ionic states and the efficient coupling of the two modes involved that $P_{\mathrm{des}}(\tau)$ is a sensitive, rapidly increasing function of τ. Along with the long lifetime inferred from comparison of the experimental data with the theoretical bias dependence ($\tau \approx 7$–20 fs; long as compared to the 0.8–5 fs CO/Cu [3] and the 0.45–3 fs H/Si [2] resonance lifetimes), Fig. 5 rationalizes the remarkable efficiency of the desorption process. Knowledge of $P_{\mathrm{des}}(\tau)$ allows estimating the excitation probability. Consistent with the above lifetime, Fig. 5 suggests relatively small excitation probabilities, in the $4 \times 10^{-6} - 6 \times 10^{-5}$ range.

Using a similar experimental procedure we find that other π-bond containing organic adsorbates on Si(100)

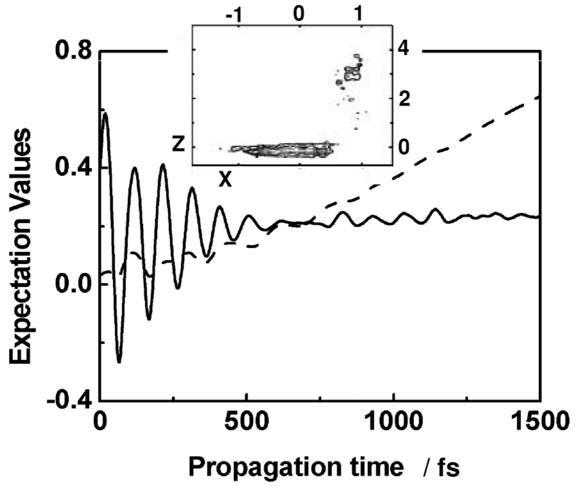

FIG. 3. Expectation values of X (solid curve) and Z (dashed curve) in the evolving neutral state wave packet subsequent to 25 fs residence in the ionic state. The wave packet dynamics are calculated quantum mechanically using the split operator technique. The inset shows a snapshot of the wave packet 750 fs after relaxation to the neutral state.

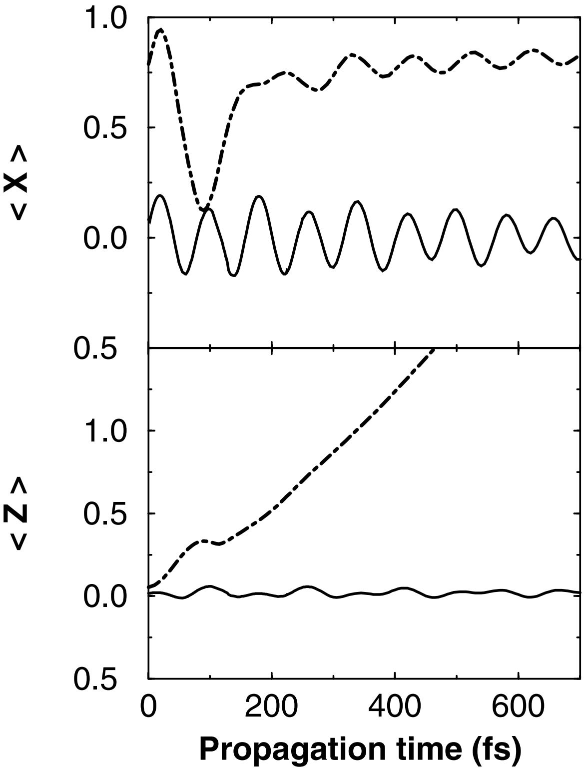

FIG. 4. Expectation values of X and Z in the evolving neutral state wave packet subsequent to 10 fs (solid line) and 40 fs (dot-dashed curve) residence in the ionic state.

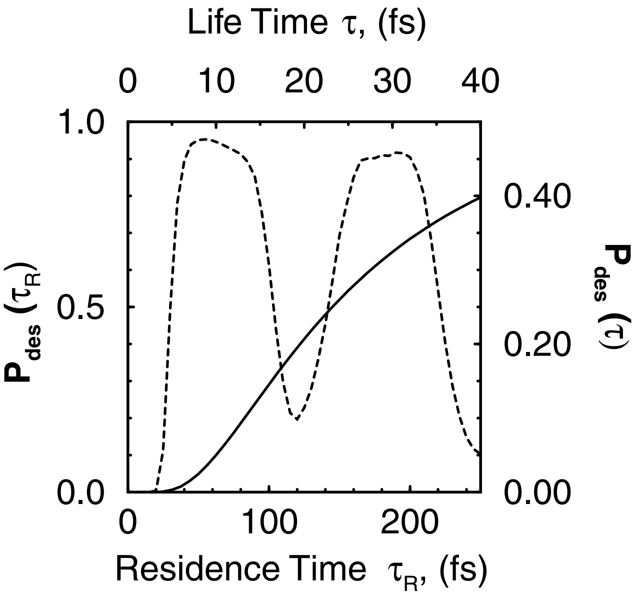

FIG. 5. The residence-time-dependent desorption probability vs τ_R (dashed curve) and the lifetime averaged desorption probability vs the resonance lifetime τ.

surface, including 1,3 cyclohexadiene and styrene, show analogous facile STM induced desorption, while organic molecules lacking π bonds are stable under similar conditions [16]. These results can be explained by extension of the model. Adsorption induces changes in hybridization of the silicon bound carbon atoms which are accompanied by geometric changes in the π-bonding backbone of the adsorbate. π-bonded systems have low-lying ionic states which σ-bonded systems generally lack. Removal (or addition) of an electron that is localized in the π system brings about geometric changes since all of the π orbitals have a large contribution to the net bonding of the system. Such equilibrium displacement leads to conversion of electron energy into vibrational excitation and ultimately to bond breaking. These results appear to suggest that organic molecule/silicon systems that offer resonance-enhanced conductance [17] would typically break at voltages exceeding 2–3 V in magnitude. Our model extends, however, to suggest π-bonded organic adsorbates that will not suffer current-induced bond breaking. In systems where only nonbonding electrons are removed by ionization, at most minor rearrangement of the nuclei is expected. This is the case, for instance, in large aromatic systems where the energetically available electrons are sufficiently delocalized over a large number of nuclei. Another example is systems where the π bond is isolated via intermediate saturated carbons from the Si-C bonds.

In summary, we studied experimentally and theoretically the STM-induced desorption of benzene from Si(100). We observe a striking threshold in the bias dependence and relatively high yields under mild conditions. A theoretical model rationalizes the observations in terms of transient ionization of a π state of the molecule and generalizes the findings to predict the behavior of different classes of organic adsorbates under similar conditions. The selective tip-induced Si-C bond breaking reported here may have implications in the area of molecular scale electronics and could prove useful in the development of nanoscale lithographic methods. STM-triggered ionic states at surfaces may find use [12] also in local control of chemical reactions.

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