

Reactions of substituted aromatic hydrocarbons with the Si(001) surface

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The interactions of toluene, *para*-xylene, *meta*-xylene and *ortho*-xylene with the (001) surface of silicon have been investigated using Fourier-transform infrared spectroscopy. Infrared spectra show that these methyl-substituted aromatic hydrocarbons are chemisorbed and oriented on the Si(001) surface at both 110 and 300 K. Peaks in the Si–H stretching region indicate that some dissociation occurs upon adsorption. Comparisons of infrared spectra of these molecules with deuterated and nondeuterated methyl groups reveal that the major source of decomposition is likely from C–H cleavage of the substituent groups, leaving the ring intact. Additionally, the striking similarity of the infrared spectra of benzene, toluene and the xylene isomers suggests that the methyl-substituted aromatic rings interact with the Si(001) surface in much the same way as benzene. Differences in relative peak intensity point to the possibility that the methyl substituent groups may steer the ring into different ratios of specific bonding geometries. © 2000 American Vacuum Society.
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I. INTRODUCTION

The Si(001) surface is the starting point for most microelectronic devices. Although present microelectronic manufacturing techniques primarily use inorganic materials, recent developments in controlling the behavior of *organic* molecules on Si(001) may provide opportunities for extending Si(001)-based microelectronics technology to new areas, such as molecular electronics and biotechnology.^{1–5}

Chemical reactions are usually controlled by the highest-occupied and lowest-unoccupied molecular orbitals (HOMO) and (LUMO), respectively, of the reactants. The HOMOs and LUMOs of the Si(001) surface are π -bonding and π^* -antibonding levels and are formed through a surface reconstruction in which adjacent atoms pair together into “dimers.”⁶ The silicon dimers have geometric and electronic structures that are similar to those of organic alkenes, suggesting that their chemistry might be similar. Subtle features, such as dimer tilting, can complicate the semiconductor-organic chemistry analogy. Nevertheless, developing an understanding of how organic molecules interact with Si(001) can provide insight into the development of new strategies for the chemical functionalization of dimerized surfaces such as Si(001), Ge(001), and diamond (001).^{7–9}

Benzene is one of the most widely studied compounds in chemistry because it possesses unusual stability. Recent studies have shown that the interaction of benzene with the Si(001) surface is complex, with evidence for multiple bonding configurations^{10–18} and transformations from one configuration to another at room temperature.^{10,15,16} Likewise, toluene also chemisorbs in multiple bonding configurations.¹⁹ At the present time, the kinetic and thermodynamic factors controlling adsorption of benzene and other aromatic hydrocarbons on Si(001) remain controversial.^{10,11,13–18,20,21}

It is well known within the field of organic chemistry that substituent groups on an aromatic ring can steer a reaction towards a particular product.²² This can be accomplished either sterically, using large unreactive substituent groups, or electronically, by making particular sites on the ring more susceptible to attack. The reaction chemistry of aromatic rings containing a pair of either electron-donating or electron-withdrawing groups is often very different depending on whether these groups are located across from one another (*para*), adjacent to one another (*ortho*) or separated by one carbon on the ring (*meta*).²² The resulting specificity in bonding often is attributed to differing degrees of stabilization of transient or ionic intermediates.

Studying the interaction of substituted aromatic hydrocarbons with the Si(001) surface can be used to elucidate how substituent groups may steer the ring into particular configurations. Here we report investigations comparing the adsorption and bonding of several substituted aromatic molecules on the Si(001) surface. Our studies focus on aromatics in which methyl groups, as electron-donating substituents, replace one or more hydrogen atoms on the benzene ring.

II. EXPERIMENT

Multiple internal reflection-Fourier-transform infrared (MIR-FTIR) spectroscopy was used to investigate the interaction of methyl-substituted benzene rings at submonolayer and monolayer coverages. Infrared light, produced by a Mattson RS-1 FTIR spectrometer, was coupled into an ultra-high vacuum (UHV) chamber (base pressure $< 1.0 \times 10^{-10}$ Torr) by BaF₂ windows and, after exiting the chamber, was collected with a cooled InSb detector. The samples were cut from *n*-type high-resistivity wafers ($> 7 \Omega \text{ cm}$, P doped, from Wacker Chemitronics) that were polished on both large (0.9 cm \times 2.0 cm) faces. The small edges (0.9 cm \times 0.5 mm) of the samples were polished 45° off the (001) face for use in a multiple internal reflection geometry.²³ The samples were rinsed in methanol and

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cleaned of residual surface carbon contamination by exposure to ozone for 15 min. After transferring to vacuum, the samples were outgassed overnight at 850 K and then annealed at 1400 K to remove the oxide layer, leaving a clean Si(001)-(2×1) surface.²⁴

Studies were performed using both “on-axis” and “off-axis” Si(001) wafers. On-axis samples oriented to (001) ± 0.5° consist of large terraces of dimer rows separated by steps one atomic layer high. Since terraces separated by monatomic steps have dimer bonds rotated 90° with respect to one another, these on-axis “two-domain” Si(001) samples contain equal amounts of the (2×1) and (1×2) domains. Off-axis Si(001) samples were intentionally miscut 4° off the (001) axis, toward the [110] direction. This miscut produces surfaces consisting of small terraces separated by bilayer steps.^{25,26} Because the dimer bond orientation is retained across a bilayer step, all the dimers in these off-axis, “single-domain” Si(001) samples are in a single (2×1) orientation.

Infrared absorption is controlled by the dot product of the electric field vector and the transition dipole corresponding to each vibrational mode. Differences between spectra obtained with *s*-polarized and *p*-polarized light reveal the tendency of molecules to orient with respect to the surface normal. For single-domain samples, *s*-polarized light with its electric field vector either parallel or perpendicular to the Si=Si dimer bond axis can additionally be used to probe the orientation of specific molecular vibrations with respect to the Si=Si dimer bond.

The molecules used for this study included benzene (99%, Aldrich), toluene (99.8%, Aldrich), *para*-xylene (99+%, Aldrich), *meta*-xylene (99+%, Arcos) and *ortho*-xylene (97%, Aldrich). Isotopically labeled molecules, in which the hydrogen atoms of the methyl (CH₃) groups were replaced with deuterium, were used to distinguish IR absorption of the C–D stretches of the methyl groups from IR absorption of the C–H stretches on the ring. Compounds with deuterated methyl groups included toluene-*d*₃ (98%, Cambridge Isotopes), *para*-xylene-*d*₆ (99+%, Aldrich), *meta*-xylene-*d*₆ (98%, CDN Isotopes) and *ortho*-xylene-*d*₆ (98%, Cambridge Isotopes). Each compound was further purified by at least three freeze-pump-thaw cycles. Purity was verified with an *in situ* mass spectrometer. The chemicals were introduced to the UHV chamber through a variable leak valve directed towards the surface. Exposures reported here are nominal exposures based on the background pressure in the chamber. Due to the geometry of the vacuum system, the actual exposures at the sample are higher.

III. RESULTS

Polarized infrared spectra were obtained on single-domain Si(001) samples. With an appropriate choice of geometry, it is possible to obtain spectra using infrared light in which the electric-field vector lies completely in the surface plane, aligned selectively along either the [110] direction (perpendicular to the dimer bonds) or the [1 $\bar{1}$ 0] direction (parallel to the dimer bonds).²⁷ The *s*-polarized infrared spectra were

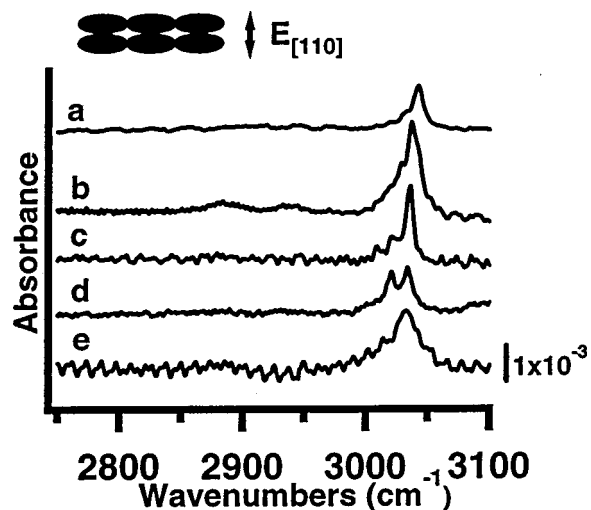


Fig. 1. Infrared spectra of molecules chemisorbed on single-domain Si(001) samples at 300 K, probed with light polarized perpendicular to the dimer bonds. Spectra of (a) 10.0 L benzene (4.0×10^{-8} Torr for 250 s); (b) 10.0 L toluene-*d*₃ (2.5×10^{-8} Torr for 400 s); (c) 1.0 L *p*-xylene-*d*₆ (1.0×10^{-8} Torr for 100 s); (d) 2.0 L *m*-xylene-*d*₆ (2.0×10^{-8} Torr for 100 s); (e) 1.0 L *o*-xylene-*d*₆ (1.0×10^{-8} Torr for 100 s).

obtained in this manner for benzene, toluene-*d*₃, *p*-xylene-*d*₆, *m*-xylene-*d*₆ and *o*-xylene-*d*₆ adsorbed onto Si(001) at 300 K and are presented in Figs. 1 and 2. Due to technical difficulties, the room temperature spectrum for *m*-xylene-*d*₆ probed with $E_{[1\bar{1}0]}$ light could not be acquired. Figure 2(d), therefore, is a spectrum of *m*-xylene-*d*₆ adsorbed to Si(001) at 110 K.

Spectra also were obtained using *p*-polarized light (not shown) for benzene, toluene-*d*₃, *p*-xylene-*d*₆, *m*-xylene-*d*₆ and *o*-xylene-*d*₆. The electric field of *p*-polarized light con-

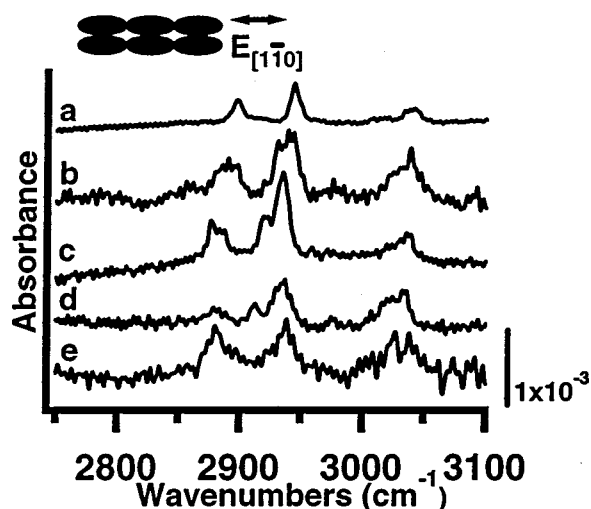


Fig. 2. Infrared spectra of molecules chemisorbed on single-domain Si(001) samples at 300 K, probed with light polarized parallel to the dimer bonds. Spectra of (a) 10.0 L benzene (2.5×10^{-8} Torr for 400 s); (b) 10.0 L toluene-*d*₃ (2.5×10^{-8} Torr for 400 s); (c) 1.0 L *p*-xylene-*d*₆ (1.0×10^{-8} Torr for 100 s); (d) 2.0 L *m*-xylene-*d*₆ (2.0×10^{-8} Torr for 100 s) [Due to technical difficulties, this spectrum was acquired on a Si(001) sample at 110 K]; (e) 1.0 L *o*-xylene-*d*₆ (1.0×10^{-8} Torr for 100 s).

tains two components: one oriented along the [001] direction and a second oriented along either the [110] or [1 $\bar{1}$ 0] direction. In all cases, the *p*-polarized spectra of benzene and the methyl-substituted rings appeared to be dominated by vibrational modes parallel to the surface plane, indicating that there are no strong vibrational modes with transition dipoles oriented directly in the [001] direction.

The spectral region between 3000 and 3100 cm^{-1} is normally associated with the C–H stretching vibrations of sp^2 -hybridized, or unsaturated, alkene-like carbons. Each of the five different spectra in Fig. 1 shows absorption peaks between 3000 and 3100 cm^{-1} when probed with light polarized in the [110] direction. The position of the main peak decreases in frequency from 3043 cm^{-1} in benzene to 3037 cm^{-1} in toluene- d_3 to 3035 cm^{-1} in *o*-, *m*-, and *p*-xylene- d_6 . This small shift in frequency occurs because the methyl groups donate electron density to the ring, thereby decreasing the force constant associated with the C–H bonds on the ring. While the main peak has nearly the same shape for benzene [Fig. 1(a)], toluene- d_3 [Fig. 1(b)] and *p*-xylene- d_6 [Fig. 1(c)], *m*-xylene- d_6 [Fig. 1(d)] shows two rather strong peaks at both 3035 and 3021 cm^{-1} , while the *o*-xylene- d_6 peak [Fig. 1(e)] is much broader, with a high-frequency tail.

When the samples were probed with light with its electric field parallel to the Si=Si dimer bond (Fig. 2), all molecules had significantly decreased absorption above 3000 cm^{-1} . The apparent splitting of the *o*-xylene- d_6 alkene-like peak in Fig. 2(e) is actually due to absorption interference from atmospheric water as a result of increased humidity during acquisition of the background spectrum.

The spectral region between 2800 and 3000 cm^{-1} is associated with C–H stretching vibrations of sp^3 -hybridized, or saturated, alkane-like carbons. When the electric field is perpendicular to the dimer bonds (Fig. 1), the spectra exhibit only weak features. In contrast, when the electric field is parallel to the dimer bonds (Fig. 2), two strong clusters of peaks emerge in this region and dominate the spectra. Again, the absorption features are shifted downward in frequency as methyl groups are added to the ring. The more intense peak shifts from 2944 cm^{-1} for benzene in Fig. 2(a), down to a broader peak at 2930–2951 cm^{-1} for toluene in Fig. 2(b). Each of the xylenes has two peaks, at 2919 and 2933 cm^{-1} for *p*-xylene- d_6 and at 2913 and 2934 cm^{-1} for *m*-xylene- d_6 . The intense peak for *o*-xylene- d_6 is located at 2938 cm^{-1} with a smaller shoulder at 2921 cm^{-1} . Similarly, the second major grouping of peaks in Fig. 2 decreases from 2899 cm^{-1} for benzene to 2890 cm^{-1} for toluene- d_3 and 2880 cm^{-1} for the deuterated xylene isomers.

Previous studies have shown that benzene chemisorbs molecularly to the surface.^{12,17} We found no indication of Si–H vibrational modes upon benzene adsorption, at either 110 K or room temperature. Furthermore, after heating to 550 K (above the desorption temperature), neither C–H nor Si–H stretching vibration modes were detectable. These observations confirm that benzene molecularly adsorbs to the Si(001) surface and desorbs as an intact molecule, leaving behind a clean surface.^{12,17} In contrast, we find some evi-

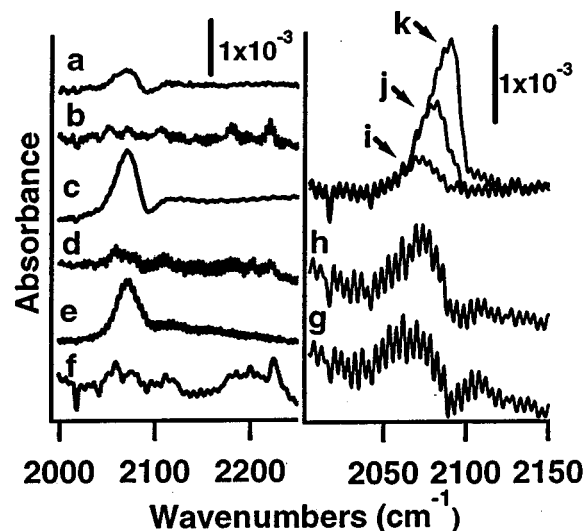


Fig. 3. Infrared spectra of nondeuterated and deuterated methyl-substituted aromatic rings chemisorbed on single-domain Si(001) samples at 300 K. The samples were resistively heated to the temperature shown for 2 min and allowed to cool to 300 K prior to spectral acquisition. Spectra of (a) 12.0 L *p*-xylene (6.0×10^{-8} Torr for 200 s); (b) 1.0 L *p*-xylene- d_6 (1.0×10^{-8} Torr for 100 s); (c) 1.0 L *m*-xylene (1.0×10^{-8} Torr for 100 s); (d) 2.0 L *m*-xylene- d_6 (2.0×10^{-8} Torr for 100 s); (e) 1.0 L *o*-xylene (1.0×10^{-8} Torr for 100 s); (f) 1.0 L *o*-xylene- d_6 (1.0×10^{-8} Torr for 100 s); (g) 10.0 L toluene- d_3 (2.5×10^{-8} Torr for 400 s); (h) same as (g), heated to 420 K; (i) 5.0 L toluene (5.0×10^{-8} Torr for 100 s); (j) same as (i), heated to 490 K; (k) same as (i) heated to 670 K.

dence for dissociation of toluene and the xylene isomers.

Figures 3(a)–(f) show the spectra in the Si–H stretching region of *p*-xylene, *p*-xylene- d_6 , *m*-xylene, *m*-xylene- d_6 , *o*-xylene and *o*-xylene- d_6 adsorbed on the two-domain Si(001) at 300 K, probed with *p*-polarized light with components in both the [1 $\bar{1}$ 0] and [001] directions. While a Si–H vibrational peak at 2070 cm^{-1} is clearly visible for the nondeuterated xylenes in Fig. 3(a), 3(c) and 3(e), the analogous compounds in which the methyl groups alone are deuterated [Figs. 3(b), 3(d) and 3(f)] show little evidence of dissociation. By comparing the Si–H peak areas of the nondeuterated xylene isomers with the peak area of a fully hydrogenated surface, we estimate that surface hydrogen coverage was approximately 0.03, 0.18 and 0.20 monolayers (ML) for *p*-xylene, *m*-xylene and *o*-xylene, respectively. A broad peak near 2220 cm^{-1} is present in Figs. 3(b), 3(d) and 3(f) and is associated with the C–D stretches of the deuterated methyl groups.

To investigate possible further decomposition at elevated temperatures, spectra were obtained of toluene- d_3 [Figs. 3(g) and 3(h)] and nondeuterated toluene [Figs. 3(i)–(k)] on Si(001) after annealing to successively higher temperatures. The toluene samples in Figs. 3(g)–(k) were probed with *p*-polarized light with components in the [110] and [001] directions. Although toluene- d_3 has a small absorption near 2070 cm^{-1} when adsorbed on a 300 K Si(001) surface [Fig. 3(g)], this absorption does not increase significantly when the temperature is increased to 420 K [Fig. 3(h)]. In contrast, the Si–H peak of normal (i.e., nondeuterated toluene) in-

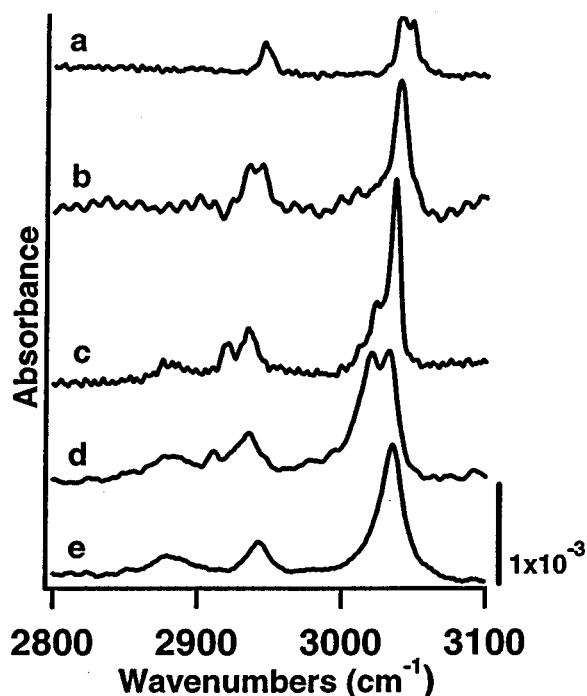


FIG. 4. Unpolarized infrared spectra of molecules adsorbed on two-domain Si(001) samples at 110 K. Spectra of (a) 0.5 L benzene (5.0×10^{-9} Torr for 100 s); (b) 1.6 L toluene- d_3 (1.0×10^{-8} Torr for 160 s); (c) 5.0 L *p*-xylene- d_6 (2.5×10^{-8} Torr for 200 s); (d) 5.0 L *m*-xylene- d_6 (2.5×10^{-8} Torr for 200 s); (e) 5.5 L *o*-xylene- d_6 (2.5×10^{-8} Torr for 220 s).

increases significantly with increasing temperature, yielding hydrogen coverages of 0.09 ML at 300 K, 0.21 ML at 490 K and 0.28 ML at 670 K.

Because previous experiments have shown that the distribution of bonding geometries for benzene is temperature-dependent,¹⁴ additional studies were performed to identify whether toluene and the xylenes exhibited different behavior at lower temperatures. Figure 4 compares the unpolarized spectra of benzene, toluene- d_3 , *p*-xylene- d_6 , *m*-xylene- d_6 and *o*-xylene- d_6 adsorbed on two-domain, on-axis Si(001) at 110 K. When benzene was adsorbed onto a cooled Si(001) surface, as in Fig. 4(a), the resulting spectrum is substantially different from spectra of benzene on a room-temperature sample. In particular, the spectrum obtained on a cold substrate shows no absorbance at 2899 cm^{-1} even after 3 h. Similarly, when toluene- d_3 was adsorbed onto Si(001) at 110 K, as in Fig. 4(b), its corresponding room-temperature peak at 2890 cm^{-1} in Fig. 2(b) is not present. After heating the benzene and the toluene- d_3 samples (not shown), the peaks at 2899 cm^{-1} for benzene and at 2890 cm^{-1} for toluene- d_3 increased in intensity until the spectra were identical to the spectra at 300 K exposure. In contrast, the spectra of *p*-xylene- d_6 [Fig. 4(c)], *m*-xylene- d_6 [Fig. 4(d)] and *o*-xylene- d_6 [Fig. 4(e)] adsorbed on Si(001) at 110 K appear nearly identical to the xylene Si(001) spectra obtained with the Si(001) samples at 300 K [Figs. 1(c)–1(e) and 2(c)–2(e)]. Surprisingly, the xylene/Si(001) spectra at 110 K are more similar to the spectra of benzene and toluene- d_3 on

Si(001) at 300 K than to the spectra of benzene and toluene- d_3 on Si(001) at 110 K.

IV. DISCUSSION

A comparative analysis of the spectra of the methyl-substituted aromatic systems addresses several fundamental issues, including the reversibility of adsorption, the possible pathways to dissociation from the Si(001) surface and the ability of the methyl substituents to direct the ring into particular bonding geometries.

The presence of peaks in the alkane-like C–H stretching region ($2800\text{--}3000 \text{ cm}^{-1}$) for benzene, toluene- d_3 and the deuterated xylene isomers indicates that at least one of the π bonds in the ring system is broken upon adsorption. When an unsaturated carbon atom bonds to the Si surface, the transformation from sp^2 to sp^3 hybridization and the donation of electron density from the silicon atom lower the force constant associated with the C–H bond. The low-frequency alkane-like vibrations in the $2800\text{--}3000 \text{ cm}^{-1}$ region almost certainly arise from carbon atoms that have been strongly perturbed by bonding to the silicon surface.³ Additionally, absorption in the region above 3060 cm^{-1} , normally associated with the C–H stretching of an aromatic ring, is absent in Figs. 1–4.^{14,28,29} The absence of these high-frequency modes and the absorption in the alkane region indicate that both benzene and the methyl-substituted compounds are chemisorbed onto Si(001) through their rings. Furthermore, the multiplicity of peaks in Figs. 1, 2, and 4 suggests that benzene, toluene and the xylenes might bond to the surface in more than one configuration or into a singular bonding configuration of low symmetry.

While our studies and previous studies show that benzene adsorbs and desorbs with no detectable dissociation,^{12,17} our data indicate that substituting one or more methyl groups onto the ring leads to some dissociation when the molecule adsorbs to the Si(001) surface. At elevated temperatures, this dissociation becomes more significant. Surprisingly, comparison of deuterated and nondeuterated methyl-substituted rings demonstrates that the major dissociation channel arises almost entirely from cleavage of C–H bonds of the methyl group.

Aromatic hydrocarbons typically interact with reactants in one of two ways. In “substitution reactions,” a C–H bond on the ring is cleaved as the reactant attacks one of the aromatic carbon atoms. In “addition reactions,” the reactant bonds directly to the ring through the π system without cleavage of the C–H bonds. For aromatic hydrocarbons, substitution reactions preserve the aromaticity of the benzene ring while in addition reactions, the aromaticity of the ring is lost. Since the aromatic nature of benzene results in high stability, we might expect that benzene and related molecules would bond to the surface with cleavage of a C–H bond from the aromatic ring. In contrast, our results show that benzene adsorbs molecularly, and that the dissociation that is observed for toluene and xylenes arises almost exclusively from the methyl groups, not from the ring. These observa-

tions suggest that the interaction of these aromatic systems and the Si(001) surface more closely mimics addition reactions.

For simple alkenes, it has been proposed that the surface reactions are facilitated by the interaction of the electron-rich π system of the alkene with the normally unoccupied π^* orbital of the silicon dimer.^{7,30,31} Tilting of the dimers leads to a charge transfer and zwitterion-like behavior, helping to facilitate the overall reaction.^{24,32,33} Aromatic systems undergo substitution reactions through similar ionic intermediate pathways. In these type of reactions, the location of substituent groups will often direct reactants to specific sites on the ring. This propensity to react at specific positions is a result of how well transient intermediates are stabilized as the molecule undergoes a reaction.²² The differences in the spectra of *p*-xylene-*d*₆, *m*-xylene-*d*₆ and *o*-xylene-*d*₆ in Figs. 1 and 2 indicate that the methyl substituent groups may exert some influence on the distribution of bonding configurations. Differences in the overall symmetry of the final bonding geometries may also influence the noted differences in peak shape.

A comparison of the low temperature and room-temperature spectra of benzene and toluene-*d*₃ indicates that the lower frequency modes at 2899/2890 cm⁻¹ [Figs. 2(a) and 2(b)] arise from a different bonding geometry than the modes near 2940 cm⁻¹ [Figs. 4(a) and 4(b)]. In contrast, the spectra of xylenes/Si(001) [Figs. 4(c)–4(e)] are nearly identical at both 110 and 300 K. This indicates that either the methyl substituent groups enhance the ability to convert from one configuration to another by stabilizing transient intermediates, or that the methyl groups prevent conversion between different configurations, possibly by stabilizing the initial adduct. In the first case, the observed species would reflect thermodynamically stable products, while in the latter they would represent the kinetically favored species.

At this time, the presence of more than one bonding geometry coupled with the difficulty in performing vibrational analysis of small peak shifts precludes making definitive statements about specific bonding geometries present on the surface. Indeed, even the surface structure and vibrational analysis for the parent molecule, benzene, on Si(001) remain controversial.^{10–13,15–17} Nevertheless, qualitative analysis of the spectra is possible. First, a comparison of Figs. 1 and 2 confirms that there is pronounced optical anisotropy between the [110] and the [1 $\bar{1}$ 0] directions. This clearly demonstrates that the molecules are chemisorbed into configurations that are strongly oriented with respect to the Si=Si dimer bond. Beyond this, we note the fact that the low-frequency, alkane-like absorbances in the 2800–3000 cm⁻¹ region are most intense when probed with light polarized in the [1 $\bar{1}$ 0] direction. This indicates that the C–H dipoles of the *sp*³-hybridized carbon atoms attached to the surface are strongly oriented parallel to the Si=Si dimer bond for all five molecules. Second, the striking similarity in the overall vibrational spectra of benzene, toluene and the xylene isomers, especially at room temperature, suggests that these mol-

ecules likely share similar types of bonding configurations on the surface.

V. CONCLUSION

Our studies demonstrate that the bonding of methyl substituted aromatic molecules, such as toluene and xylene, are strongly controlled by the directional nature of the dimer bonds. This anisotropy results in oriented vibrational modes that were detected using polarized light. The similarity of the spectra for benzene, toluene and *p*-, *m*- and *o*-xylene adsorbed on Si(001) suggests that, spatially, the methyl-substituted molecules bond in much the same way as benzene. The presence of additional vibrational features, however, indicates more than one bonding geometry is present on the surface. Dissociation of substituted aromatic molecules arises almost entirely by C–H bond cleavage of the functional group *external* to the aromatic ring. It is not clear from the FTIR data that the additional methyl groups strongly steer the ring into unique bonding configurations. These substituent groups, however, may work to influence the distribution of the different geometries.

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