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Room-temperature chemisorption of chloroethylenes on Si(1 1 1)7×7: formation of surface vinyl, vinylidene and their chlorinated derivatives

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Abstract

Chemisorption of a family of six chloroethylenes (C_2H_3Cl, 1,1-$C_2H_2Cl_2$, *cis*-1,2-$C_2H_2Cl_2$, *trans*-1,2-$C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_4) on Si(1 1 1)7×7 at room temperature (RT) has been investigated by vibrational electron energy loss spectroscopy (EELS). The characteristic vibrational EELS features have been used to identify the prominent surface species upon RT adsorption. Like ethylene, C_2H_3Cl has been found to predominantly adsorb in a di-σ bonding geometry to the Si surface, while 1,1-$C_2H_2Cl_2$, *cis*- and *trans*-1,2-$C_2H_2Cl_2$, C_2HCl_3 and, to a lesser extent, C_2Cl_4 appear to undergo dechlorination upon adsorption to form chlorinated vinyl adspecies involving single-σ bonding structures. Evidence of vinylidene ($>C{=}CH_2$) has been obtained for the first time on a semiconductor surface for the adsorption of 1,1-$C_2H_2Cl_2$. The present work illustrates that the molecular structure and the Cl content of chloroethylenes play a crucial role in controlling not only the adsorption geometry but also the extent of dechlorination and the resulting adspecies upon RT adsorption on Si(1 1 1).

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The interaction of chlorinated hydrocarbons and derivatives with silicon surfaces is of practical interest to the semiconductor industry due to their important role as common industrial chemicals for processing and treatment of silicon wafers [1–3]. With most of these compounds being known carcinogens and mutagens, the proper release and destruction of these potentially hazardous chemicals after use has also become an important health and environmental issue. Despite a considerable amount of work on metal-catalyzed degradation of chlorinated ethylenes [4–10], little is known about the interactions of these compounds with silicon. The studies on metal surfaces focus primarily on multilayer (physi-)adsorption near liquid-nitrogen temperature and chemisorption behaviour upon annealing toward room temperature (RT). In particular, using vibrational electron energy loss spectroscopy (EELS) and thermal desorption spectrometry (TDS), Grassian et al. showed that

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for monolayer and submonolayer adsorption at 110 K *cis*- and *trans*-dichloroethylenes form di-σ bonds with Pt(1 1 1) in staggered, alkane-like geometries, and undergo dechlorination above 200 K resulting in a vinylene (1,2-ethenediyl, $H\dot{C}{=}\dot{C}H$ adspecies [1] [5]. Later, Cassuto et al. concluded from their XPS study that on Pt(1 1 1) and Pt(1 1 0) dichloroethylenes (*cis*, *trans* and *iso* isomers), trichloroethylene and tetrachloroethylene are weakly bonded molecularly at 95 K (with the molecular plane parallel to the surface) and they could be desorbed intact above 120–130 K [6]. Furthermore, Yang et al. studied the bonding and reactions of a series of chloroethylenes (vinyl chloride, *cis*- and *trans*-dichloroethylene, and trichloroethylene) on Cu(1 0 0) using TDS and near-edge X-ray absorption fine structure technique [7], and found that molecular adsorption at 95 K involves π-bonding interaction with the Cu surface. Unlike vinyl chloride, which was found to desorb molecularly upon annealing, dechlorination appears to increase with the Cl content for the heavier chloroethylenes, and the resulting dissociated hydrocarbon species (acetylene) could lead to benzene evolution in the case of *cis*- and *trans*-dichloroethylene, and trichloroethylene [7]. On Cu(1 1 0), however, Jugnet et al. proposed, on the basis of their EELS data, a di-σ bonding geometry for *trans*-dichloroethylene chemisorbed at 135 K, which forms acetylene upon annealing to ~200 K with C–Cl bond cleavage [8]. The formation of benzene has also been reported upon further annealing the acetylene-like adspecies or direct adsorption of *trans*-dichloroethylene at 300 K [8]. Benzene evolution by trimerization involving vinylene ($H\dot{C}{=}\dot{C}H$) and ethynyl (–C≡CH) adspecies at low temperature (150 K) was also observed above 370 K upon complete dechlorination of trichloroethylene on Cu(1 1 0) by Laroze et al. [9]. Unlike *trans*-dichloroethylene, the adsorption of trichloroethylene at 140 K was further proposed not to involve a di-σ bonding geometry due to steric hindrance of the Cl ligands. Recently, vinyl chloride was found to desorb molecularly at 119 K in a first-order process after exposure to Ag(1 1 1) at 90 K [11]. Above 126 K, a small portion of the adsorbed molecules apparently dissociates into vinyl and Cl adspecies, which undergo recombinative desorption (as vinyl chloride) in a second-order process upon further annealing above 155 K [11].

Unlike metal surfaces, low-Miller-index single-crystal surfaces of silicon offer unique covalent bonding opportunities for surface reconstruction and chemistry involving directional surface dangling bonds. The interactions of simple unsaturated (π-bonded) hydrocarbons such as ethylene and acetylene on such model surfaces as Si(1 1 1)7×7 and Si(1 0 0)2×1 with one and two directional dangling bonds per surface Si atom, respectively, have been studied extensively [12–16]. As the simplest unsaturated chlorinated hydrocarbons, the family of chloroethylenes is built up from only three basic bonding components (C=C, C–H, and C–Cl), which makes a comparative study of their vibrational spectra manageable yet illuminating, especially about their adsorption properties on Si surfaces. Chloroethylenes are also of fundamental interest because this family of compounds not only is chemically stable at RT but also provides an ideal platform for studying geometric isomeric effects and the effects of halogen substitution on organosilicon chemistry. Of special interests are the possible surface chemical processes involving these three basic bonding components upon chemisorption, which include π-bond saturation, dehalogenation, surface etching and polymerization. In the present work, we present a comparative study of the chemisorption properties of vinyl chloride ($H_2C{=}CHCl$), *iso*-dichloroethylene (1,1-dichloroethylene or vinylidene chloride, $H_2C{=}CCl_2$), (1,2-)*cis*- and *trans*-dichloroethylene ($HClC{=}CHCl$), trichloroethylene ($HClC{=}CCl_2$), and tetrachloroethylene ($Cl_2C{=}CCl_2$) on Si(1 1 1)7×7 at RT by using vibrational EELS.

All the experiments were carried out in a home-built ultra-high vacuum chamber with a base pressure better than 1×10^{-10} Torr [17], which was equipped with an ion(-sputtering) gun, a 4-grid retarding-field optics for reverse-view low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), a differentially pumped 1–300 amu quadrupole mass spectrometer for TDS

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[1] We use “·” or “–” to denote an unpaired electron available for bonding with a substrate atom.

studies, and a home-built multitechnique electron spectrometer for both electronic and vibrational EELS measurements [18,19]. All of the present EELS measurements were conducted with the sample held at RT under specular reflection scattering condition of 45° from the surface normal [17]. A routine energy resolution of 12–20 meV (or 97–160 cm^{-1}) full-width at half-maximum with a typical count rate of 100,000 counts/s for the elastic peak could be achieved with our spectrometer operated at 5 eV impact energy. It should be noted that the calibration and tuning of the EELS spectrometer typically limit the reproducibility of the measured peak positions to 2 meV (or 16 cm^{-1}) in the present work. The Si(1 1 1) sample (p-type boron-doped, 50 Ω cm, 8 mm × 6 mm × 0.5 mm thick) with a stated purity of 99.999% was purchased from Virginia Semiconductor Inc. The Si(1 1 1) sample was cleaned by using a standard procedure involving repeated cycles of Ar^+ sputtering and annealing to 1200 K until a sharp 7 × 7 LEED pattern was observed. The cleanliness of the 7 × 7 surface was further verified in situ by the lack of any detectable vibrational EELS feature attributable to unwanted contaminants, particularly the Si–C stretching mode at 800–850 cm^{-1}. The sensitivity of this SiC feature as an indicator of surface cleanliness was found to be far superior to that achievable by AES using our LEED optics (5% at best). Vinyl chloride (98% purity) was purchased from Matheson, while the liquid samples, *iso*-dichloroethylene (99% purity), *cis*- and *trans*-dichloroethylenes (98% purity), trichloroethylene (99.5% purity), and tetrachloroethylene (99.9% purity) were obtained commercially from Sigma-Aldrich. All the liquid samples were degassed using freeze–pump–thaw cycles before individually dosed to the Si(1 1 1) surface at a typical pressure of 1×10^{-6} Torr by a variable leak valve.

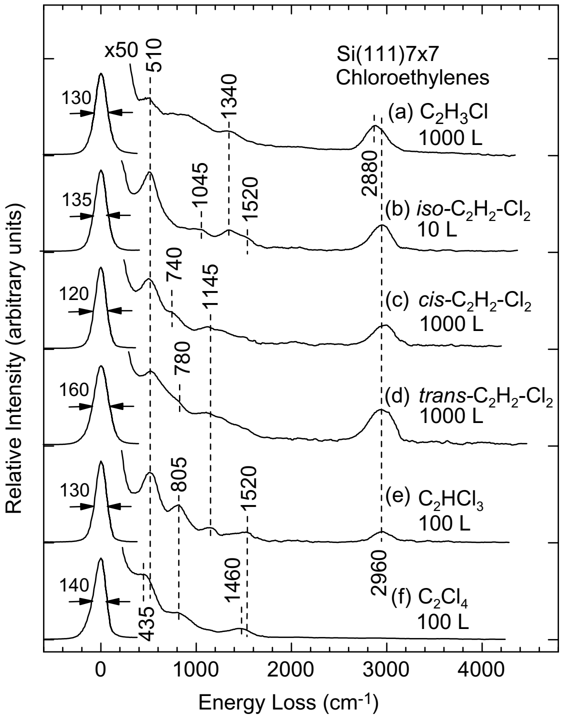

Fig. 1. Vibrational electron energy loss spectra for Si(1 1 1)7 × 7 exposed to (a) 1000 L of C_2H_3Cl, (b) 10 L of 1,1-$C_2H_2Cl_2$, (c) 1000 L of *cis*-$C_2H_2Cl_2$, (d) 1000 L of *trans*-$C_2H_2Cl_2$, (e) 100 L of C_2HCl_3, and (f) 100 L of C_2Cl_4.

Fig. 1 shows the vibrational EELS spectra for a saturation coverage of chloroethylenes on Si(1 1 1)7 × 7 at RT. To facilitate spectral assignments, we compare the surface vibrational EELS data obtained in the present work with the corresponding infrared and Raman spectroscopic data of chloroethylenes obtained in the gas or liquid phase [20–27]. Except for C_2Cl_4, all the chloroethylenes adsorbed on the 7 × 7 surface exhibit a well-defined feature near 2900 cm^{-1}, which is found to correspond well with the characteristic C–H stretching mode. The plateauing of the relative intensity of this vibrational mode has been used to identify the approximate saturation exposure, as depicted in units of Langmuir (1 L = 1 × 10^{-6} Torr s) for individual chloroethylenes shown in Fig. 1. The other more prominent feature, observed at 510 cm^{-1}, is found to be in accord with the characteristic frequency for Si–Cl stretching mode commonly found in 500–540 cm^{-1} [28], and it can be used to indicate the relative surface Cl moiety and the extent of dechlorination upon adsorption. The dissociation of Cl from chloroethylenes is also supported by the evolution from a sharp 7 × 7 LEED pattern for the clean surface to a 1 × 1 pattern upon a saturation exposure. Furthermore, the lack of a Si–H stretching mode commonly found near 2100 cm^{-1} [29] suggests that hydrogen abstraction of chloroethylenes does not play a prominent role on Si(1 1 1)7×7. The observed Cl dissociation is generally consistent with the stronger bond strength of Si–Cl (377 kJ/mol) relative to C–Cl (339 kJ/mol) [1,30]. The generally stronger C–H bond strength (414 kJ/mol) relative to Si–H bond strength (314 kJ/mol) also supports the lack of H abstraction in the present case [30].

The EELS spectrum of adsorbed vinyl chloride shown in Fig. 1a reveals several interesting features. In particular, the C–H stretching mode at 2880 cm^{-1} is found to be at a considerably lower energy than the corresponding mode in the liquid phase (3040–3120 cm^{-1}), which is in good accord with the change in the effective hybridization of the C atoms from sp^2 (liquid phase) to sp^3 (adsorbed phase) [23]. The feature at 1340 cm^{-1} can be assigned to CH_2 scissoring mode while the unresolved structure in the 600–1300 cm^{-1} region may be attributed to C–Cl stretching, C–C stretching, C–H bending, and CH_2 bending (wag, twist and rock) modes [20,21]. The presence of the Si–Cl stretching mode at 510 cm^{-1} suggests partial dissociation of the C_2H_3Cl molecules with C–Cl bond cleavage upon adsorption. However, the lack of any substantial intensity near 1500 cm^{-1} that is commonly attributed to the C=C stretch [23] suggests that the dechlorinated single-σ bonded vinyl adspecies ($H\dot{C}{=}CH_2$) plays only a minor role. Instead, C_2H_3Cl predominantly adsorbs on the 7×7 surface molecularly with a di-σ bonding structure, which is similar to the adsorption structure of ethylene on Si(1 1 1)7×7 [31,32]. These structures are shown schematically in Fig. 2a. In the case of adsorption of ethylene on a well-defined surface, the di-σ adsorption geometry leads to the saturation of the C=C bond and rehybridization of the carbon atoms from sp^2 to sp^3, giving rise to a generally lower C–H stretching frequency in the 2800–3000 cm^{-1} region [31,32].

For *iso*-dichloroethylene on Si(1 1 1)7×7, several distinct features at 2960, 1520, 1340, 1045 and 510 cm^{-1} (Fig. 1b) could be assigned to CH_2 stretching, C=C stretching, CH_2 scissoring, CH_2 rocking, and Si–Cl stretching modes, respectively [23]. The presence of Si–Cl and C=C stretching modes clearly indicates that *iso*-$C_2H_2Cl_2$ dissociates with C–Cl bond cleavage on the silicon surface producing most likely a single-σ bonded 1-chlorovinyl adspecies ($Cl\dot{C}{=}CH_2$), which may lead to vinylidene (>C=CH_2) upon further dechlorination (Fig. 2b). The lack of notable intensity at 700–850 cm^{-1} [23] suggests that the C–Cl stretching mode does not play a prominent role, which provides support for nearly complete dechlorination of the adsorbed *iso*-$C_2H_2Cl_2$ molecules with vinylidene as the favoured adspecies. It should be noted that vinylidene has been identified by Ormerod et al. as the likely adspecies following acetylene adsorption on Pd(1 1 1) at 300 K [33]. The present work provides the first evidence for the presence of vinylidene on a semiconductor surface through total dechlorinated adsorption of *iso*-dichloroethylene. The adsorption of vinylidene is physically plausible via a back-bond breaking mechanism [15], which could create additional bonding sites between an adatom and a pedestal atom or between two pedestal atoms. Such back-bond breaking mechanism has been proposed for oxygen [34] and chlorine insertion on Si(1 1 1) [35], and we believe that a similar mechanism is responsible for Cl dissociation observed in the present work. The discernible difference of 80 cm^{-1} observed in the C–H stretch between the adsorbed *iso*-$C_2H_2Cl_2$ (2960 cm^{-1}, Fig. 1b) and C_2H_3Cl (2880 cm^{-1}, Fig. 1a) confirms the difference in the carbon hybridization between sp^3 in the di-σ bonded C_2H_3Cl and sp^2 either in the single-σ bonded 1-chlorovinyl or double-σ bonded vinylidene adsorption structures.

The surface vibrational features for *cis*-$C_2H_2Cl_2$ (Fig. 1c) and *trans*-$C_2H_2Cl_2$ (Fig. 1d) adsorbed on Si(1 1 1)7×7 are strikingly similar. In particular, the common features at 2960, 1145, 740–780 and 510 cm^{-1} could be assigned to C–H stretching, CH in-plane bending, C–Cl stretching, and Si–Cl stretching modes, respectively [23]. The similar locations of the C–H stretching mode (at 2960 cm^{-1}) for *iso*-$C_2H_2Cl_2$ and the *cis* and *trans* isomers again suggest sp^2 hybridization for the C atoms. The presence of the strong peak at 510 cm^{-1} indicates C–Cl cleavage likely with the 2-chlorovinyl surface species ($H\dot{C}{=}CHCl$), while the lack of Si–H peak near 2100 cm^{-1} [29] suggests that C–H bond cleavage is not preferred. Indeed,

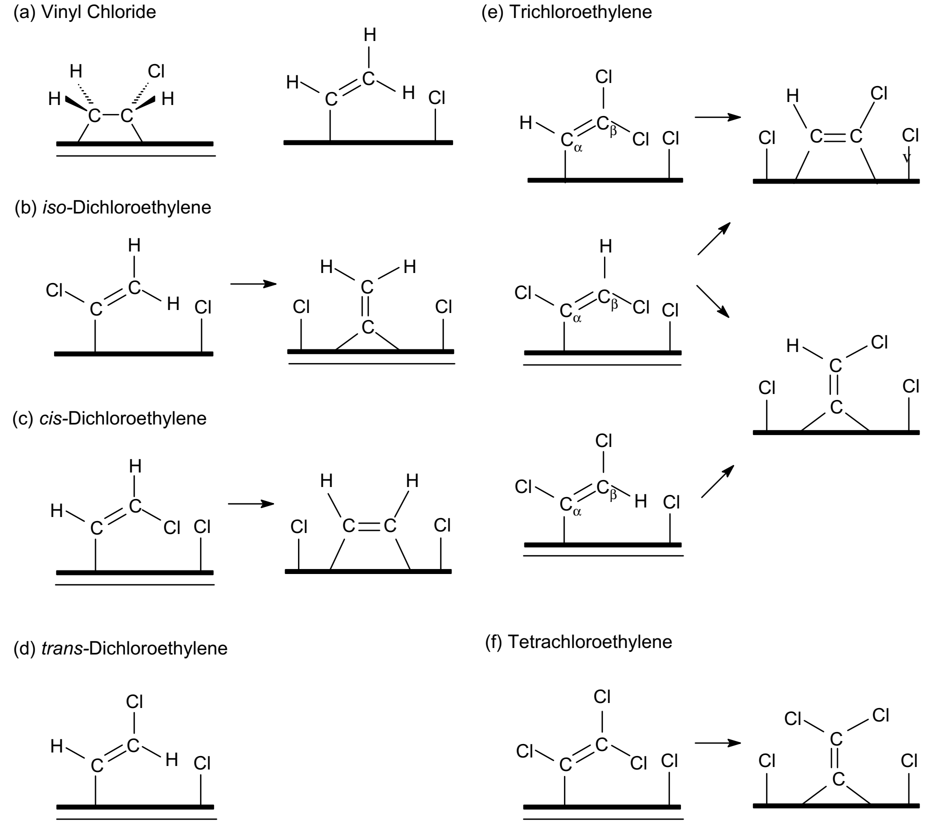

Fig. 2. Schematic diagrams of the plausible adsorption structures for Si(1 1 1)7×7 exposed to (a) 1000 L of C_2H_3Cl, (b) 10 L of 1,1-$C_2H_2Cl_2$, (c) 1000 L of *cis*-$C_2H_2Cl_2$, (d) 1000 L of *trans*-$C_2H_2Cl_2$, (e) 100 L of C_2HCl_3, and (f) 100 L of C_2Cl_4. The preferred adsorption geometries are underlined.

the general similarity of the EELS spectra for the *cis* and *trans* isomers further supports that they both involve a common adsorption species such as the single-σ bonded $H\dot{C}{=}CHCl$ (Fig. 2c and d). In the case of *cis*-$C_2H_2Cl_2$, further dechlorination of $H\dot{C}{=}CHCl$ could lead to a di-σ bonded vinylene (1,2-ethenediyl) adspecies $H\dot{C}{=}\dot{C}H$ (Fig. 2c), similar to the adsorption structure found for acetylene [14,16]. It should be noted that for *cis*-$C_2H_2Cl_2$ adsorbed on Cu(1 0 0), the corresponding TDS data obtained by Yang et al. [7] suggests that once the first C–Cl bond breakage occurs (at 185 K), the second C–Cl bond cleavage could follow promptly. The absence of a CH_2 group in the *cis* and *trans* isomers is clearly reflected by the weaker EELS intensity at 1340 cm^{-1} (Fig. 1c and d), which corresponds to the CH_2 scissoring mode in their *iso* homolog (Fig. 1b). Furthermore, the apparently stronger relative intensity for the Si–Cl stretching mode at 510 cm^{-1} relative to that for the C–Cl stretching mode near 750 cm^{-1} in *iso*-$C_2H_2Cl_2$ in comparison with the *cis* and *trans* isomers supports our earlier hypothesis that the di-σ bonded vinylidene ($>C{=}CH_2$) structure is a plausible adsorption structure for *iso*-$C_2H_2Cl_2$ (Fig. 2b), in contrast to the *cis* and *trans* isomers for which the single-σ-bonded $H\dot{C}{=}CHCl$ adsorption structure is more likely (Fig. 2c and d). The absence of intensity for the C–Cl stretching mode near 750 cm^{-1} in *iso*-$C_2H_2Cl_2$ (Fig. 1b), in contrast to the presence of notable intensity in the same region in the *cis* and *trans* isomers (Fig. 1c and d), further reinforces support for the vinylidene bonding model (Fig. 2b).

Like dichloroethylenes, the well-defined features observed at 2960, 1520, 1145, 805, and 510 cm^{-1} for trichloroethylene on Si(1 1 1)7×7 shown in Fig. 1e can be attributed to C–H stretching, $C{=}C$ stretching, CH in-plane bending, C–Cl stretching, and Si–Cl stretching modes, respectively [23]. Given the presence of Cl dissociation (as indicated by the Si–Cl stretching mode at 510 cm^{-1}) and the absence of C–H bond cleavage (as indicated by the lack of Si–H stretching mode near 2100 cm^{-1}), the plausible surface species could only include the single-σ bonded 2,2-dichlorovinyl ($H\dot{C}{=}CCl_2$) and 1,2-dichlorovinyl ($Cl\dot{C}{=}CHCl$, with the *cis* and *trans* conformers depending on whether the Cl atom on the C_β atom is closer to the surface—see Fig. 2e). The corresponding bonding (C_α) side of the $H\dot{C}_\alpha{=}CCl_2$ and $Cl\dot{C}_\alpha{=}CHCl$ adspecies are similar to the adsorption structures for *cis* and *trans*-dichloroethylene ($H\dot{C}_\alpha{=}CHCl$) and for *iso*-dichloroethylene ($Cl\dot{C}_\alpha{=}CH_2$), respectively. However, the saturation exposure for *cis* and *trans*-dichloroethylene on the 7×7 surface (>600 L) is found to be considerably higher than that for *iso*-dichloroethylene (∼10 L), which suggests that the latter adsorption structure $Cl\dot{C}{=}CHCl$ is likely the more prominent structure. Moreover, the relative intensity of the Si–Cl stretch (at 510 cm^{-1}) to that of the C–H stretch feature (at 2960 cm^{-1}) for trichloroethylene on the 7×7 surface (Fig. 1e) is closer to that for *iso*-dichloroethylene (Fig. 1b) than its corresponding *cis* (Fig. 1c) and *trans* isomers (Fig. 1d). This observation is also consistent with a preferred adsorption structure that involves $Cl\dot{C}{=}CHCl$ with one Cl attached to the C_α atom upon adsorption (Fig. 2e), similar to the proposed adsorption geometry of the *iso*-dichloroethyene (Fig. 2b). Furthermore, as in the case of 1-chlorovinyl adspecies ($Cl\dot{C}{=}CH_2$) resulting from *iso*-dichloroethylene adsorption, the 1,2-dichlorovinyl adspecies ($Cl\dot{C}{=}CHCl$) from trichloroethylene adsorption could undergo further dechlorination to form either chlorovinylidene ($>C{=}CHCl$) or chlorovinylene ($H\dot{C}{=}CCl$)—See Fig. 2e. Further dechlorination of the less probable structure $H\dot{C}{=}CCl_2$ would also produce chlorovinylene (Fig. 2e).

Finally, Fig. 1f shows the EELS spectrum for tetrachloroethylene adsorbed on Si(1 1 1)7×7. The three notable features observed at 1460, 805 and 435 cm^{-1} can be assigned to $C{=}C$, C–Cl, and Si–Cl stretching modes, respectively [23]. However, the small shift of the feature at 435 cm^{-1} relative to 510 cm^{-1} (commonly assigned to Si–Cl stretch) suggests the presence of other vibrational modes such as various lower-lying CCl_2 bending modes [23]. These EELS features are consistent with the presence of a single-σ bonded trichlorovinyl ($Cl\dot{C}{=}CCl_2$) adsorption species, which could further dechlorinate to a dichlorovinylidene ($>C{=}CCl_2$) structure (Fig. 2f). The generally weaker vibrational features of adsorbed C_2Cl_4 (Fig. 1f) relative to the other chloroethylene homologes (Fig. 1a–e) suggest weaker adsorption of tetrachloroethylene on Si(1 1 1)7×7, which may be related to the non-polar nature and the molecular symmetry of the adsorbate. Furthermore, the weak adsorption may also be related to the relatively large size of the Cl atoms that produce sufficient steric effects to prevent adsorption via a di-σ bonded geometry as observed for ethylene [13] and vinyl chloride (Fig. 2a).

In summary, we have obtained the EELS spectra of six chloroethylene compounds (vinyl chloride, *iso*-, *cis*-, and *trans*-dichloroethylenes, trichloroethylene, and tetrachloroethylene) adsorbed on Si(1 1 1)7×7 at RT. Although di-σ bonding appears to be preferred for vinyl chloride, the single-σ bonding structure with Cl dissociation predominates in the case of the heavier chloroethylenes: (*iso*-, *cis*- and *trans*-)dichloroethylenes, trichloroethylene, and to a lesser extent tetrachloroethylene. The presence of novel vinyl ($H\dot{C}{=}CH_2$) and vinylidene adspecies ($>C{=}CH_2$) as well as their chlorinated derivatives as plausible adsorption products could be inferred from the characteristic vibrational features. The present work demonstrates the important roles of molecular symmetry and Cl content of the adsorbate on the RT chemisorption of this family of chloroethylenes on Si(1 1 1)7×7, which ultimately control the surface chemistry of these important unsaturated chlorinated hydrocarbons.

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