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Stereo-selective binding of chlorobenzene on Si(111)-7×7

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The adsorption and binding of chlorobenzene (C_6H_5Cl) on clean and D-modified Si(111)-7×7 surfaces have been investigated using high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). On a clean surface, both chemisorbed and physisorbed C_6H_5Cl are observed at an adsorption temperature of 110 K. The HREEL spectra show direct evidence for the presence of both sp^2 and sp^3 carbon atoms in chemisorbed C_6H_5Cl molecules on Si(111)-7×7. Upon D-modification, the chemisorption of C_6H_5Cl decreases rapidly with increasing D-coverage (θ_D). At $\theta_D = 1/3$ ML, only physisorbed chlorobenzene is detected, which strongly suggests the involvement of rest-atoms in the chemisorption of C_6H_5Cl. Combined with the scanning tunneling microscopy (STM) results by Chen *et al.* [Surf. Sci. **340**, 224 (1995)] showing the participation of adatoms in the binding, we propose that the 2,5-carbon atoms in C_6H_5Cl are stereo-selectively di-σ bonded to a pair of adjacent adatom and rest-atom on the Si(111)-7×7 surface, yielding a 2,5-chlorocyclohexadienelike surface adduct. *© 2000 American Institute of Physics.* [S0021-9606(00)70610-6]

I. INTRODUCTION

In recent years, halogen-containing hydrocarbons have attracted increasing attention due to their potential applications in photochemical etching for device fabrication[1–6] or as precursors in low-temperature chemical vapor deposition (CVD) of diamond coatings on various nondiamond substrates.[7] A fundamental understanding on the binding of halogen-containing molecules with well-defined surfaces is of great importance in developing these industrial processes.

Chlorobenzene (C_6H_5Cl) was chosen as a probing molecule for the study of photo- or electron-induced chemistry of adsorbates on Ag(111),[8,9] where its bonding structure as well as dissociation mechanisms under photon- or electron-irradiation have been extensively studied. In contrast, only a few studies have been carried out to study the interaction of chlorobenzene with silicon surfaces. Flaum *et al.*[10] measured the chemisorption probability (S) of a monoenergetic C_6H_5Cl beam on the technologically important Si(100)-2×1 surface. Their results suggest a precursor-mediated chemisorption mechanism, in which the molecule is first trapped into a weakly bound precursor state and then makes a transition to a more stable chemisorption state. More recently, Chen *et al.*[11] investigated the adsorption of chlorobenzene on Si(111)-7×7 at room temperature using scanning tunnelling microscopy (STM). It was found that the center adatoms are more reactive than the corner adatoms, and the faulted half of the unit cell is more favored for C_6H_5Cl adsorption compared to the unfaulted side. To achieve further insight into this particular adsorption system, the information on the vibrational structures of adsorbed C_6H_5Cl is desired, providing direct evidence about the chemical bonding involved in the adsorption process.

The structure of Si(111)-7×7, well studied with a variety of spectroscopic techniques,[12] can be described by the dimer-adatom-stacking fault (DAS) model proposed by Takayanagi *et al.*,[13] shown in Fig. 1. It presents several chemically distinguishable types of surface atoms,[12] including the center and corner adatoms in the inherently different faulted and unfaulted halves, rest atoms and corner holes. Thus, the surface provides a rich array of chemically and spatially inhomogeneous reaction sites. Upon adsorption, C_6H_5Cl is expected to react with the dangling-bonds at these sites on the Si(111)-7×7 surface. The objective of this report is to carry out a vibrational study for better understanding the structural geometry of chemisorbed chlorobenzene on the basis of the STM work by Chen *et al.*[11]

In this paper, we present a systematic investigation of C_6H_5Cl adsorption on both clean and D-modified Si(111)-7×7 surfaces at room temperature as well as at 110 K using thermal desorption spectroscopy (TDS) and high resolution electron energy loss spectroscopy (HREELS). It was found that C_6H_5Cl initially chemisorbs on Si(111)-7×7 at low exposures at 110 K. The increase in exposure leads to the physisorption of C_6H_5Cl. For the room temperature adsorption, only the chemisored state was observed. Both TDS and HREELS results show a nondissociative adsorption of chlorobenzene on the Si(111)-7×7 surface. The structure of

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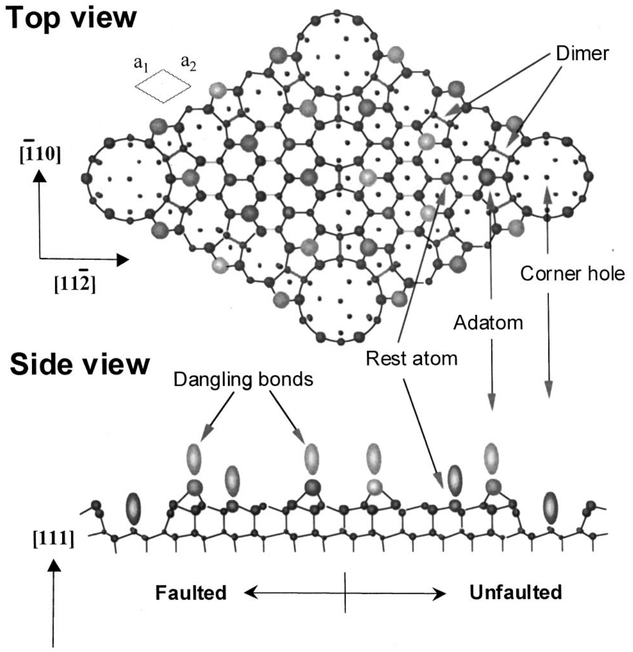

FIG. 1. Dimer-adatom-stacking-fault (DAS) model of the Si(111)-7×7 unit cell proposed by Takayanagi *et al.* (Ref. 13). Only adatoms, rest atoms, and corner hole atoms have dangling bonds. Faulted and unfaulted halves of the (7×7) unit cell are marked.

chemisorbed C_6H_5Cl was found to be similar to that of benzene on Si(111)-7×7.[14] Two well-resolved vibrational features at 2926 (C(sp^3)–H) and 3022 cm^{-1} (C(sp^2)–H) were observed, suggesting the presence of both the sp^3 and sp^2 carbon in the chemisorbed C_6H_5Cl molecules. The premodification of the Si(111)-7×7 surface by atomic-D inhibits the subsequent chemisorption of C_6H_5Cl. Our results demonstrate that the chemisorption is completely blocked when the surface is precovered with 1/3 ML of D-atoms. Based on the previous[11] and present experimental results, we propose that the 2,5-carbon atoms in adsorbed chlorobenzene are stereoselectively di-σ bonded to the pair of adjacent adatom and rest-atom on Si(111)-7×7, yielding a 2,5-chlorocyclohexadienelike structure.

II. EXPERIMENT

The experiments were conducted in a three-level stainless-steel ultrahigh vacuum chamber with a base pressure $<2\times10^{-10}$ Torr.[15] The vacuum chamber is equipped with a high resolution electron spectrometer (LK-2000-14R) for HREELS and a quadrupole mass spectrometer (UTI-100) for TDS and gas analysis. The EEL spectrometer consists of a double-pass 127° cylindrical deflector analyzer (CDA) for the monochromator and a single-pass 127° CDA for the analyzer. For HREELS measurements, a primary energy (E_p) of 5.0 eV, an energy resolution of 5–7 meV [full-width at half-maximum (FWHM)] and an incident angle θ_i of 60° from the surface normal were used. The spectra were taken at the specular direction. In TDS studies, the ionizer of the mass spectrometer is enclosed in a glass envelope with a 4 mm diam aperture located 2 mm from the sample surface. A temperature ramping rate of $dT/dt=2\ \mathrm{K\,s^{-1}}$ employed in the experiment is provided by a RHK temperature controller controlling the power supply to the crystal through a feedback circuit. The controller is capable of producing a reproducible and linear temperature ramp in the region between 110 K and 1200 K.

The Si(111) samples (9 mm×14 mm×0.38 mm) were cut from *n*-type (*P*-doped) silicon wafers with a resistivity of 1–15 Ω cm (Goodfellow, Cambridge). A Ta foil (thickness~0.025 mm) was sandwiched between two experimental samples with a set of Ta clips, and in turn was spot-welded to two Ta posts (diameter~1.5 mm) at the bottom of a Dewar-type LN_2-cooled sample holder. The sample was heated through resistive heating of the Ta foil. Its temperature was measured by a W/Re5%–W/Re26% thermocouple (C-type) attached to the edge of the sample using a high temperature ceramic adhesive (Aremco 516), and confirmed with an optical pyrometer (Minolta, $\epsilon=0.74$). The sample surface was carefully cleaned by Ar^+ sputtering and annealing to 1200 K for 10 min.[14] At least ten cycles of such Ar^+ bombardment and annealing are needed to obtain a carbon-free clean Si(111)-7×7 surface. Surface cleanliness was routinely checked by HREELS since a clean Si(111)-7×7 surface is characterized by a featureless background in the range of 240–4000 cm^{-1}. The (7×7)-reconstruction structure was confirmed by LEED and STM in a separate chamber.

To study the effect of precovered D-atoms on the chemisorption of chlorobenzene, a D-atom doser was fabricated. During the exposure of atomic-D, the Si(111) crystal was placed 3 cm in the line-of-sight from a coiled tungsten filament (Goodfellow, wire diameter=0.25 mm, coil diameter=12 mm) heated to ~1900 K in a D_2 (*g*) background pressure of 2.0×10^{-8} Torr. In order to avoid the irradiation of electrons and light onto the sample, the hot tungsten filament was covered by a tantalum shield with an 8 mm diam hole in the front. Because the dissociation degree of D_2 at 1900 K is not determined, all the D-atom exposures quoted in this report are relative, estimated from the D_2 background pressure and the dosing time.

Chlorobenzene (99.8%) was purchased from Aldrich. It was further purified by freeze–pump–thaw cycles with liquid nitrogen before being dosed onto the crystal through a doser. This procedure gives chlorobenzene free of impurities, confirmed by the mass spectrometer. The vapor of chlorobenzene was introduced into the chamber via a 6 mm diam doser located at 2 mm from the sample surface. Typical background pressure rise in the chamber was $(1-2)\times10^{-10}$ Torr during the dosing process. The chlorobenzene exposures quoted here are normalized to background exposures by comparing the respective thermal desorption spectra after doser and background exposures.

III. RESULTS

A. C_6H_5Cl adsorption on Si(111)-7×7 at 300 K

Figure 2 shows the TDS spectra of $C_6H_5^+$ ($M/e=77$) from the Si(111)-7×7 surface exposed to an increasing amount of C_6H_5Cl ranging from 0.12 L to 10 L at 300 K. Identical desorption features with much lower intensities were also obtained for the $C_6H_5Cl^+$ ($M/e=112$) parent ion,

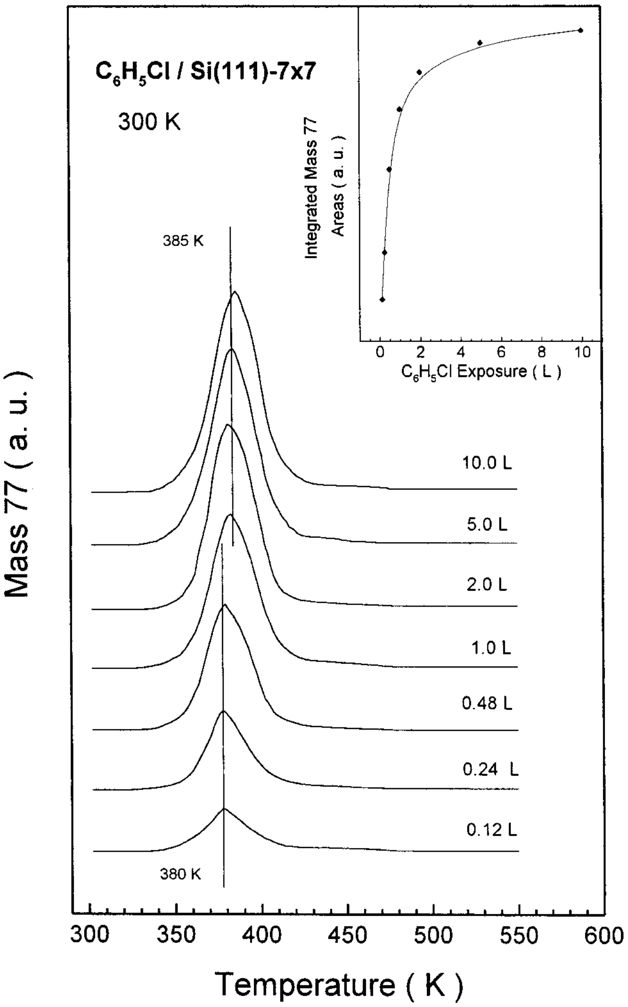

FIG. 2. Thermal desorption spectra of $C_6H_5^+$ ($m/e=77$) from Si(111)-7×7 as a function of C_6H_5Cl exposure at 300 K. Inset plots the desorption peak area as a function of exposure. A heating rate of 2 K s^{-1} was employed.

suggesting the molecular desorption of chemisorbed C_6H_5Cl. There are no $SiCl^+$ ($M/e=63$) ions detected, possibly indicating the nondissociative adsorption of chlorobenzene. At low exposures of 0.12–0.24 L, the observed desorption peak at 380 K is in good agreement with the previous STM study by Chen *et al.*[11] With increasing C_6H_5Cl exposure, the TDS peak slightly shifts towards a higher temperature of 385 K. In addition, a slight tailing in the high temperature side is noticed. This is plausibly attributable to the existence of electronically-unequivalent active sites in the (7×7) unit cell on Si(111).

The inset in Fig. 2 plots the desorption peak intensity for the C_6H_5Cl from Si(111)-7×7 as a function of exposure. There is an almost linear increase of the peak intensity at low exposures (<1 L). The adsorption gradually reaches its saturation at ~10 L. The activation energy for the C_6H_5Cl desorption from Si(111)-7×7 is estimated as $E_{des}=97.5$ kJ/mol, assuming the first order kinetics and a pre-exponential factor of $10^{13}\,s^{-1}$.[16] It is noted that the desorption peak temperature for chlorobenzene is ~20 K higher than that of benzene on Si(111)-7×7,[14] which can be attributed to the electrophilic substitution effect of chlorine atom on the benzene ring.

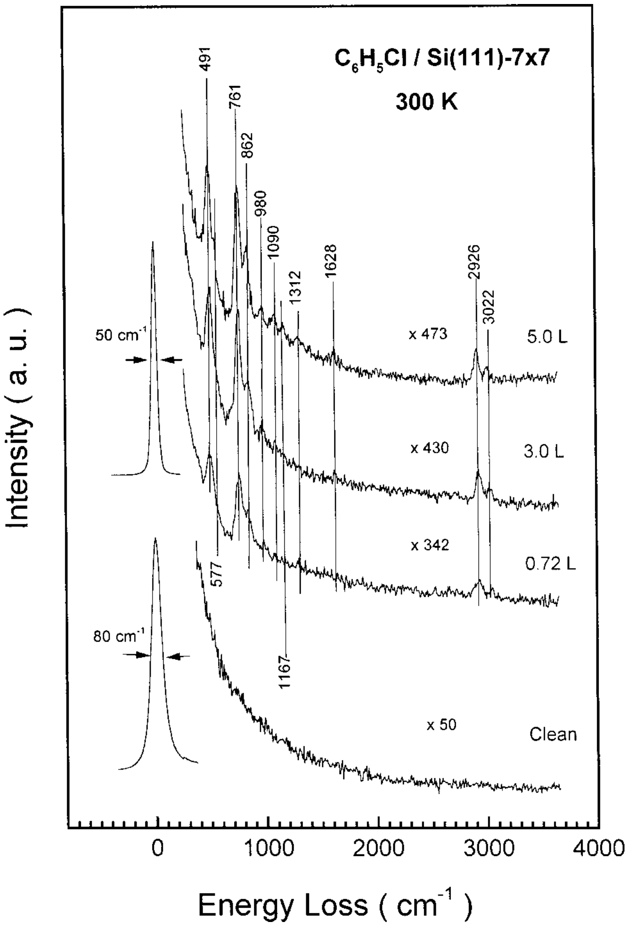

FIG. 3. HREEL spectra as a function of C_6H_5Cl exposure to Si(111)-7×7 at 300 K.

Figure 3 shows the HREELS spectra taken at the specular detection with $E_p=5.0$ eV for the clean Si(111)-7×7 as well as the surface exposed to various amounts of C_6H_5Cl. For the clean surface, the elastic peak has an intensity of $\sim 1\times 10^4$ counts/s and a full-width at half-maximum (FWHM) of ~80 cm^{-1}. Apart from a loss continuum decaying rapidly towards higher loss energies, the clean surface is characterized by a featureless background in the region of 240–4000 cm^{-1}.

Upon C_6H_5Cl adsorption, the elastic peak is significantly enhanced together with the reduction in the loss continuum. After exposing the (7×7) surface to 0.72 L C_6H_5Cl, the elastic peak (FWHM) ≅56 cm^{-1}) becomes much narrower than that of the clean surface. The vibrational energy losses at 3022, 2926, 1090, 980, 862, 761, and 491 cm^{-1} are observed. Upon increasing the C_6H_5Cl exposure up to 5.0 L, additional losses at 1628, 1312, 1167, and 577 cm^{-1} gradually appear. Compared to the literature results and the standard IR data for gas- or liquid-phase C_6H_5Cl, which is summarized in detail in the next section, the typical EEL spectrum for chemisorbed C_6H_5Cl is markedly different, suggesting a significant modification of the molecular structure as C_6H_5Cl is chemically bonded to Si(111)-7×7.

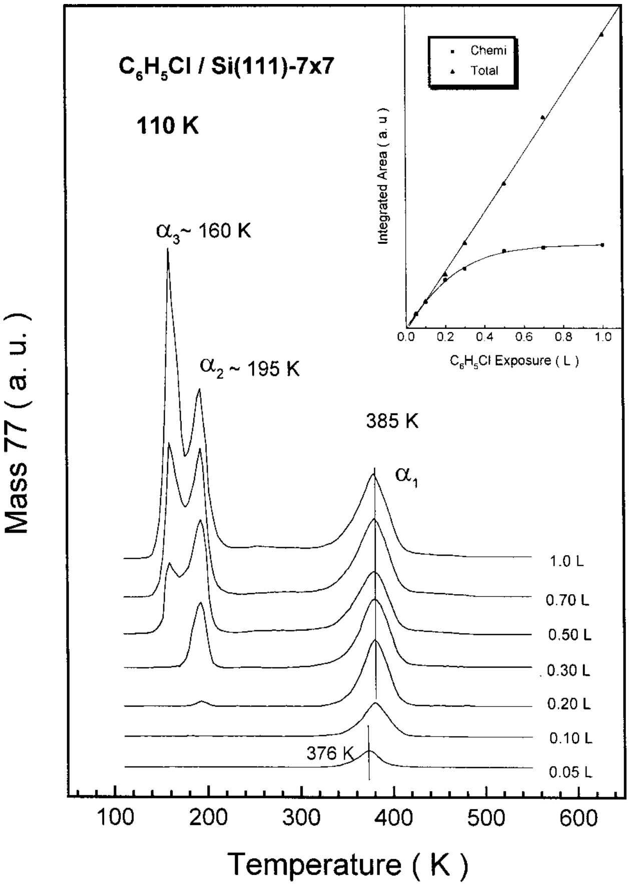

FIG. 4. Thermal desorption spectra of $C_6H_5^+$ ($m/e=77$) as a function of C_6H_5Cl exposure at 110 K. Inset plots the desorption peak areas of $C_6H_5^+$ as a function of C_6H_5Cl exposure; (a) chemisorbed C_6H_5Cl; (b) total amount of adsorbed C_6H_5Cl.

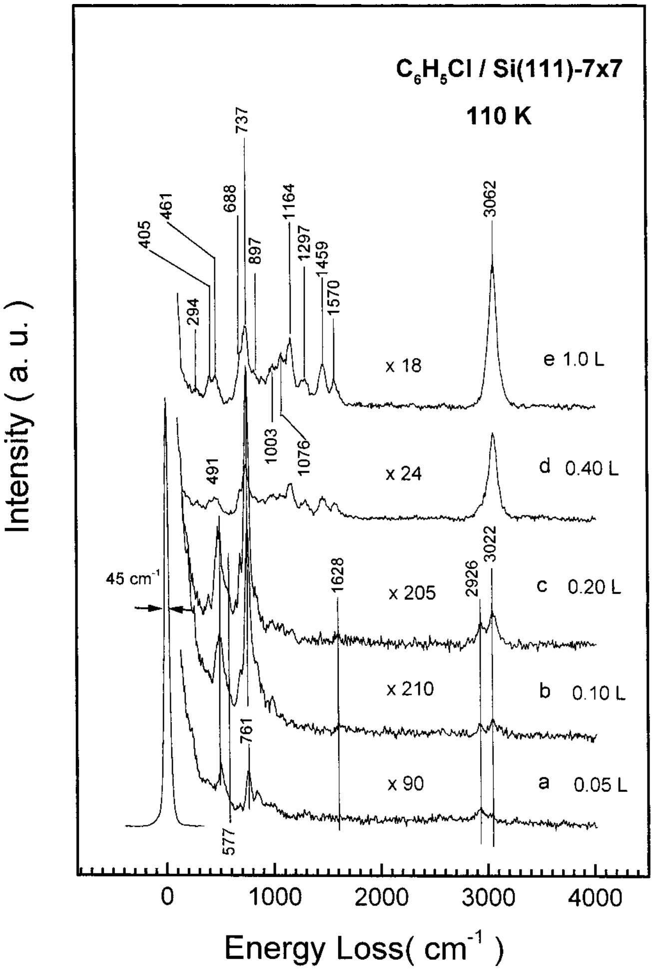

FIG. 5. HREEL spectra as a function of C_6H_5Cl exposure at 110 K.

B. C_6H_5Cl adsorption on Si(111)-7×7 at 110 K

Figure 4 shows the TDS spectra obtained after exposing the Si(111)-7×7 surface to an increasing amount of C_6H_5Cl at 110 K. A total of three molecular desorption peaks were observed. The peak at 376 K (α_1) is initially observed at a low exposure of 0.05 L. Upon increasing exposure, the 376 K peak shifts to 385 K. At 0.2 L, a peak at 195 K (α_2) can be clearly resolved, which saturates at an exposure of ~0.5 L. Higher exposures lead to the observation of a new peak at 160 K (α_3). This low temperature feature (α_3) grows linearly with the C_6H_5Cl exposure without saturation, attributed to the ''bulklike'' multilayers. The α_1 state at 385 K is assigned to the chemisorbed state of C_6H_5Cl on Si(111)-7×7, while the α_2 peak at 195 K is attributed to the first layer of physisorbed chlorobenzene.

The inset in Fig. 4 presents the changes in chemisorption and total amount of adsorption as a function of exposure, obtained from the measurements shown in Fig. 4. The plot indicates that chemisorbed chlorobenzene reaches its saturation at an exposure of 0.5 L. However, the first physisorbed layer starts to appear on top of the chemisorbed C_6H_5Cl at exposures $\geqslant 0.2$ L, indicating the formation of 3D islands, similar to the case of benzene adsorption on Si(111)-7×7.[14] The linear dependence of the total integrated peak area as a function of exposure suggests the unitary sticking coefficient for chlorobenzene adsorption on Si(111)-7×7 at 110 K.

The EEL spectra obtained after C_6H_5Cl adsorption at 110 K are reported in Fig. 5. On a multilayer C_6H_5Cl-covered surface, loss features are readily identified at 294, 405, 461, 688, 737, 897, 1003, 1076, 1164, 1297, 1459, 1570, and 3062 cm^{-1}, shown in Fig 5(e). These loss energies compare well with the vibrational structures of liquid phase chlorobenzene[17] within ~20 cm^{-1}. The peak at 3062 cm^{-1} is assigned to C–H stretching mode, while the losses at 1570 and 1459 cm^{-1} are associated with the combined modes of the C_6 ring stretching and deformation. The losses at 1164, 1076, 1003 cm^{-1} are attributed to the in-plane C–H bending modes, and intensities at 897 and 737 cm^{-1} are related to the C–H out-of-plane bending modes. The feature at 461 cm^{-1} is assigned to the C–Cl out-of-plane bending mode, and the peaks at 405 and 294 cm^{-1} are for the ring out-of-plane and in-plane deformation modes, respectively. In addition, the ring torsion (688 cm^{-1}) and stretching modes (1297 cm^{-1}) are also observed. The detailed assignments for physisorbed chlorobenzene on the Si(111) surface together with the IR data of liquid-phase C_6H_5Cl (Ref. 17) are summarized in Table I.

For exposures <0.2 L, our TDS studies (Fig. 4) show that chemisorption of chlorobenzene is the predominant process. Three additional losses at 577, 1628, and 2926 cm^{-1}

TABLE I. Vibrational assignments of physisorbed and chemisorbed chlorobenzene on Si(111)-7×7 at $T = 110$ K. The vibrational frequencies (cm^{1}) of liquid chlorobenzene are also included for comparison (Ref. 17).

Vibrational assignment	C_6H_5Cl (liquid phase)[a]	Physisorbed C_6H_5Cl/Si(111)-7×7	Chemisorbed C_6H_5Cl/Si(111)-7×7
ring deform	297	294	314
ring deform	400	405	⋯
CCl bend (γCCl)	467	461	491
CSi str (υCSi)	⋯	⋯	577
ring torsion	682	688	⋯
CH bend (γCH)	740	737	761
CH bend (γCH)	902	897	862
CH bend (δCH)	1003	1003	980
CH bend (δCH)	1068	1076	1090
CH bend (δCH)	1174	1164	1167
ring str (υCC)	1271	1297	1312
ring str (δCC) and deform	1445	1459	⋯
ring str (δCC) and deform	1580	1570	1628
CH str (υCH)	⋯	⋯	2926
CH str (υCH)	3071	3062	3022

[a] Reference 17.

are observed in the EEL spectra for exposures <0.2 L (Fig. 5), which are associated with the chemisorbed C_6H_5Cl. Furthermore, the energy loss at 737 cm^{-1} observed for multilayer shifts to 761 cm^{-1} for chemisorbed C_6H_5Cl. All these changes indicate the direct formation of chemisorbed chlorobenzene at a cryogenic temperature of 110 K on the Si(111)-7×7 surface. With increasing exposure of chlorobenzene, the losses associated with chemisorption are gradually screened by the subsequent coverage of physisorbed chlorobenzene.

To further confirm the vibrational structures of chemisorbed chlorobenzene, the EEL spectra were also taken after annealing the multilayer C_6H_5Cl-covered surface to higher temperatures (Fig. 6). Figure 6(a) shows the adsorbed multilayer-C_6H_5Cl features obtained after exposing the sample to 0.4 L C_6H_5Cl at 110 K. Upon annealing to 300 K to desorb physisorbed chlorobenzene molecules, a pure chemisorbed layer on Si(111)-7×7 is prepared. Losses at 314, 491, 577, 761, 862, 980, 1090, 1167, 1312, 1628, 2926, and 3022 cm^{-1} are clearly observed for the chemisorbed molecules. For the convenience of comparison, the assignments of the EEL spectrum of chemisorbed C_6H_5Cl are also summarized in Table I. Two separate vibrational features at 2926 cm^{-1} ($C(sp^3)-H$) and 3022 cm^{-1} ($C(sp^2)-H$) suggest the rehybridization in chemisorbed chlorobenzene. The 1628 cm^{-1} loss is attributed to the nonconjugated $C{=}C$ stretching vibration. The 1167, 1090, 980 cm^{-1} losses are related to the CH in-plane bending modes. The 761 and 577 cm^{-1} peaks are assigned to CH out-of-plane bending mode and Si–C stretching mode, respectively.[14] The energy loss at 491 cm^{-1} is attributable to the out-of-plane C–Cl bending mode.[17] The intensity at 314 cm^{-1} is for the in-plane ring deformation mode. No features at ~2055 cm^{-1} associated with the SiH stretching mode can be observed, indicating the molecular adsorption of chlorobenzene on the Si(111)-7×7 surface. It should be noted that the absence of the 491 cm^{-1} peak after annealing at 400 K implies the C–Cl bond cleavage possibly attributable to the presence of the trace amount of defective sites on our well-prepared sample. The clean surface spectrum of the Si(111)-7×7 surface can be easily recovered without deposition of carbon species by heating the sample to above 500 K further confirming the molecular desorption of chemisorbed chlorobenzene.

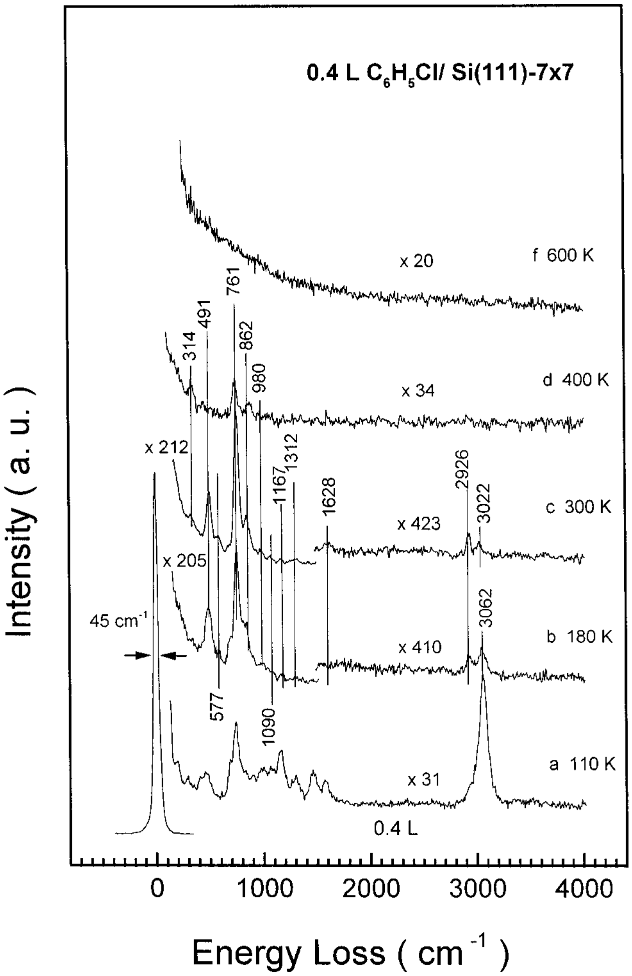

FIG. 6. The temperature dependence of the HREEL spectra for a 0.4 L C_6H_5Cl exposed Si(111)-7×7 at 110 K.

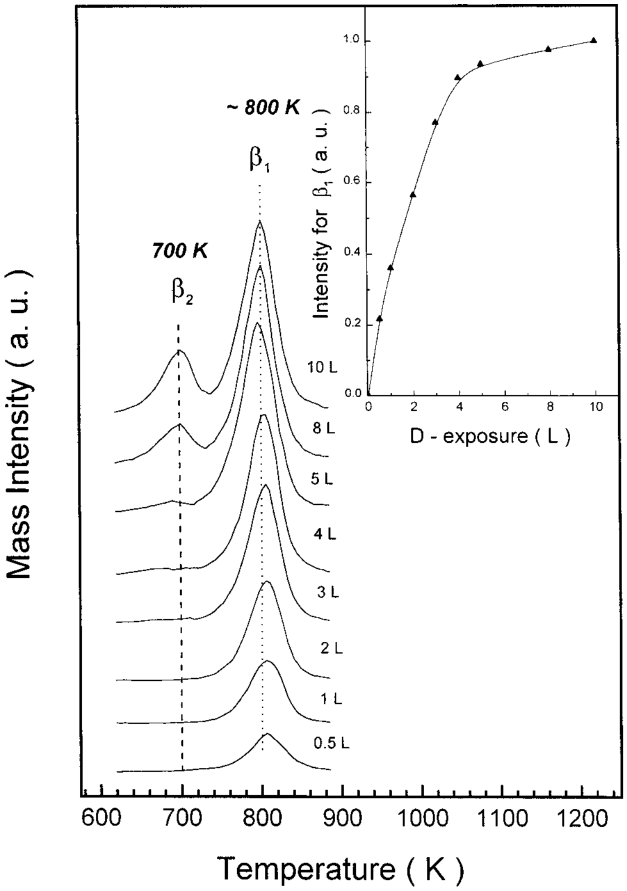

FIG. 7. Thermal desorption spectra of D_2 from Si(111)-7×7 as a function of D-atom exposure. Inset plots the normalized β_1 peak intensity as a function of D-atom exposure.

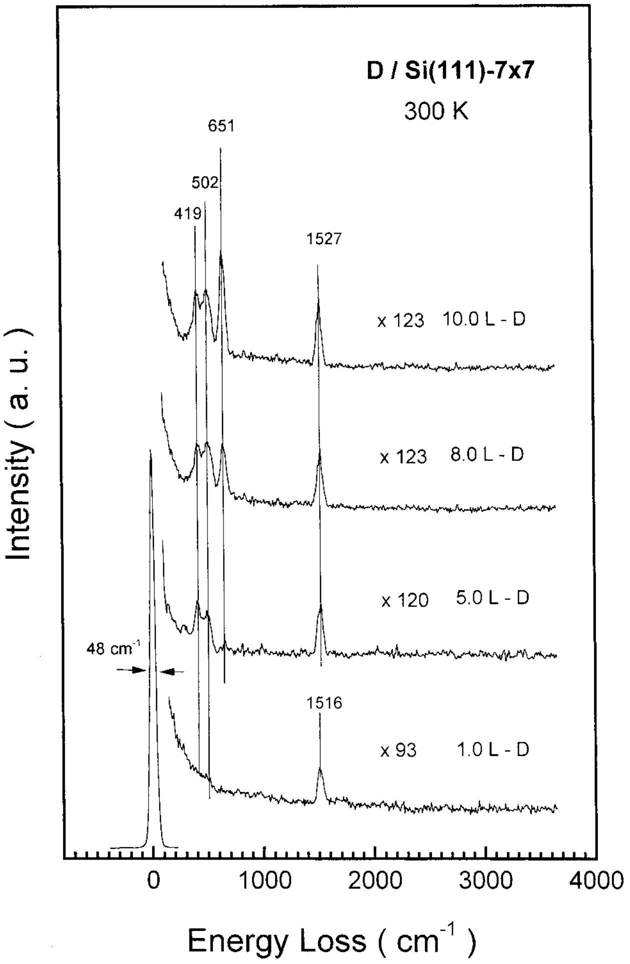

FIG. 8. HREEL spectra as a function of D-atom exposure at 300 K.

C. C_6H_5Cl adsorption on D/Si(111)-7×7

To further understand the surface binding sites involved in the reaction, the adsorption of chlorobenzene was also carried out on D-precovered surfaces. Figure 7 presents the thermal desorption of D_2 from the Si(111)-7×7 surface exposed to various amounts of D-atoms. At low D-exposures, only a single desorption peak at ~800 K is observed, which is labeled as β_1. As the D-exposure is increased, an additional peak (β_2) located at ~700 K appears. This result is in good agreement with the previous work on the desorption behavior of H_2 from H/Si(111)-7×7.[18]

To obtain the nature of the adsorption states of D-atoms, the EEL spectra of the D-covered Si(111)-7×7 surface were taken, shown in Fig. 8. At a low exposure of 1.0 L D-atoms, the strong energy loss at 1516 cm^{-1} together with two weak peaks around 502 and 419 cm^{-1} are observed. At a higher D-exposure of 5.0 L, the losses at 502 and 419 cm^{-1} are intensified and an additional weak loss at 651 cm^{-1} appears. At the saturation exposure, the peak at 651 cm^{-1} develops into the most intensified among all the four losses. Based on the previous work on H(D)/Si(111)-7×7 surface, the loss at 1516 cm^{-1} is assigned to the Si–D stretching mode,[19] attributable to the Si–D species formed at low D-exposures. Because losses at 651, 502, and 419 cm^{-1} are developed with the formation of the β_2 state in the thermal desorption spectra, they are assigned to the $-SiD_2$ scissors modes, the symmetric or asymmetric deformation modes of $-SiD_3$ species.[19] At high D-exposures, the surface species including $-SiD$, $-SiD_2$, and $-SiD_3$ contribute to the 1527 cm^{-1} peak. Combined with our thermal desorption results in Fig. 7, the losses at 419, 502, and 651 cm^{-1} can be readily attributed to the β_2 state of silicon multideuterides, while the peak at 1516 cm^{-1} corresponding to the β_1 state of silicon monodeuteride (Si–D). The inset in Fig 7 plots the normalized β_1 peak intensity as a function of D-exposure. The saturation of the β_1 state shows the complete passivation of the surface dangling bonds by D-atoms, forming monodeuteride on the Si(111) surface. Hence the normalized value for the β_1 state corresponds to the fractional coverage of the atomic D (θ_D) on the surface. It is noted that a D-exposure of 1.2 L results in a $\theta_D \sim 0.3$ ML (monolayer), while the saturation exposure at 10.0 L corresponding to $\theta_D = 1.0$ ML.

Figure 9 shows the thermal desorption of C_6H_5Cl obtained after exposing the clean as well as D-precovered surfaces to 0.2 L at 110 K. On a clean Si(111)-7×7 surface, both physisorbed and chemisorbed states are observed. The chemisorbed state at ~380 K is the dominant feature while the small peak at ~195 K suggests the formation of the first physisorbed layer. However, on D-modified Si(111) surfaces, remarkable changes in the thermal desorption of C_6H_5Cl occur. With increasing D-atom pre-exposure, there is

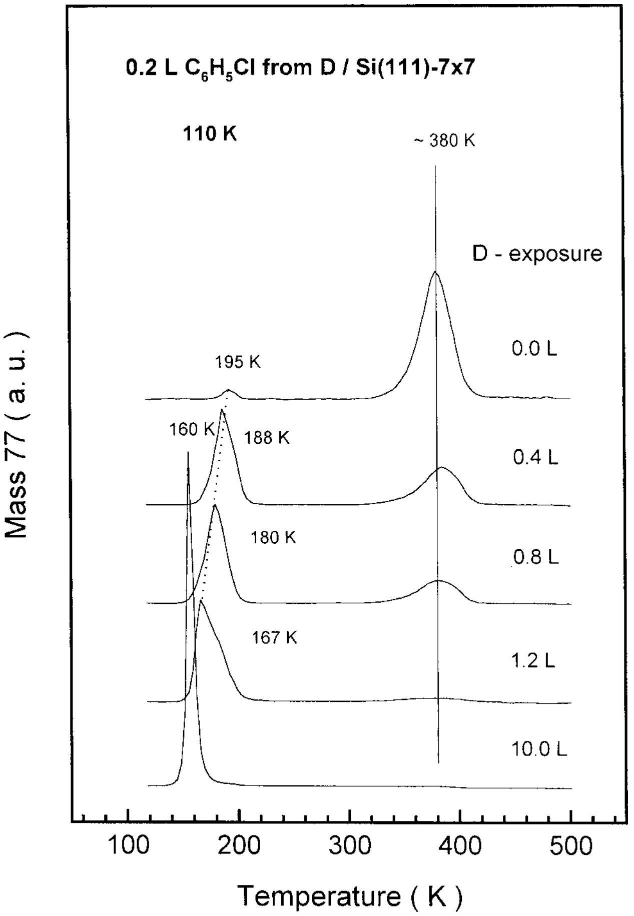

FIG. 9. Thermal desorption spectra for C_6H_5Cl on D-modified Si(111)-7×7.

a rapid attenuation of the chemisorbed peak at 380 K as well as a continuous growth for the lower temperature desorption peak. On a 1.2 L D-atom ($\theta_D = 0.3\,\mathrm{ML}$) predosed surface, the chemisorption is almost totally inhibited, while the peak at 167 K becomes the dominant feature. This clearly demonstrates the direct involvement of the silicon dangling bonds in the chemisorption of chlorobenzene. Since the preferential adsorption of D-atoms onto the rest atoms occurs in the initial stages, which is discussed in the next section, our work further supports the participation of rest atoms in the chemisorption of chlorobenzene. This information can not be provided by the STM studies.

It is also interesting to note that with increasing intensity for the physisorbed peak, there is a continuous shift of the peak maximum to a lower temperature on the D-passivated surface. In addition, the low temperature peak related to physisorbed molecules shifts from 195 to 167 K as increasing the D-exposure to 1.2 L. On a fully D-passivated (10.0 L D_2) Si(111)-7×7 surface, the only chlorobenzene desorption feature is a peak at ~160 K, similar to the desorption of multilayer on a clean surface (Fig. 4). The 195 K peak detected for the first physisorbed layer on a clean surface is not observed for the completely passivated surface. This in turn suggests that sillicon dangling bonds are even involved in the adsorption of the first physisorbed layer of chlorobenzene on a clean surface.

IV. DISCUSSIONS

For the Si(111)-7×7 clean surface, the broad elastic peak as well as the loss continuum observed in the EEL spectrum are attributable mainly to the excitations of two dimensional plasmons associated with the dangling bond electrons and of surface state interband/interband transitions with significant electron–phonon coupling.[20] Upon chlorobenzene adsorption, the intensity of the loss continuum and the width of the elastic peak is markedly reduced. These results indeed show that the dangling bonds of the surface are involved in the formation of the adsorbate complex. The HREELS results of chemisorbed chlorobenzene on Si(111)-7×7 are quite comparable to our previous study of benzene adsorption on Si(111)-7×7,[14] where the coexistence of both sp^3 and sp^2 carbon states in chemisorbed benzene molecules was identified. In the present study, we observed two separate vibrational losses of 2926 and 3022 cm^{-1} for chemisorbed chlorobenzene on the Si(111)-7×7 surface, assigned to the stretching vibrations of $\mathrm{C}(sp^3)-\mathrm{H}$ and $\mathrm{C}(sp^2)-\mathrm{H}$, respectively. This rehybridization in chemisorption is accompanied with the observation of the 577 and the 1628 cm^{-1} losses for Si–C and nonconjugated C═C stretching vibrations, respectively.

The present experimental finding clearly suggests that chemical bonds may form between two carbon atoms in chlorobenzene and two adjacent Si atoms with dangling bonds. Here we adopt the ‘‘bridging configuration’’ proposed by Chen *et al.*,[11] but with a di-σ bonding geometry. We propose that chlorobenzene is di-σ bonded to a pair of neighboring adatoms and rest-atoms on Si(111)-7×7. The proposed model is shown in Fig. 10, where the 2,5-carbon atoms in chlorobenzene bind to a pair of nearest Si atoms having dangling bonds, stereoselectively forming a 2,5-chlorocyclohexadienelike structure. The selective addition of two adjacent Si adatom and rest-atom to the 2,5-sites instead of 1,4-sites in chlorobenzene can be inferred as no significant shift is observed for the out-of-plane C–Cl bending mode in chemisorbed C_6H_5Cl. A slight blue shift for the C–Cl out-

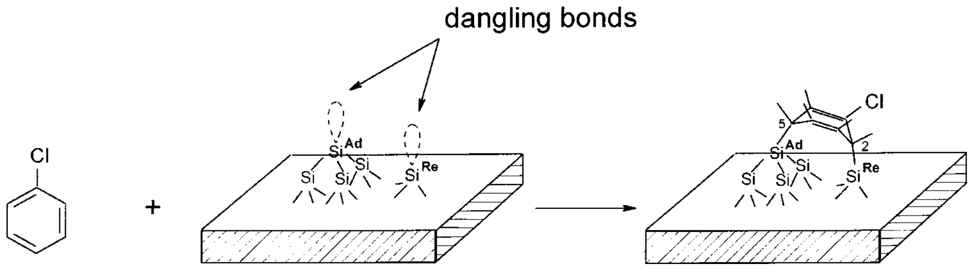

FIG. 10. The schematic diagram of chlorobenzene adsorption on Si(111)-7×7. Note that the 2,5-carbon atoms in C_6H_5Cl are stereoselectively bonded to two adjacent adatom-rest atom sites in the (7×7) unit cell.

of-plane bending mode in the chemisorbed C_6H_5Cl compared to the gas phase molecule can be attributed to the loss of aromaticity in the adsorbed C_6H_5Cl molecule. In addition, the formation of 1,4-adduct would result in a C–Cl bond nearly normal to the surface, resulting in a strong loss peak for the C–Cl stretching vibration. However, no losses related to the C–Cl stretching mode are observed for the monolayer C_6H_5Cl in the EEL spectrum.

The binding of C_6H_5Cl at 2,5-carbon sites can also be argued in terms of the effect of electron rich Cl on subsequent electrophilic addition/substitution reactions of C_6H_5Cl. The adatom and rest-atom on the surface act sequentially as a pair of electrophiles to react with the chlorobenzene molecule. At the first stage of adsorption may form a single-σ bonded transition state involving one adatom or rest-atom site. The two-carbon atom in chlorobenzene would be the most preferred site for the reaction,[21] considering the stability of the single-σ bonded complex formed with the two-carbon atom in C_6H_5Cl. Then, the most energetically favored route is to involve the five-carbon atom in forming the second σ-bond, based on the resonance theory in organic chemistry.

According to the DAS model[13] of Si(111)-7×7 in Fig. 1(a), the direct distance between two adjacent adatom and rest-atom is ~4.5 Å, the closest Si-atom pair with dangling bonds. On the other hand, the distance between two opposite carbon atoms in chlorobenzene is 2.78 Å, and the typical bond length of SiC is 1.8–2.1 Å.[22] Thus, it is reasonable to make the di-σ bond between the chlorobenzene molecule and the adjacent adatom and rest-atom without inducing much strain in the adsorption complex. The bonding of chlorobenzene to the silicon surface through two adjacent carbon atoms would yield a 2,3- or 4,5-cyclohexadienelike complex. However, this structure is energetically unfavorable since the C–C bond in chlorobenzene is 1.39 Å, much smaller than the adatom-rest atom distance.

The energy loss in forming our proposed structure is actually well compensated by the formation of two Si–C bonds. In organosilicon chemistry, the typical bond energy for Si–C ($D_{\mathrm{Si-C}}$) is 75.95 kcal/mol,[23] much greater than 48 kcal/mol [(resonance energy[24]+one double bond)/2=(36+60)/2 kcal/mol].[25] Hence, The di-σ bonding of chlorobenzene to two adjacent adatom and rest-atom is energetically favorable.

It is noted that the chemisorbed chlorobenzene on Si(111)-7×7 is slightly tilted by ~13° with respect to the surface plane according to the present di-σ bonding model, since the adatom is about 1 Å above the rest atom.[26] In contrast, both parallel and tilted orientations for adsorbed C_6H_5Cl were observed on metal surfaces. The HREELS study of C_6H_5Cl adsorbed on Ag(111) was carried out by Song *et al.*[8] The absence of in-plane C–H bending (δ(C–H)) and the C–C stretch modes in specular EEL spectrum showed that the chemisorbed C_6H_5Cl molecules were oriented with their aromatic ring planes parallel to the Ag(111) surface. Using the near edge x-ray absorption fine structure spectroscopy (NEXAFS), the aromatic rings in adsorbed C_6H_5Cl and C_6H_5I were found to be tilted by 45±5° away from the Cu(111) surface.[27]

The STM studies[11] unambiguously showed the participation of adatoms in the chemical bonding of C_6H_5Cl with Si(111)-7×7. Our experiment of C_6H_5Cl adsorption on D-precovered surfaces lends us the further support for the involvement of rest atoms in chemisorption. Both density-functional calculations by Vittadini and Selloni[28] and the STM study by Lo *et al.*[29] have shown that the most stable sites for H-atoms adsorption are the rest atoms on the Si(111)-7×7 surface. Thus, at low D-exposures to Si(111)-7×7 in our experiments, D-atoms are expected to preferentially adsorb on the rest-atom sites. Indeed, a rapid attenuation of the chemisorbed state is observed on the D-passivated surface, especially at $\theta_D < 0.3$ (Fig. 9), indicating the blocking of active sites for C_6H_5Cl adsorption by D-adatoms. The complete inhibition of the C_6H_5Cl chemisorption occurs at $\theta_D \sim 0.3$ ML, at which all the rest-atoms on Si(111)-7×7 are passivated with D-atoms although adatom sites are still not. The "fractional coverage" of rest-atoms in the 7×7 structure is roughly ~0.3 [rest-atoms/(adatoms+rest-atoms+cornerholes)=6/(12+6+1)=6/19]. This observation strongly suggests that the rest-atom sites are necessary for the formation of chemisorption intermediates. Hence, the adsorption studies of C_6H_5Cl on the D/Si(111)-7×7 surface give further support to our di-σ bonding model mentioned above.

The present model for chemisorbed chlorobenzene on Si(111)-7×7 may also account for the observed preferential occupation of center adatom sites rather than corner adatom sites observed in the previous STM work by Chen *et al.*[11] According to the DAS model,[13] a center adatom has two neighboring rest-atoms, but only one for each corner adatom. Thus, for the di-σ bond formation, the probability of a center adatom combining with a rest-atom is two times of that for a corner adatom. In addition, only six adatoms in a 7×7 unit cell can be involved in the reaction, limited by the number of rest-atoms. Thus, the predicted saturation coverage of di-σ bonded chlorobenzene on Si(111)-7×7 is ~0.12 (~6/49). This is in excellent agreement with the value of ~0.14 ML determined in the STM study by Chen *et al.*[11]

V. CONCLUSIONS

The adsorption of chlorobenzene on clean and D-modified Si(111)-7×7 has been investigated using high resolution electron energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). At 300 K, both TDS and HREELS show that C_6H_5Cl chemisorbs nondissociatively on Si(111)-7×7. At 110 K, the physisorption of C_6H_5Cl occurs in addition to chemisorption for exposures $\geqslant$0.2 L. The physisorbed C_6H_5Cl desorbs at 160 K (mutilayer) and 195 K (first layer), while the chemisorbed molecules desorb at a temperature around 385 K. The HREEL study demonstrates the coexistence of both sp^2 and sp^3 carbon in chemisorbed C_6H_5Cl. Upon atomic-D modification of Si(111)-7×7, the chemisorption of C_6H_5Cl is rapidly inhibited. The complete inhibition of the chemisorbed state occurs at $\theta_D \sim 0.3$, at which nearly all the rest-atoms are preferentially passivated. This result strongly suggests the involvement of the rest-atoms in C_6H_5Cl chemisorption. Combined with the previous STM work[11] and our HREELS and TDS results, we propose that the chemisorbed C_6H_5Cl is stereoselectively di-σ bonded through its 2,5-carbon atoms to a pair of neighboring adatoms and rest atoms of Si(111)-7×7, yielding a 2,5-chlorocyclohexadienelike complex.

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