Methyl chloride and trichlorosilane adsorption on Cu(110)

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The adsorption of methyl chloride (CH₃Cl) and trichlorosilane (HSiCl₃) on Cu(110) was studied by temperature-programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and ultraviolet photoelectron spectroscopy (UPS). Methyl chloride interacts weakly with Cu(110) at 100 K, and we estimate from TPD that the adsorption energy is only 8–10 kcal/mol. It adsorbs nondissociatively and reversibly on Cu(110) under these conditions; no evidence of thermal decomposition was observed. HREELS indicates that chemisorbed CH₃Cl adopts a bonding geometry with a symmetry lower than C₃v, presumably bonded to the surface through the Cl atom with the methyl group tipped over with respect to the surface normal. In contrast, HSiCl₃ interacts strongly with Cu(110) at 100 K. Trichlorosilane is initially dissociatively adsorbed, but most of the HSiCl₃ in the chemisorbed monolayer adsorbs molecularly and reversibly due to the strong poisoning of the Cu(110) surface by Cl adatoms. Thermal decomposition, which leaves some Si–Cl and Si–H bonds intact, occurs readily at 140–300 K. Silicon deposited on the Cu(110) surface during HSiCl₃ decomposition is in a metallic bonding environment, directly bonded to the Cu. Low coverages of HSiCl₃ form an H₂ desorption state near 300 K that is attributed to the decomposition of an SiH surface species with an activation energy for decomposition of 18 kcal/mol. This H₂ desorption state is not observed for the thermal decomposition of large coverages of HSiCl₃ on Cu(110) nor for pre-chlorinated Cu(110) surfaces. On pre-chlorinated Cu(110), HSiCl₃ is only weakly adsorbed with an adsorption energy of 8 kcal/mol and is adsorbed nondissociatively with complete reversibility. The importance of these results for understanding the Cu-catalyzed direct synthesis reaction between CH₃Cl and Si to form methylchlorosilanes is discussed.

1. Introduction

Fundamental studies of methyl chloride adsorption and reaction on Cu, Si, and Cu–Si alloy surfaces are important for understanding the Cu-catalyzed direct synthesis of methylchlorosilanes from solid Si and gaseous CH₃Cl. Dimethylchlorosilane ((CH₃)₂SiCl₂), the precursor of linear long chain silicone polymers, is formed selectively in the presence of Cu in the industrial reaction of CH₃Cl with Si [1]. Copper increases the selectivity for (CH₃)₂SiCl₂ from less than 1% on Si to 90% on Cu–Si alloys at 598 K. Understanding how CH₃Cl interacts with Cu is necessary for a basic understanding of the catalytic effect of Cu on the direct synthesis reaction.
Previous studies at high exposures (> $10^7$ L) and 300–600 K have shown that CH$_3$Cl chemisorbs weakly on Cu, Si, and Cu–Si alloy surfaces [2–4]. Methyl chloride has also been coadsorbed with hydrogen on an evaporated thin film of Cu at pressures of 1–30 mTorr [5]. Unfortunately, surface contamination was a problem in this study, since the Cu film was prepared at pressures higher than $10^{-7}$ Torr. No previous studies of the interaction of CH$_3$Cl with Cu single crystal surfaces in UHV conditions are available.

A few previous studies have used electron spectroscopic techniques to study the adsorption of CH$_3$Cl on well-characterized metal single crystal surfaces. A series of methyl halides were adsorbed on Pt(111) and Ni(100) and studied by HREELS and TPD [6,7]. On these surfaces, methyl chloride does not thermally decompose but desorbs intact with a desorption peak temperature of 145 K on Pt(111) and 165 K on Ni(100). Methyl chloride has also been coadsorbed with CO on Cu(100) [8]. The presence of CH$_3$Cl on the Cu(100) surface increases the C–O stretching frequency above the gas-phase value.

Anderson and McConkey [5] reported that CH$_3$Cl, at high pressures (1–30 mTorr) in the presence of H$_2$, decomposed on a thin film of Cu to form gas-phase CH$_4$ and H$_2$ along with Cl adatoms. Methyl chloride was partially dehydrogenated upon adsorption on the Cu film, since some H$_2$ desorbed during the initial adsorption process. Some chemisorbed hydrogen may also have remained, bonded to Cu. The H/C ratio of the adlayer on the film decreased as the surface temperature increased from 273 to 473 K. Thus, after CH$_3$Cl and H$_2$ exposure, hydrogen, chlorine and carbon were present on the Cu film.

Using a $1.7 \times 10^4$ L exposure of CH$_3$Cl, Meyer and Sparnaay [2] found that CH$_3$Cl adsorbs dissociatively on Si(100) and Si(111) surfaces. Adsorption occurs by occupation of uncompensated (dangling) surface bonds. The Si crystal face affects the identity of the adsorbed species formed; CH$_3$Cl dissociates on Si(111) to form the surface species Si$_2$–CH$_3$, Si–Cl, and Si–H, whereas on Si(100), CH$_3$Cl dissociates to form the surface complex H–Si–CH$_3$–Si–Cl.

Trichlorosilane adsorption on Cu(110) is of interest because HSiCl$_3$ initiates a two-step reaction between CH$_3$Cl and Si (with evaporated thin films of Cu) to produce the partially-hydrogenated methylchlorosilane (CH$_3$)$_2$HSiCl with a selectivity of 90% [9]. Without surface Cu, the reaction of Si and mixtures of HSiCl$_3$ and CH$_3$Cl yields other methylchlorosilanes. Copper dramatically increases the selectivity of this reaction for (CH$_3$)$_2$HSiCl, and thus HSiCl$_3$ adsorption on well-defined Cu surfaces may provide insight into this reaction on Cu–Si surfaces. The only previous adsorption study of HSiCl$_3$ was done by Podgorny et al. [4] on polycrystalline Si and Cu–Si alloy surfaces. They reported that trichlorosilane adsorbed reversibly and desorbed at 300 K. Changes in the work function suggested that HSiCl$_3$ adsorbed through a Cl atom. These surfaces were not clean before exposure, however, and these results may have been influenced by surface contamination.

In this paper, we report on studies of the adsorption and reaction of CH$_3$Cl and HSiCl$_3$ on Cu(110) surfaces. We find weak, reversible adsorption of CH$_3$Cl and strong, irreversible adsorption of HSiCl$_3$. The adsorption of HSiCl$_3$ on pre-chlorinated Cu(110) surfaces is briefly investigated. Some comments are also given concerning the nature of the surface chemical bonds for the adsorbed species formed.

2. Experimental

The UHV chamber used in these studies was equipped with instrumentation for high resolution electron energy loss spectroscopy (HREELS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature programmed desorption (TPD) and has been described in detail elsewhere [10].

The Cu(110) crystal (Atomergic Chemetals, 99.999% Cu) was cleaned by repeated cycles of Ar$^+$ ion bombardment (30 min, 300–520 K, 1 kV, and $3 \times 10^{-5}$ Torr Ar) and annealing (1 min, 870 K). Sulfur was the major impurity that diffused to the surface with heating. Thus, some of the cleaning cycles were performed at 520 K to maximize the rate of S segregation to the surface and mini-
The methyl chloride (Matheson, 99.5% purity) was purified by flowing through a 5 Å molecular sieve at 273 K to remove methanol. Trichlorosilane (Petrarch Chemicals, 99.9%), a liquid at 298 K, was degassed by several freeze–pump–thaw cycles. Each gas was dosed through a leak valve from a stainless steel tube doser that was capped by a microcapillary array made of borosilicate glass. This doser provided a significant flux enhancement at the Cu(110) surface and minimized contamination from CH₂Cl and HSiCl₃ decomposition in the UHV chamber. An enhancement factor of 40 was measured for CH₂Cl and assumed for HSiCl₃. The CH₂Cl exposures were also corrected for ion gauge sensitivity [11]. The HSiCl₃ exposures are uncorrected, since the ion gauge sensitivity for HSiCl₃ has not been reported. All CH₂Cl and HSiCl₃ exposures are reported in Langmuir (1 Langmuir (L) = 1 × 10⁻⁶ Torr · s).

Thermal desorption spectra were obtained by using a constant heating rate of 8.3 K/s. The ions monitored during TPD of CH₂Cl were CH₂Cl (50 amu), Cl (35 amu), C (12 amu), and H₂ (2 amu). The ions monitored during TPD of HSiCl₃ were HSiCl₃ (134 amu), HSiCl₂ (99 amu), HSiCl (64 amu), HCl (36 amu), Cl (35 amu), Si (28 amu), C (12 amu), and H₂ (2 amu). Atomic carbon and chlorine ions were monitored in order to insure that we had fully accounted for all C-containing and Cl-containing species that desorbed.

All HREELS and UPS spectra were obtained with the crystal at 100 K. In HREELS, we used a primary beam energy of 1.8 eV. The resolution was typically 77 cm⁻¹ FWHM, with 10⁴ counts/s for the elastic peak from clean Cu(110). The UPS data were taken by using He I (21.2 eV) and He II (40.8 eV) radiation with a double-pass cylindrical mirror analyzer operated in the constant resolution mode with a pass energy of 25 eV (0.4 eV resolution). Work function changes were determined from the changes in kinetic energy for the onset of secondary electron emission after gas adsorption.
be used to give approximate activation energies for comparisons.) Methyl chloride exposures were also made at 300, 450, and 600 K to determine if activated adsorption processes could be observed under UHV conditions. No CH₃Cl decomposition was detected; no desorption occurred in subsequent TPD experiments and the surface was clean as determined by AES measurements after CH₃Cl exposure at elevated temperatures.

Fig. 2 shows vibrational spectra obtained by using HREELS for a 5 L CH₃Cl exposure on Cu(110) at 100 K. Spectra for both specular and off-specular scattering geometries are shown. The four major loss peaks observed are due to the C–Cl symmetric stretch, \( \nu(C-Cl) \), at 696 cm⁻¹, CH₃ rock, \( \rho(CH_3) \), at 1009 cm⁻¹, C–H bend, \( \delta(CH_3) \), at 1428 cm⁻¹, and the C–H stretch, \( \nu(CH_3) \), mode at 3032 cm⁻¹. Table 1 compares the vibrational frequencies of gas-phase CH₃Cl [13] to those of CH₃Cl(a) on Cu(110) and Pt(111) [6,7]. The \( \delta(CH_3) \) and \( \nu(CH_3) \) peaks have been deconvoluted approximately into symmetric and asymmetric contributions in table 1. The frequencies of the CH₃Cl vibrations are not significantly altered in energy from the gas-phase values upon adsorption on either Cu(110) or Pt(111) because CH₃Cl interacts weakly with these metal surfaces. We can also conclude that the adsorption geometry for CH₃Cl(a) on Cu(110) has a symmetry lower than \( C_{3v} \), since we observe a strong, dipole active peak due to the \( \rho(CH_3) \) mode at 1009 cm⁻¹. (This mode is not dipole active within the \( C_{3v} \) point group.) This assignment is supported by other features of the spectra. The peaks for CH₃Cl(a) on Cu(110) in fig. 2a due to the modes \( \delta(CH_3) \) at 1428 cm⁻¹ and \( \nu(CH_3) \) at 3032 cm⁻¹ are much broader (nearly twice) than the instrumental resolution. This can be explained by the contribution of both the symmetric and asymmetric bending and stretching modes to the respective peaks. These asymmetric bending and stretching modes are not dipole active within the \( C_{3v} \) point group, and only become dipole active if the adsorption complex symmetry is reduced to lower than \( C_{3v} \). This also explains the absence of a shift of the \( \delta(CH_3) \) peak at 1428 cm⁻¹ and the \( \nu(CH_3) \) peak at 3032 cm⁻¹ between curves (a) and (b) in fig. 2. After a brief anneal of the CH₃Cl(a) monolayer on Cu(110) to 200 K, the HREELS spectrum was featureless and the surface was clean by AES; CH₃Cl had desorbed completely.

He I and He II UPS spectra are shown in fig. 3. Curves (a) and (c) are the appropriate clean
Cu(110) spectra. The Cu d-band gives rise to intense emission at 2.3 and 3.3 eV binding energy (BE), dominating the clean Cu(110) spectra, with the sp band causing only a small intensity near $E_F$. Adsorption of 5 L CH$_3$Cl produced new peaks (curves (b) and (d) in fig. 3) at 5.7, 9.3, 10.2, and 16.6 eV BE. The UPS spectra of CH$_3$Cl(a) on Cu(110) can be assigned by comparison to the gas phase CH$_3$Cl spectrum [14], which is shown as an insert in fig. 3. We have rigidly shifted the gas phase spectrum to lower binding energy to account for final state relaxation effects and aligned the C(2s) peak at 21.5 eV BE for CH$_3$Cl(g) with the peak at 16.6 eV BE for CH$_3$Cl(a). Emission from the Cl lone pair orbitals at 5.7 eV BE is a very intense feature in the He I spectrum. The broad peak near 10 eV BE can be decomposed into peaks at 9.3 and 10.2 eV, corresponding to the unresolved emission from orbitals derived from the a$_1$ (CCl) and e(CH$_3$) orbitals in CH$_3$Cl(g). Since no additional shifts due to bonding interactions with the surface are observed, weak chemisorption is indicated. A saturation coverage of chemisorbed CH$_3$Cl decreased the work function by 1.1 eV relative to clean Cu(110). Warming the crystal to 200 K reproduced the spectrum of the clean Cu(110) surface.

3.2. Adsorption of trichlorosilane

3.2.1. Trichlorosilane TPD

Fig. 4 shows TPD spectra after 0.03, 0.2, and 0.5 L exposures of HSiCl$_3$ on clean Cu(110). The ionization fragment HSiCl (64 amu) was used to monitor desorption of molecular HSiCl$_3$, since this ion signal is larger than the molecular ion HSiCl$_3$ (134 amu). The ion signals for Si (20 amu), Cl (35 amu), HCl (36 amu), HSiCl$_2$ (99 amu), and HSiCl$_3$ (134 amu) gave the same desorption profiles as HSiCl (64 amu) with the intensities expected from HSiCl$_3$ fragmentation in the mass...
spectrometer. In particular, the 35 amu signals in fig. 4 are associated with fragmentation of HSiCl$_3$. No Cl$_2$ desorption was observed. At the lowest exposure, no signals were detected for 35 or 64 amu, and H$_2$ desorption was barely detectable; HSiCl$_3$ is completely irreversibly adsorbed for this exposure. After 0.2 and 0.5 L exposure, TPD yielded significant amounts of H$_2$, and reversible desorption of chemisorbed HSiCl$_3$ is observed as broad 35 and 64 amu peaks near 150 K. The H$_2$ desorption peak maximum is 290 K for 0.2 L exposure and 300 K for 0.5 L exposure (fig. 1), and the areas for these peaks are the same within experimental error. For 0.5 L exposure, reversibly adsorbed HSiCl$_3$ desorbs from both a chemisorbed state ($T_p = 150$ K) and a weakly bound, physically adsorbed multilayer ($T_p = 125$ K).

The H$_2$ desorption state near 300 K is attributed to the rate-determining unimolecular decomposition of SiH$_x$ surface species, since we will show later by using HREELS that Si--H bonds exist at 300 K. Assuming a preexponential factor of 10$^{13}$ s$^{-1}$, the H$_2$ desorption peak at 300 K corresponds to an activation energy of 18 kcal/mol for decomposition of SiH$_x$ surface species. Still, rate-limiting H$_2$ desorption from Cu(110) may occur near this temperature when H is coadsorbed with Cl and Si, and so the 18 kcal/mol barrier for Si--H bond breaking should be considered best as an upper limit.

The AES spectrum in fig. 5, obtained after a 19 L HSiCl$_3$ exposure and heating to 873 K, shows clearly that HSiCl$_3$ decomposes and deposits Cl(a) and Si(a) on the Cu(110) surface. The Si(LVV) Auger transition was split into two peaks at 90 and 94 eV; this splitting has been observed for bulk Cu$_3$Si [15] and is indicative of Cu--Si bonding. The Si coverage is estimated as $\Theta_{Si} = 0.17$. The Cl coverage is estimated as $\Theta_{Cl} = 0.5$. The Cl(181 eV)/Cu(60 eV) AES peak intensity ratios obtained after TPD are plotted versus exposure in fig. 6. The coverage of Cl increases rapidly at low exposures. Both AES and TPD indicate that decomposition is strongly inhibited after 0.5 L of HSiCl$_3$ exposure.

Fig. 7 shows the TPD spectra obtained after a 0.7 L exposure of HSiCl$_3$ on a chlorine-precovered Cu(110) surface with $\Theta_{Cl} = 0.5$. This represents the largest amount of Cl(a) that is produced by HSiCl$_3$ decomposition. No H$_2$ desorption was observed, and the 35 and 64 amu TPD peaks are those expected for molecular desorption of HSiCl$_3$. This clearly shows that adsorbed Cl inhibits decomposition of HSiCl$_3$ on the Cu(110) surface, and indicates that the reversible HSiCl$_3$ adsorption seen in fig. 4 is due to deactivation of the surface by decomposition fragments. The desorption peak temperatures of the chemisorbed state at 150 K and the physisorbed state at 125 K were not noticeably affected by prechlorination of the
Fig. 7. TPD spectra for saturation coverage of HSiCl$_3$ adsorbed on Cl-precovered Cu(110) with $\theta_1 = 0.5$ ML. H$_2$ (2 amu), Cl (35 amu), and HSiCl (64 amu) ion signals are shown.

surface. Since HSiCl$_3$ chemisorption is completely reversible on Cl-precovered Cu(110), an increase in the area of the TPD peak for chemisorbed HSiCl$_3$ is observed relative to the area associated with physisorbed HSiCl$_3$.

3.2.2. Trichlorosilane HREELS

Vibrational spectra obtained using HREELS are shown in fig. 8 for a multilayer of HSiCl$_3$ adsorbed on Cu(110) at 100 K and for the same layer after heating to 147 and 300 K. The vibrational frequencies of HSiCl$_3$ adsorbed on Cu(110) are compared with those of gas phase HSiCl$_3$ in table 2. For HSiCl$_3$(s) (condensed as ice at 100 K), the intense peaks at 590 and 791 cm$^{-1}$ are assigned to the asymmetric Si–Cl stretch, $\nu_3$(SiCl$_3$), and the Si–H bend, $\rho$(SiH), modes respectively. The peak at 2265 cm$^{-1}$ is assigned to the symmetric Si–H stretch, $\nu_5$(SiH), mode. The peaks at 1200 and 1605 cm$^{-1}$ are either the first overtones or double losses of the 590 and 791 cm$^{-1}$ modes. The peak at 1392 cm$^{-1}$ may be a combination band from the 590 and 791 cm$^{-1}$

modes. The overtone bands are observed in the vibrational spectrum of gas phase HSiCl$_3$, but the combination band is not [16]. The shoulder near 250 cm$^{-1}$ may be the symmetric SiCl$_3$ deformation mode, $\delta_3$(SiCl$_3$).

Table 2

<table>
<thead>
<tr>
<th>Mode No. and symmetry (gas phase)</th>
<th>Vibration</th>
<th>HSiCl$_3$(g) [16]</th>
<th>HSiCl$_3$/Cu(110) 100 K</th>
<th>147 K $^a$</th>
<th>300 K $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1(SiH)$</td>
<td>2265 (s)</td>
<td>2265</td>
<td>2265</td>
<td>2265</td>
<td>2265</td>
</tr>
<tr>
<td>$\rho$(SiH)</td>
<td>1609 (m)</td>
<td>1605</td>
<td>1605</td>
<td>1605</td>
<td>1605</td>
</tr>
<tr>
<td>$\nu_2 + \nu_8$</td>
<td>$\nu_4$(SiCl$_3$)</td>
<td>not obs.</td>
<td>1392</td>
<td>1392</td>
<td>1392</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>$\nu_{as}$(SiCl$_3$)</td>
<td>1207 (w-m)</td>
<td>1200</td>
<td>1200</td>
<td>1109 1062</td>
</tr>
<tr>
<td>$\rho$(SiH)</td>
<td>811 (vs)</td>
<td>791</td>
<td>802</td>
<td>850</td>
<td></td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>$\nu_{as}$(SiCl$_3$)</td>
<td>600 (vs)</td>
<td>590</td>
<td>555</td>
<td></td>
</tr>
<tr>
<td>$\nu_3$(SiH)</td>
<td>$\nu_{as}$(SiCl$_3$)</td>
<td>499 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>$\delta_3$(SiCl$_3$)</td>
<td>254 (m)</td>
<td>250</td>
<td>250</td>
<td>271</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>$\delta_6$(SiCl$_3$)</td>
<td>176 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Dissociative adsorption of HSiCl$_3$ occurs at these temperatures.
Upon warming the surface to 147 K and desorbing any condensed multilayers, the peak at 590 cm\(^{-1}\) appears to shift to 555 cm\(^{-1}\) and the peak at 791 cm\(^{-1}\) shifts to 802 cm\(^{-1}\). While there is a large decrease in the intensity of the \(\nu_{as}(\text{SiCl}_3)\) and \(\rho(\text{SiH})\) modes relative to the losses above 1000 cm\(^{-1}\), the intensity ratio between these peaks remains roughly the same as it was at 100 K. The major new peak that appears is the one at 1109 cm\(^{-1}\), but also the peak at 250 cm\(^{-1}\) is now much sharper. The \(\nu_1(\text{SiH})\) peak at 2265 cm\(^{-1}\) is unshifted and losses at 1200, 1392, and 1605 cm\(^{-1}\) can still be observed. These results suggest that dissociation occurs upon warming the surface to 147 K, but that some undissociated HSiCl\(_3\) is also adsorbed on the surface.

The peak at 555 cm\(^{-1}\) observed at 147 K is broader than the peak at 590 cm\(^{-1}\) in the multilayer HSiCl\(_3\) spectrum at 100 K. This suggests that the adsorbed species formed during HSiCl\(_3\) dissociation have vibrational frequencies very similar to the \(\nu_{as}(\text{SiCl}_3)\) and \(\rho(\text{SiH})\) modes of adsorbed HSiCl\(_3\). Some evidence for this comes from previous infrared studies. The gas phase H\(_2\)SiCl\(_2\) frequencies for the \(\nu_{as}(\text{SiCl}_2)\), \(\nu_1(\text{SiCl}_2)\) and \(\rho(\text{SiH})\) modes are 592, 531 and 953 cm\(^{-1}\) respectively [17]. In H\(_2\)SiCl, the Si–Cl stretch occurs at 551 cm\(^{-1}\) and the Si–H bend occurs at 949 cm\(^{-1}\) [18]. The \(\nu_{as}(\text{SiCl}_2)\) and \(\nu_1(\text{SiCl}_2)\) modes for matrix isolated SiCl\(_2\) are observed between 480 and 500 cm\(^{-1}\) (for various isotopes of Si and Cl) [19,20]. In fig. 8, the peak at 250 cm\(^{-1}\) is most likely an SiCl\(_x\) bending vibration similar in frequency to the SiCl\(_3\) deformation mode observed for HSiCl\(_3\). Assignment of the peak at 1109 cm\(^{-1}\) to the SiH bending mode in an adsorbed HSiCl\(_x\) species is made by comparison with the spectra for gas phase HSiCl and matrix isolated SiH\(_2\) and SiH\(_3\) radicals [21,22]. The H–Si–Cl bending, the Si–Cl stretching, and the Si–H stretching frequencies in HSiCl (formed by flash photolysis of HSiCl\(_3\)) are 808, 522 and \(\approx 1500\) cm\(^{-1}\) respectively [21]. The Si–H bend is observed at 1004 cm\(^{-1}\) in SiH\(_3\), and the \(\delta(\text{SiH}_2)\) and \(\delta_{as}(\text{SiH}_3)\) modes in SiH\(_3\) occur at 926 and 996 cm\(^{-1}\), respectively [22].

Large changes in the vibrational spectrum occur upon heating to 300 K. The \(\nu_1(\text{SiH})\) peak is still present at 2265 cm\(^{-1}\), but the peak at 248 cm\(^{-1}\) shifts to 271 cm\(^{-1}\), the peak at 550 cm\(^{-1}\) disappears, and the peak at 802 cm\(^{-1}\) shifts to 850 cm\(^{-1}\). A new intense peak appears at 1062 cm\(^{-1}\) with a shoulder at 1109 cm\(^{-1}\). The peaks at 1392 and 1605 cm\(^{-1}\) are still present. These changes are due to the formation of HSiCl\(_x\) (where \(x = 1\) or 2), and SiH\(_x\) species due to Si–Cl bond cleavage and SiCl\(_x\) species due to Si–H bond cleavage. Importantly, some Si–Cl, SiCl\(_x\), and Si–H bonds remain intact at this temperature.

### 3.2.3. Trichlorosilane UPS

Fig. 9 and 10 show He I and He II UPS spectra obtained after an exposure of HSiCl\(_3\) on Cu(110) at 100 K (some multilayer could be present) and after the crystal was heated. At 100 K, intense peaks are observed in the He I spectrum at 5.0 and 8.6 eV BE, with smaller peaks occurring at 6.5 and
Fig. 10. HeII UPS spectra for 65 L HSiCl₃ exposure (HSiCl₃ ice) on Cu(110) at 100 K. The crystal was subsequently warmed to 140, 190, and 250 K. Also shown is the HeI UPS spectrum for gas phase HSiCl₃ rigidly shifted to approximately account for final state screening effects. The peaks at 2.5 and 3.4 eV arise from Cu(3d) band emission. In the HeII spectrum, peaks are observed at 6.5, 8.6, 10.0, 12.4, and 13.6 eV BE. The lower intensity of the 5.0 eV peak in HeII compared to HeI spectra indicates significant p-character of the orbitals that comprise this peak.

Also shown in figs. 9 and 10 is the HeI UPS spectrum of gas phase HSiCl₃ [23]. The gas phase spectrum has been rigidly shifted to align the peak at 12.4 eV in our data with emission from the σ_{HSiCl₃} level at 18.5 eV in HSiCl₃(g) to approximately account for final state relaxation effects. Consequently, the following assignments were made for molecular HSiCl₃ on Cu(110) at 100 K: 13.6 eV (σ_{HSiCl₃}), 10.0 eV (σ_{SiCl}), and 6.5 eV (Cl). The peak at 12.4 eV does not correlate with any HSiCl₃(g) molecular orbital and is therefore assigned to some product of HSiCl₃ decomposition in the chemisorbed layer at 100 K. In addition, the 12.4 eV peak persists at 250 K, well above the temperature where TPD indicates HSiCl₃ begins to decompose. Warming the surface to 140 K produces only minor changes in the UPS spectra; no large shifts are observed. Warming to 190 K increases the intensity of Cu(3d) band emission due to HSiCl₃ desorption. In the HeI spectrum, all of the adsorbate-derived peaks are reduced in intensity, but otherwise unchanged. In the HeII spectrum, however, the peak at 13.6 eV (corresponding to emission from the σ_{HSiCl₃} framework molecular orbital in the gas phase) has disappeared; this disappearance is consistent with HSiCl₃ decomposition. By 250 K, adsorbate peaks are observed at 5.0, 8.6, and 10.0 eV BE in HeI spectra and 6.5, 8.6, 9.7, and 12.4 eV BE in HeII spectra.

4. Discussion

4.1. Methyl chloride adsorption

The TPD, HREELS, and UPS spectra all indicate that CH₃Cl adsorbed nondissociatively and reversibly on Cu(110) at 100 K. Methyl chloride was the only species desorbing during TPD experiments; it is weakly bonded to the surface (8–10 kcal/mol) and desorbs intact by 200 K. The vibrational frequencies in HREELS for CH₃Cl(a) were similar to those reported for gas phase CH₃Cl. In addition, the orbital spacings for adsorbed CH₃Cl observed by UPS were nearly unchanged with respect to the gas phase spacings. This confirms that no major bonding change occurs within the molecule due to adsorption. Weak adsorption of CH₃Cl has also been observed on Pt(111) [6], Ni(100) [7], and on thin films of Cu, Ni, W, Pt, Cu, Mn, Al, and Ag [5]. Even for CH₃Cl exposures on Cu(110) at higher temperature, no dissociation occurs at low pressures.

Since all vibrational modes of CH₃Cl are observed both on specular and off-specular in HREELS, CH₃Cl is adsorbed with less than C₃ᵥ symmetry on Cu(110). The 1.1 eV decrease in the work function that accompanies CH₃Cl adsorption suggests that the negative end of the molecular dipole is toward the surface; i.e., the chlorine
atom is closer to the surface than the methyl group. This is consistent with CH$_3$Cl forming a weak dative bond between nonbonding electron pairs on chlorine and unfilled (sp) bands on Cu. We propose a bonding geometry that has less than C$_{3v}$ symmetry with the Cl in the same site that Cl(a) or O(a) adopts on Cu(110).

4.2. Trichlorosilane adsorption

Unlike CH$_3$Cl, which is unreactive, HSiCl$_3$ thermally decomposes on Cu(110). For HSiCl$_3$ exposures up to 0.5 L, adsorption is partially irreversible; HSiCl$_3$ decomposes and H$_2$ desorbs. AES shows that the concentration of Cl(a) rapidly builds up on the surface as a function of HSiCl$_3$ exposure. Trichlorosilane exposures in excess of 0.5 L saturate the surface with Cl(a). We propose that this inhibits further HSiCl$_3$ decomposition, and subsequent exposures on the chlorinated Cu(110) surface result in completely reversible HSiCl$_3$ adsorption.

HREELS and UPS both suggest that HSiCl$_3$ decomposition occurs by (presumably sequential) Si–Cl bond cleavage. The 12.4 eV binding energy peak appears in the HeII UPS spectrum of an HSiCl$_3$ multilayer at 100 K, and persists to 250 K. This observation, coupled with the HREELS spectrum for a HSiCl$_3$ multilayer warmed to 300 K, suggests that HSiCl$_4$, and/or SiCl$_x$ or Si$_x$ species are formed during HSiCl$_3$ decomposition. Unfortunately, the exact identity of the surface species cannot be deduced from HREELS or UPS. The $\nu$(SiH) HREELS peak at 2265 cm$^{-1}$ may be similar to that observed on Cu/Si(111) after exposure to 1000 L of H$_2$ [24]; this peak was attributed to Cu–Si–H surface species. Since the UPS peak at 13.6 eV for HSiCl$_3$/Cu(110) disappears above 140 K, weakly adsorbed intermediates such as H$_2$SiCl$_2$ and H$_2$SiCl were not formed during HSiCl$_3$ decomposition. The binding energies for the $\sigma$ molecular framework orbitals of these molecules are within a few tenths of an eV of those for HSiCl$_3$ [23], and a peak close to 13.6 eV would be expected in each case (assuming a similar final state relaxation shift for these molecules when adsorbed on Cu(110)). This clearly does not occur. Unfortunately, there are no reference spectra to assign the UPS features of adsorbed species that would exist as radicals in the gas phase, such as HSiCl.

After TPD for HSiCl$_3$ exposures greater than 0.5 L, the surface contains approximately 50 at% Cl and 17 at% Si. These AES measurements are another indication of HSiCl$_3$ decomposition. Silicon is in a metallic environment, exhibiting the characteristic Si(LVV) doublet at 90 and 94 eV in AES [15,25–28]. The full-width at half maximum of this doublet is similar to that observed for Cu$_3$Si and for a thin layer of Cu (0.1–0.6 nm) evaporated onto Si(111) [29].

4.3. Comparison of CH$_3$Cl and HSiCl$_3$ on Cu(110)

The differences in reactivity between CH$_3$Cl and HSiCl$_3$ on Cu(110) lend important insight into how these molecules behave during the direct synthesis reaction that forms methylchlorosilanes. One can first consider the bond strengths in each of these molecules in the gas phase. In CH$_3$Cl, the C–H bond strength (D(H,ClC–H) = 101 kcal/mol) is much stronger than the C–Cl bond (D(H,C–Cl) = 83 kcal/mol). Dissociative adsorption would probably occur by breaking the C–Cl bond first, but this cleavage apparently has a relatively high activation barrier since CH$_3$Cl is only weakly adsorbed and neither the Cu–C nor Cu–Cl bonds formed in the products are strong. In trichlorosilane, the Si–Cl bond strength (D(Cl,HSi–Cl) $\approx$ 110 kcal/mol) is much stronger than the Si–H bond strength (D(Cl,Si–H) = 91 kcal/mol). It is difficult to guess whether dissociative adsorption occurs by cleavage of the Si–Cl bond or Si–H bond first, since the Cu–Cl bond is stronger compared to the Cu–H bond. Based on our experimental observations, we propose that Si–Cl bond cleavage occurs first. We also propose that trichlorosilasine is more reactive than CH$_3$Cl because the strengths of the relevant bonds formed in the products (the Cu–Si bond versus the Cu–C bond) provides a greater thermodynamic driving force for dissociation of trichlorosilasine. However, when $\theta_{Cl} = 0.5$, the activation energy for HSiCl$_3$ decomposition increases sufficiently that desorption rather than decomposition occurs. In the ultrahigh vacuum (UHV) environment of our ex-
periments, this results in no further HSiCl₃ decomposition. At atmospheric pressure, however, the situation is somewhat different.

When an evaporated Cu film on Si is exposed to CH₃Cl at 598 K and atmospheric pressure, no reaction to form methylchlorosilanes occurs [9]. The addition of HSiCl₃ activates these Cu/Si surfaces and methylchlorosilanes form. While both CH₃Cl and HSiCl₃ will decompose on the Cu/Si surfaces at 598 K and atmospheric pressure, only HSiCl₃ forms the SiClₓ species (identified by a Si AES transition at 84 eV [9]) that appear to be necessary for methylchlorosilane formation.

The results from our study of CH₃Cl and HSiCl₃ on Cu(110) are consistent with the chemistry observed at atmospheric pressure and furthermore, suggest a model for HSiCl₃ activating the Cu/Si surfaces for direct synthesis. Methyl chloride is less reactive toward Cu than HSiCl₃. Importantly, CH₃Cl does not chlorinate the Cu(110) surface in vacuum, and therefore, may not be reactive enough to chlorinate the Cu/Si surfaces either. Trichlorosilane, on the other hand, is more reactive and provides a source of the SiClₓ(a) fragments that are necessary for methylchlorosilane synthesis on the otherwise rather unreactive Cu/Si surface. The role of SiH(a) fragments formed during HSiCl₃ decomposition, though less clear, may be related to the selectivity observed for formation of (CH₃)₂HSiCl on the Cu/Si surfaces [9].

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