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Strongly bound state of benzene on cleaved Si(111): Vibrational modes and chemisorption bonds

M. N. Piancastelli
Istituto di Chimica Generale, Università degli Studi di Roma, I-00185 Roma, Italy

G. Margaritondo*
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

J. Anderson, D. J. Frankel, and G. J. Lapeyre
Department of Physics, Montana State University, Bozeman, Montana 59717
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A unique, strongly bound chemisorption state is formed upon room-temperature exposure of cleaved Si to benzene, while no room-temperature benzene chemisorption is observed on Ge, GaAs, and annealed Si(111). Surface vibrational spectra show that the chemisorption process involves the breaking of benzene C—H bonds and formation of Si—C bonds. This process results in a "tilted" chemisorption geometry not observed when benzene is chemisorbed on metal surfaces. Spectra taken on cleaved Si covered by deuterated benzene confirm the above analysis. Sequential C_6H_5 (or C_6D_6) and hydrogen exposure experiments indicate that benzene chemisorption primarily occurs at cleavage steps.

I. INTRODUCTION

A recent synchrotron-radiation photoemission experiment[1] unexpectedly revealed the existence of a strongly bound chemisorption state for benzene on cleaved Si(111)2×1. This state exhibits rather interesting and unique characteristics. It is the only known stable chemisorption state for C_6H_6 on semiconductor surfaces at room temperature. Its saturation coverage is reached for exposures as low as 10^2 L (1 L$\equiv10^{-6}$ Torr sec), and it corresponds to photoemission spectra dominated by C_6H_6 features. For comparison, much larger exposures (up to 10^6 L) fail to introduce C_6H_6 features in the spectra of cleaved GaAs and Ge. Similarly, vibrational measurements do not reveal any evidence of benzene chemisorption on *annealed* Si(111) after large exposures. Furthermore, the C_6H_6 chemisorption geometry on Si(111)2×1 is "tilted" rather than with the benzenic ring parallel to the substrate as on most single-crystal metals.[2]

The above, interesting characteristics are stimulating extensive experimental studies of the Si(111)2×1-C_6H_6 system. We present here the results of high-resolution low-energy electron-loss surface vibrational measurements. Vibrational modes in the energy range up to 4000 cm^{-1} were measured for Si(111)2×1 exposed to C_6H_6 or to deuterated benzene. Changes in the vibrational spectra were monitored upon exposure to atomic hydrogen of some of those surfaces. Our results demonstrate that the chemisorption process involves breaking of C—H bonds and formation of C—Si σ bonds. This process produces a large angle between the benzene-ring plane and the Si(111) surface. Furthermore, the hydrogen chemisorption experiments demonstrate that the saturation chemisorption of benzene leaves a large number of unsaturated silicon dangling bonds on the surface. This fact and the unreactivity of annealed Si indicate that benzene chemisorption occurs at cleavage steps. A qualitative correlation between sticking coefficient and step density supports this hypothesis.

II. EXPERIMENTAL PROCEDURE

The high-resolution electron energy-loss experiments were performed at the Montana State University Center for Research in Surface Science, while the preliminary photoemission experiments[1] were performed at the University of Wisconsin Synchrotron Radiation Center (Stoughton, Wisconsin). The energy-loss instrumentation included a Leybold-Heraeus ELS-22 spectrometer mounted in an ultrahigh-vacuum chamber equipped with a low-energy electron-diffraction system and with an x-ray photoemission spectrometer. The experiments were performed at a typical pressure of 5×10^{-11}-Torr ranges. Single-crystal Si samples were cleaved *in situ* in a benzene or deuterated-benzene atmosphere with pressure in the 10^{-7}-Torr range. The atmosphere composition was monitored by means of a residual gas analyzer. Photoemission experiments[1] demonstrated that this procedure results in a chemisorption state equivalent to that obtained by cleavage in vacuum and subsequent exposure to benzene. The saturation character of the chemisorption state was tested by measuring vibrational or photoemission spectra after further exposure to benzene or deuterated benzene. One benzene-covered surface and one C_6D_6-covered surface were exposed to atomic hydrogen, obtained by admitting ultrapure hydrogen in the vacuum chamber in presence of a W filament at 2000 °C.

Experiments were also performed on annealed Si(111). After repeated annealing cycles, the clean surfaces exhibited sharp 7×7 low-energy electron-diffraction patterns. Room-temperature exposure of these surfaces up to 10^5 L of benzene did not produce any visible benzene-related feature in the surface vibrational spectra. This shows that the room-temperature sticking coefficient of benzene on annealed Si is very small, like those on Ge and GaAs.[1]

The high-resolution energy-loss measurements were performed with a typical primary energy of 6.5 eV. The experiments were performed with an angle of incidence of 45°, both in the specular and off-specular modes. The resolution was optimized by a fine tuning of the parameters of the spectrometer, and it depended on the quality and area of the cleaved surface. The corresponding full width at half maximum of the primary peak ranged between 13 and 22 meV. Data averaging over periods of time from a few minutes to several hours was performed by means of Tektronic 4051 minicomputer with Transera interfaces. The overall performance of the energy-loss spectrometer was tested by taking spectra on ultraclean silicon surfaces and reproducing previously published results.[3]

III. RESULTS AND DISCUSSION

Figure 1 shows typical surface vibrational spectra for clean cleaved Si(111) (top), and for cleaved Si(111) with a saturation coverage of benzene. The top and bottom spectra were recorded in the specular scattering geometry while the middle spectrum was taken at a scattering angle 12° off the specular direction. The saturation coverage was achieved with a 10^3-L exposure to benzene, and the spectra were not modified by further exposures. Comparison with the clean Si(111)2×1 spectrum shows that the spectral features of the middle and bottom spectra in Fig. 1 are related to the adsorbate molecule and to its chemisorption bonds. These features are labeled as peaks *A*, *B*, *C*, *D*, *E*, *F*, and *G*, and the corresponding energy losses are 540, 780, 1060, 1250, 1610, 2055, and 3060 cm^{-1}. We attribute the weak peak *H* at 3630 cm^{-1} to a slight water contamination.[4] The identification of the benzene-related modes was performed based on the electron-energy-loss selection rule[5] and on comparison with vibrational spectra of benzene chemisorbed on metal surfaces.[5–7]

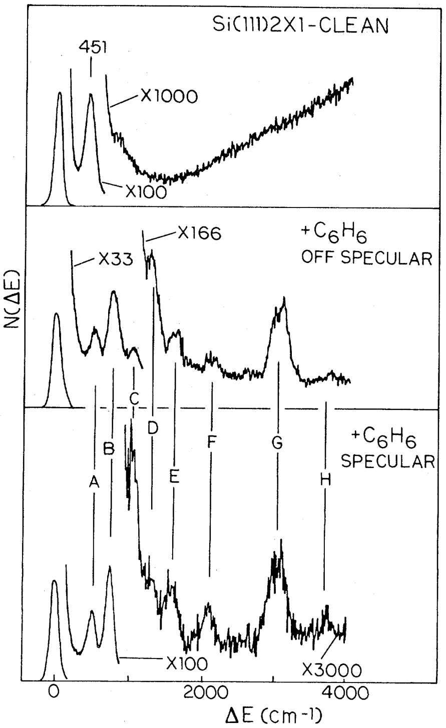

FIG. 1. High-resolution energy-loss spectra taken on clean cleaved Si (top curve), and cleaved Si with a saturation benzene coverage (middle and bottom curves). The angle of incidence was 45°. The top and bottom spectra were taken in a specular scattering geometry. The middle spectrum was taken 12° off the specular geometry. The primary energy was 6.5 eV. The energy resolution (full width at half maximum of the primary peak) was 17.5 meV ($\sim 140\ \text{cm}^{-1}$) for the top and middle curves and 15 meV ($\sim 120\ \text{cm}^{-1}$) for the bottom curve. The surface vibrational features of the benzene-coverage spectra are identified and discussed in the text.

We examined two possible chemisorption bonding processes for the benzene molecules. The first process occurs through their aromatic π molecular-orbital systems, and it corresponds to the formation of a π donor bond involving those π orbitals and substrate states of suitable symmetry. The second process implies the removal of a hydrogen atom from the benzene molecule and formation of a σ bond between a carbon atom of the aromatic ring and a substrate atom. On the metal surfaces investigated until now[2,5–7] benzene has been found to form chemisorption bonds through the first mechanism, π-donor-bond formation. The corresponding chemisorption geometry is with the plane of the benzene ring parallel to the surface. On the contrary, the σ-bonding process results in a chemisorption geometry with the ring tilted at a large angle (up to 90°) with respect to the surface. Previous photoemission data[1] suggested the tilted geometry as the most likely for Si(111)2×1-C_6H_6. One of the goals of the present experiment was to test that suggestion. This was done by theoretically identifying the active molecular benzene modes under the assumption of tilted geometry, establishing a correspondence between those modes and most of our spectral features—and finally justifying the remaining spectral features in terms of the σ-bonding chemisorption process. The data analysis was helped by comparison of our results with those obtained for benzene on metal surfaces.[5–7]

Under the assumption of a tilted geometry, the symmetry of the benzene chemisorption site is C_s.[8] The only symmetry element is a plane perpendicular to the substrate surface and bisecting the ring. Table I identifies the totally symmetric, i.e., dipole active modes in the C_s symmetry. These are the modes contributing to the specular energy-loss spectra. Table II emphasizes the correspondence between those modes and our spectral features. We see in general a shift of the modes to higher vibrational frequencies on going from the free C_6H_6 molecule to benzene chemisorbed on Si(111)2×1. This is due to electronic density changes, again indicative of a strong chemisorption bonding process. The correspondence emphasized by Table II supports the hypothesis of a tilted geometry. Further support to this hypothesis is given by the observed differences between our chemisorbed benzene spec-

TABLE I. Vibrational modes of molecular benzene and deuterated benzene which are dipole active in the C_s symmetry (data from Ref. 8).

Mode	C_6H_6 frequency (cm^{-1})	C_6D_6 frequency (cm^{-1})	Character
ν_1	3062	2293	C—H stretching
ν_2	992	943	C—C stretching
ν_4	673	497	C—H bending
ν_5	3068	2292	C—H stretching
ν_6	1010	969	C—C—C bending
ν_7	995	827	C—H bending
ν_8	703	601	C—C—C bending
ν_{11}	849	662	C—H bending
ν_{12}	3063	2287	C—H stretching
ν_{13}	1486	1335	C—C stretching
ν_{14}	1038	814	C—H bending
ν_{15}	3047	2265	C—H stretching
ν_{16}	1596	1552	C—C stretching
ν_{17}	1178	867	C—H bending
ν_{18}	606	577	C—C—C bending
ν_{19}	975	795	C—H bending
ν_{20}	410	352	C—C—C bending

tra and those of benzene chemisorbed on metal surfaces.[5–7] In particular, the position of some of our spectral features is different from those observed on metal surfaces. Furthermore, our spectra include more features related to molecular-benzene modes than to the metal-C_6H_6 spectra. This is consistent with the lower symmetry of the tilted geometry with respect to the "parallel" geometry—although nondipole excitation[8] cannot be excluded as discussed below.

Peaks *A* and *F* in the Si(111)2×1-C_6H_6 spectra do not correspond to molecular-benzene modes. These peaks are explained in terms of the σ-bonding chemisorption process leading to the tilted geometry. In fact, peak *A* at 540 cm^{-1} is in the typical energy range of the vibrational modes related to σ bonds between a Si atom and a phenyl group.[9] In particular, molecules containing one or more of these bonds always exhibit an infrared absorption peak around 515 cm^{-1}, most likely due to the Si—phenyl stretching.[10] Correspondingly, we attribute peak *A* to a Si—C stretching mode. The formation of Si—C bonds requiring the removal of a hydrogen atom from the benzene molecule is independently supported by the splitting of the π-orbital peak *C* in the photoemission spectra.[1] The removal of H atoms from the benzene molecule is also consistent with the presence of peak *F* in our spectra. In fact, the H atoms released from the benzene molecules are likely to form chemisorption bonds with Si atoms due to the large density of unsaturated dangling bonds on the silicon surface. The vibrational frequency for the Si—H stretching mode of atomic H on cleaved Si is 2015 cm^{-1}, close to that of peak *F*.[3]

Additional evidence for a tilted chemisorption geometry is provided by the comparison of the specular and off-specular Si(111)2×1-C_6H_6 spectra in Fig. 1. The off-specular spectrum shown in Fig. 1 does not exhibit additional peaks with respect to the specular spectrum.[8] This would be consistent with a tilted chemisorption geometry since with the plane of the benzene molecule parallel to

TABLE II. Correspondence between the vibrational modes of molecular benzene and the electron energy-loss spectral features for benzene on Si(111)2×1.

Molecular benzene		C_6H_6 on Si	
Character	cm^{-1}	Peak	cm^{-1}
C—C—C bending	606,703	*B*	780
C—H bending	673		
C—H bending	975,995,1038		
C—C stretching	992	*C*	1060
C—C—C bending	1010		
C—H bending	1178	*D*	1250
C—C stretching	1486,1596	*E*	1610
C—H stretching	3047,3062,3063,3068	*G*	3060

the surface there are dipole-excited modes not active in the specular spectrum but active in the off-specular spectrum. This argument, however, is not *per se* strong evidence of a tilted geometry since we cannot exclude nondipole excitations[8] for some of the modes seen in the specular spectrum, e.g., impact excitation or excitation due to ineffective screening of parallel modes. There is an intensity enhancement of the high-energy peaks in the middle spectrum of Fig. 1 with respect to the specular spectrum. This is due to the electron impact scattering contributions which become more effective as the energy loss ΔE increases, thereby enhancing the off-specular high-energy peaks.[11]

Experiments on chemisorbed deuterated benzene were performed to test the above analysis of the Si(111)2×1-C_6H_6 spectral features. A typical Si(111)2×1-C_6D_6 spectrum is shown in Fig. 2. The spectrum exhibits four features, peaks *A*, *B*, *C*, and *D*, at 500, 1170, 1540, and 2190 cm^{-1}, respectively. Peak *A* is due to a superposition of the features corresponding to the 540- and 780-cm^{-1} losses of Si(111)2×1-C_6H_6. In fact, the C—Si stretching mode at 540 cm^{-1} is not expected to shift much when C_6H_6 is substituted by C_6D_6. On the contrary, the 780-cm^{-1} loss is due to ν_4, ν_8, and ν_{18} modes which shift to lower frequency when deuterium replaces hydrogen (see Table I). Peaks *B*, *C*, and *D* in Fig. 2 correspond to peaks *D*, *E*, and *G* of the Si(111)2×1-C_6H_6 spectra, as suggested by the C_6H_6-C_6D_6 shifts of the corresponding molecular modes in Table I. In particular, the largest shift to lower frequencies is observed for the C—H stretching-mode peak *G*, as should be expected. Peak *C* in Fig. 1 probably merges with peak *A* in Fig. 2, which is asymmetric due to a strong high-energy tail. Following the above interpretatation of peak *F* in terms of formation of Si—H bonds, we should expect to see a Si-D peak in Fig. 2. However, due to the shift to lower frequencies, this peak is expected to merge with peak *C* at 1540 cm^{-1}. Off-specular Si(111)2×1-C_6D_6 spectra confirm the information given by the corresponding spectra involving C_6H_6.

We find no evidence of benzene condensation and multilayer formation as is the case for chemisorbed benzene on Ni and Pd.[5] The fact that benzene sticks on cleaved Si while it does not stick on annealed Si suggests that the cleavage steps of the Si(111)2×1 surface play an important role in the chemisorption process. A qualitative support for this hypothesis comes from the fact that cleaved surfaces with a "rough" appearance typically require two orders of magnitude smaller exposures to reach saturation than "smooth" surfaces (10^2 versus 10^4 L). To provide a further, empirical test of the role of cleavage steps, we monitored the absorption of hydrogen on a surface with a saturation C_6H_6 coverage. The hydrogen exposure (2000 L in presence of a hot W filament) resulted in an intensity increase of the Si—H, stretching peak *F* by about one order of magnitude. Similarly, exposure to hydrogen of a surface with a C_6D_6 saturation coverage produced a low-energy shoulder in peak *D*, in the spectral position of the Si—H stretching mode.[3] These experimental findings demonstrate that a saturation coverage by C_6H_6 or C_6D_6 leaves a high density of unsaturated dangling bonds on the surface. This is consistent with the hypothesis that the C_6H_6 or C_6D_6 chemisorption primarily occurs at cleavage steps.

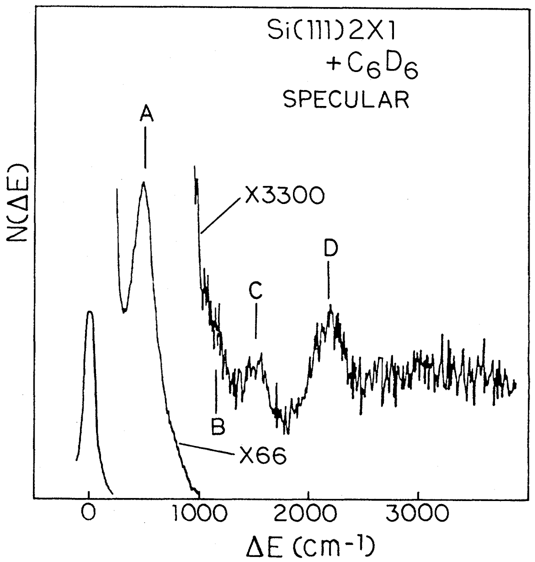

FIG. 2. Surface vibrational spectrum of cleaved Si with a saturation coverage of deuterated benzene. The spectrum was taken in a specular scattering geometry with a primary energy of 6.5 eV. The resolution in this case was 22 meV ($\sim$180 cm^{-1}). The spectral features and their relation to those of Fig. 2 are discussed in the text.

IV. CONCLUSIONS

Our present study confirms the uniqueness of the strongly bound chemisorption state for benzene on cleaved Si at room temperature. In particular, it shows that benzene does not stick on annealed Si(111) at room temperature, suggesting that the chemisorption process involves the cleavage steps of the Si(111) surface. The surface vibrational spectra are consistent with the following hypotheses. The chemisorption process involves the breaking of a C—H bond in the benzene molecule and the formation of a Si—C bond. The resulting chemisorption geometry is with the benzene ring tilted at a large angle with respect to the silicon surface. The hydrogen released during the chemisorption process remains on the Si surface and forms Si—H chemisorption bonds. The saturation coverage by benzene or deuterated benzene leaves a large density of Si dangling bonds on the surface, in agreement with the hypothesis that the molecules are chemisorbed at Si(111)2×1 cleavage steps.

The unique character of the room-temperature chemisorption systems here investigated stimulates further exploration of their properties. Further experiments are planned to investigate the geometric properties of the system and the dependence of the chemisorption process on parameters such as the substrate temperature and the density of cleavage steps.

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[*] To whom all correspondence should be addressed.

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