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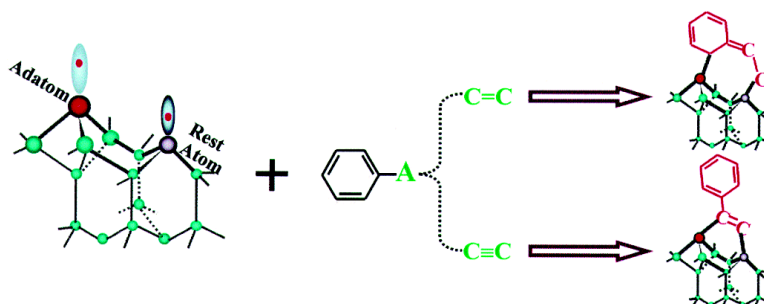# Attachment of Styrene and Phenylacetylene on Si(111)-7×7: The Influence of Substitution Groups on the Reaction Mechanism and Formation of -Conjugated Skeletons

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Attachment of Styrene and Phenylacetylene on Si(111)-7×7: The Influence of Substitution Groups on the Reaction Mechanism and Formation of π-Conjugated Skeletons

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Abstract: The interactions of styrene and phenylacetylene and their isotope substitutions with a Si(111)-7×7 surface have been studied as model systems to mechanistically understand the chemical binding of conjugated π-electron systems to *di*-radical-like silicon dangling bonds of the adjacent adatom-rest atom pair. Vibrational studies show that styrene mainly binds to the surface through a diradical reaction involving both the external C=C and its conjugated internal C=C of the phenyl ring with an adjacent adatom−rest atom pair, forming a 5-ethylidene-1,3-cyclohexadiene-like skeleton. On the other hand, phenylacetylene was shown to be covalently attached to Si(111)-7×7 through the external C≡C, forming a styrene-like conjugation system. These experimental results are consistent with density functional theory calculations. The different binding mechanisms for styrene and phenylacetylene clearly demonstrate that reaction channels for multifunctional organic molecules are strongly dependent on the chemical and physical properties of the functional groups. The resulting π-electron conjugation structures may possibly be employed as intermediates for further organic syntheses and fabrication of multilayer organic films on semiconductor surfaces.

I. Introduction

Recently, there has been growing interest in the functionalization of semiconductor surfaces with organic molecules[1−9] to modify the interfacial properties of silicon systems. Through covalent attachment, molecular properties such as chirality, molecular recognition, conductivity, nonlinear optical properties, and biosensitivity, can be readily introduced onto silicon surfaces. A successful example for the application of organic-modified Si surfaces is the fabrication of sensitive Si-based nanosensors.[10] Another important motivation for binding organic molecules on semiconductors is to grow multilayer organics in a controllable fashion.[1] Starting from the surface-bound monolayer with an ordered two-dimensional (2-D) structure, one can then develop strategies to construct 3-D materials by subsequent covalent attachment of organic layers. Successful fabrication of ultrathin organic films will create molecular architectures for advanced optical, electronic, and biorelated systems.[7−10]

For achieving these objectives, the most important step is to gain a detailed understanding of the reaction selectivity,

configuration, and formation mechanisms of functional organic molecules on Si surfaces and create precursor templates with desired functionalities for developing multilayered Si-based molecular systems. Most of the previous work in this area focused on the studies of attachment chemistry of some simple unsaturated hydrocarbons on Si surfaces.[2] However, to extend the organic modification and functionalization to allow for the next-layer covalent attachment, multifunctional molecules are preferred for the initial binding. Upon covalent attachment, this layer acting as a precursor, in turn, should retain or newly produce (during the interaction with Si surfaces) one or more reactive functional groups for the further binding of other organic molecules. The formation of surface intermediates containing delocalized π-electron structures is of special interest due to the possibility of synthesizing larger oligomers and polymers known as semiconductors or metals[11,12] in a vacuum through their conjugated structures.

Si(111)-7×7, the so-called dimer-adatom-stacking (DAS) faulted model,[13] can be employed to serve as a model template for understanding the interaction between organic molecules and Si surfaces due to its multiple reactive sites with different electronic structures and spatial distributions in one unit cell. Nineteen dangling bonds in every unit cell are located at 12 adatoms, 6 rest atoms, and 1 corner hole. The charge transfer

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occurs preferentially from adatoms to rest atoms, thereby resulting in completely occupied dangling bonds at rest atoms and the corner hole as well as partially occupied or empty dangling bonds at adatoms.[14]

Both experimental and theoretical studies showed that the adjacent adatom−rest atom pair can serve as a *di*radical to react with unsaturated organic functionalities.[15−23] The covalent binding of three typical unsaturated hydrocarbons, including ethylene, acetylene, and benzene, on Si(111)-7×7 has been extensively investigated. Ethylene and acetylene are both *di*-σ-bonded to the neighboring adatom−rest atom pair (diradical), yielding "ethanic"- or "ethylenic"-like adsorbates, respectively.[22,23] Being a π-conjugated system, however, benzene is selectively bound to Si(111)-7×7 with a reaction scheme involving two conjugated C=C bonds of benzene and the adjacent adatom and rest atom pair, forming an unsaturated 1,4-cyclohexadiene-like reaction structure on the surface.[19] Choosing the reaction pathway involving a conjugated "diene", but not a single C=C bond, is mainly attributable to the smaller strain in the resulting adduct.

Phenylacetylene and styrene are two conjugated π-electron molecules made of a phenyl ring and C≡C/C=C groups. In fact, they can be considered as monosubstituted benzene. Thus, investigating their interactions with Si surfaces will provide the correlation of reaction selectivity and binding configuration with the functional groups in the molecule, offering the necessary flexibility in the functionalization and modification of silicon surfaces.

In this paper, the covalent attachment chemistry of styrene and phenylacetylene on Si(111)-7×7 was systematically studied with the aim of elucidating the influence of functional modification of the phenyl ring on the reaction channel of π-conjugated multifunctional molecules on Si surfaces and developing functional intermediates suitable for further fabrication of molecular architectures. HREELS was used to characterize the vibrational properties of styrene and phenylacetylene and their isotope substitutions on Si(111)-7×7. DFT calculations (pBP/DN** in Spartan 5.1) were carried out to optimize the chemisorption geometries and calculate their adsorption energies and vibrational frequencies. Our experimental results together with the DFT calculations show that (a) styrene is chemically attached to Si(111)-7×7 through the reaction involving both the external C=C bond and its conjugated C=C bond of the phenyl ring, producing a 5-ethylidene-1,3-cyclohexadiene-like conjugated skeleton at the organic/silicon interface and (b)

phenylacetylene is covalently bonded to Si(111)-7×7 through an addition reaction of the C≡C with the neighboring adatom−rest atom pair, forming a styrene-like conjugation structure. The two π-electron conjugation structures formed may be considered as precursors for further syntheses, modification, and growth of multilayer molecular architectures on silicon surfaces.

II. Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure lower than 2×10^{-10} Torr. The chamber is equipped with an HREELS (LK2000-14R) spectrometer and mass spectrometer (UTI-100) for gas analyses. The HREELS spectrometer consists of a double-pass 127° cylindrical deflector analyzer (CDA) as the monochromator and a single-pass 127° CDA for energy analysis. For HREELS measurements, an electron beam with a primary energy (E_p) of 4.5 eV collides on the surface at an incident angle (θ_i) of 60° from the surface normal. The energy resolution of the spectrometer shown with fwhm (full width at half-maximum) was determined to be ∼5 meV (40 cm⁻¹). The off-specular spectra were collected at Δθ off-specular directions, where Δθ refers to the angle of $\theta_{analyzer} - \theta_{specular}$.[25,26]

The Si(111) samples (9 mm × 18 mm × 0.38 mm) were cut from n-type (p-doped) silicon wafers with a resistivity of 1−30 Ω·cm and purity of 99.999% (Goodfellow). A Ta foil with a thickness of 0.025 mm was sandwiched between two identical 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 LN₂-cooled sample holder. The sample was heated through resistive heating of the sandwiched Ta foil. The sample was carefully cleaned by cycles of Ar⁺ sputtering and annealing to 1200 K for 15 min. Styrene (99%, Aldrich), styrene-α,α,β-d_3 (99 atom % D, C/D/N Isotopes Inc.), phenylacetylene (99%, Aldrich), and phenylacetylene-α-d_1 (99 atom % D, Aldrich) were further purified by several freeze−pump−thaw cycles before being dosed onto the silicon surface through a Varian adjustable leak valve. Exposures were calculated and reported in langmuirs (1 langmuir = 10⁻⁶ Torr·s) without ion gauge sensitivity calibration.

III. Results and Discussion

III.A. Styrene Binding on Si(111)-7×7. Figure 1 shows the high-resolution electron energy loss spectra of Si(111)-7×7 exposed to styrene at 110 K as a function of exposure. The vibrational frequencies and their assignments for physisorbed and chemisorbed molecules are listed in Table 1. For the physisorbed multilayer, vibrational features at 410, 440, 707, 780, 905, 990, 1180, 1308, 1427, 1492, 1633, and 3061 cm⁻¹ are unambiguously resolved. Table 1 clearly shows that the vibrational features of physisorbed styrene (Figure 1d) are in excellent agreement with the IR spectrum of liquid styrene.[24] Among these vibrational signatures, the peak at 3061 cm⁻¹ is assigned to the C^{sp^2}H stretching mode; intensities around 1633, 1492, and 1308 cm⁻¹ are associated with the characteristic vibrational modes of the monosubstituted phenyl ring.

The vibrational features of chemisorbed styrene at low exposures (Figure 1a) or obtained by annealing the multilayer styrene-exposed sample to 300 K to drive away all the physisorbed molecules and only retain the chemisorbed molecules (Figure 2b), however, are significantly different. Losses at 515, 708, 772, 2912, and 3040 cm⁻¹ can be readily resolved. The absence of a detectable Si−H stretching feature around

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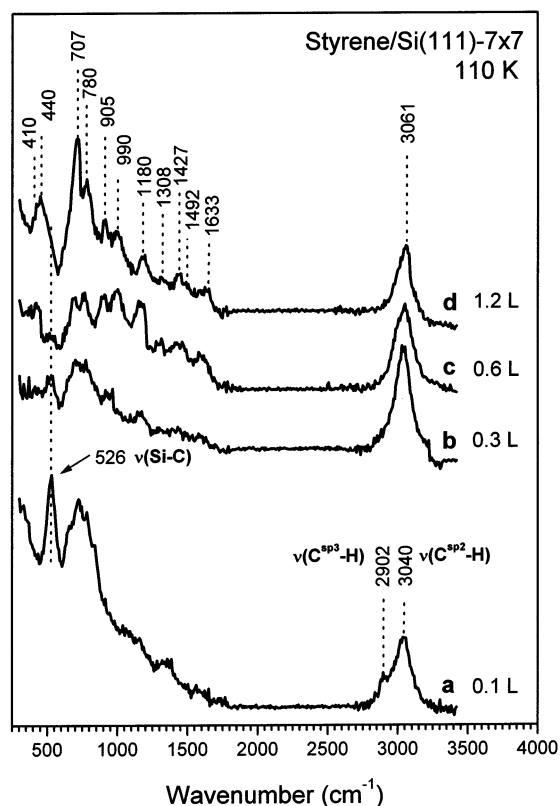(26) Condirston, D. A.; Laposa, J. D. *J. Mol. Spectrosc.* **1976**, *42*, 466−477.

Figure 1. HREELS spectra of styrene-exposed Si(111)-7×7 at 110 K as a function of exposure.

Figure 2. HREELS spectra of the physisorbed multilayer (a) and saturated chemisorbed monolayer (b) and the off-specular ($\Delta\theta = -5°$) spectrum (c) of the saturated chemisorbed monolayer (b) of styrene on Si(111)-7×7.

2000−2100 cm^{-1} [27,28] (Figures 1a and 2b) rules out the dissociative nature of chemisorbed styrene by forming a Si−C bonded σ-complex and a Si−H bond through the breakage of the C−H bond of styrene. Compared to physisorbed molecules with C−H stretching at 3061 (C^{sp2}H), the chemisorbed molecules present two vibrational peaks at 2902/2912 and 3040 cm^{-1} (Figures 1a/2b), attributable to C^{sp3}H and C^{sp2}H stretching modes,[28] respectively. This demonstrates the rehybridization of some carbon atoms from sp^2 to sp^3 in the chemisorbed molecules due to the surface covalent binding. Another major change is the appearance of a new peak at 510−530 cm^{-1}, ascribed to the Si−C stretching mode, consistent with the previous studies on the binding of unsaturated hydrocarbons on Si(111)-7×7.[19] This peak (Figure 1) is gradually weakened with an increase of exposure due to the screening effect of the physisorbed multilayer on the chemisorbed monolayer.[27] Furthermore, the characteristic vibrational modes of the monosubstituted phenyl ring ν(C−C) around 1580−1650, 1450−1525, and 1300−1350 cm^{-1} [28,29] are absent in the HREELS spectra of chemisorbed styrene (Figure 2b). This suggests the loss of aromaticity of the phenyl ring, possibly showing the involvement of the phenyl ring in the reaction with Si surface dangling bonds. The inset of Figure 2 is the enlargement of the spectrum for saturated chemisorbed styrene in the range of 1000−1700 cm^{-1}. Five weak intensities at 1568, 1402, 1287, 1172, and 1075 cm^{-1}
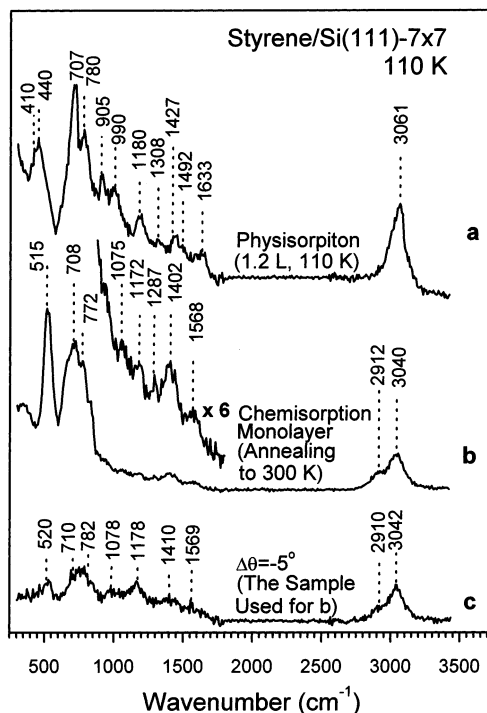
can be observed, assigned to CC stretching, CH scissors, CH wagging, CH twisting, and =CH− in-plane bending, respectively. This assignment is further confirmed by the DFT calculations that will be discussed in section III.C.

The off-specular spectrum (Figure 2c) was taken at the $\Delta\theta$ = −5° direction. Compared to the spectrum of the saturated chemisorption monolayer collected at specular geometry (Figure 2b), the intensities of 515 (ν(Si−C)), 708 (φ(C−C)), and 772 cm^{-1} (γ(C−H)) losses are significantly reduced, suggesting the main contribution of the dipole scattering mechanism for these modes, while other losses have large contributions from the impact excitation mechanism.[25] The comparison between the spectra obtained at specular and off-specular geometries suggests a nearly parallel configuration with respect to the surface plane for chemisorbed styrene.

Styrene is a π-conjugated multifunctional molecule. It may covalently bond to Si(111)-7×7 through seven possible modes as shown in Figure 3. Modes I−III are the reaction products between one C=C bond of the phenyl ring and an adjacent adatom−rest atom pair. The possible reaction occurring at the external C=C is described in mode IV. Modes V and VI are the products of reaction schemes involving two conjugated C=C bonds of the phenyl ring, similar to benzene on Si(111)-7×7.[19] In mode VII, both the external C=C and its neighboring C=C of the phenyl ring take part in an addition strategy to produce a 5-ethylidene-1,3-cyclohexadiene-like species. The absence of characteristic vibrational modes of a monosubstituted phenyl ring in the spectra of chemisorbed styrene shows the direct participation of the phenyl ring of styrene in the reaction with Si surface dangling bonds. This result rules out the occurrence of the reaction between the external −CH=CH$_2$ and adjacent adatom−rest atom pair (mode IV). However, the above vibrational properties of styrene chemisorbed on Si(111)-7×7 cannot

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Table 1. Assignments of HREELS Spectra of Physisorbed and Chemisorbed Styrene on Si(111)-7×7[d]

Designation	Description	Liquid[a]	Phys.	Chem.	Calcu.	Isotope[b]	Phys.	Chem.
ν_1	νC–H	3106		3040*		3104		3025*
ν_2	ν_{as}=CH(D)$_2$	3091				2329	2306	
ν_3	νC–H	3084				3084		
ν_4	νC–H	3061	3061			3061	3045	3025*
ν_5	νC–H	3055		3040*	3061	3051		
ν_6	νC–H	3029				3026		
ν_7	ν=CH(D)-	3009				2244		2210
ν_8	ν_s=CH(D)$_2$	2981				2207	2220	
	νC^{sp3}-H			2912	2936			2134
ν_9	νC=C	1630	1633			1562		
ν_{10}	νC–C	1600				1602	1586	
ν_{11}	νC–C	1575		1568[c]	1533	1585		1542
ν_{12}	νC–C	1494	1492			1491	1480	
ν_{13}	νC–C	1450	1427			1445		
ν_{14}	β_s=CH(D)$_2$	1411		1402[c]	1416	1048	1040	927
ν_{15}	νC–C	1334				1332	1339	
ν_{16}	β=CH(D)-	1303	1308	1287[c]	1267	1003	995	
ν_{17}	βC–H	1289				1290	1300	1292
ν_{18}	νC-CH(D)CH(D)$_2$	1203				1225		
ν_{19}	βC–H	1181	1180	1172[c]	1200	1181	1185	
ν_{20}	βC–H	1156				1156	1152	
ν_{21}	βC–H	1083		1075[c]	1102	1081		
ν_{22}	β_{as}=CH(D)$_2$	1032				831	834	
ν_{23}	βC–H	1019				1027	1040*	
ν_{24}	ring	999				1003	995*	
ν_{30}	γ=CH*-	992	990			788		778
ν_{31}	γC–H	985				986	995*	
ν_{32}	γC–H	970				970		
ν_{33}	γC–H	909	905			913		
ν_{34}	γ_s=CH(D)$_2$	909				710		
ν_{35}	γC–H	841				840	834*	
ν_{36}	γC–H	776	780	772	784	742	742	
ν_{25}	αC-C-C	776				735		
ν_{37}	ϕC–C	699	707	708	720	692	703	700
ν_{38}	γ_{as}=CH(D)$_2$	640				571		
ν_{26}	αC-C-C	621				622		
ν_{27}	β-C=C	554				510		510
	νSi-C			515	541			510*
ν_{28}	αC-C-C	442	440			442		
ν_{39}	ϕC–C	433				407	411	
ν_{40}	ϕC–C	407	410			398		
ν_{29}	βC-CH(D)CH(D)$_2$	241				220		
ν_{41}	γC-CH(D)CH(D)$_2$	212				192		
ν_{42}	torsion	76				66		

[a] Reference 24. [b] Styrene-α,α,β-d_3 in ref 24. [c] Assignments given in section III.A. [d] All frequencies are in cm^{-1}. Phys. = physisorbed molecules; Chem. = chemisorbed molecules; Calcu. = DFT calculations. Asterisks indicates frequencies used again.

exclusively resolve the remaining six binding modes, that is, modes I–III and V–VII.

To further clarify the reaction mechanism of styrene on Si(111)-7×7, styrene-α,α,β-d_3 was also studied in our HREELS experiments. Parts a and b of Figure 4 present the vibrational features of the physisorbed styrene-α,α,β-d_3 and saturated chemisorption molecules on Si(111)-7×7, respectively. In Figure 4a, vibrational peaks at 411, 703, 742, 834, 995, 1040, 1152, 1185, 1300, 1339, 1480, 1586, 2220, 2306, and 3045 cm^{-1} are clearly resolved. Their assignments are listed in Table 1. These assignments show that the vibrational signatures of physisorbed

molecules are very consistent with the IR spectrum of liquid styrene-α,α,β-d_3.[24] Among these vibrational features, the two peaks at 2306 and 2220 cm^{-1} are assigned to C$^\alpha$–D and C$^\beta$–D (in −C$^\beta$D=C$^\alpha$D$_2$) stretching modes, respectively. The peak at 3045 cm^{-1} is attributed to the C^{sp2}–H stretching related to the phenyl ring. Compared to physisorbed styrene-α,α,β-d_3, significant differences are observed for chemisorbed molecules in the regions of C−H and C−D stretching modes. The peak at 2306 cm^{-1} (C^{sp2}–D of the =C$^\alpha$D$_2$ group) previously observed for physisorbed molecules disappears upon chemisorption. A new peak appears at 2134 cm^{-1}, attributable to the C^{sp3}–D
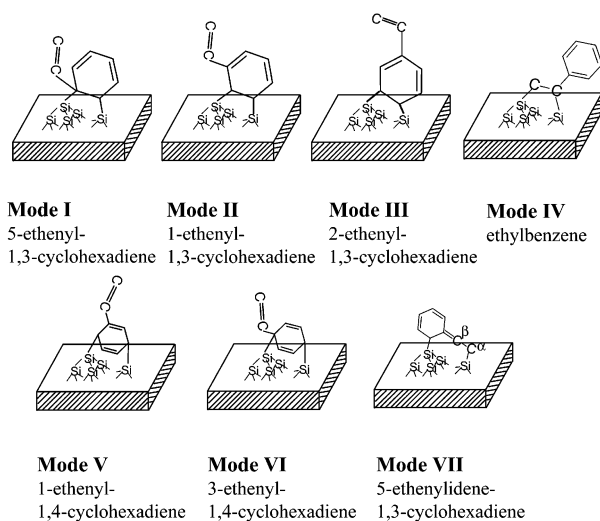
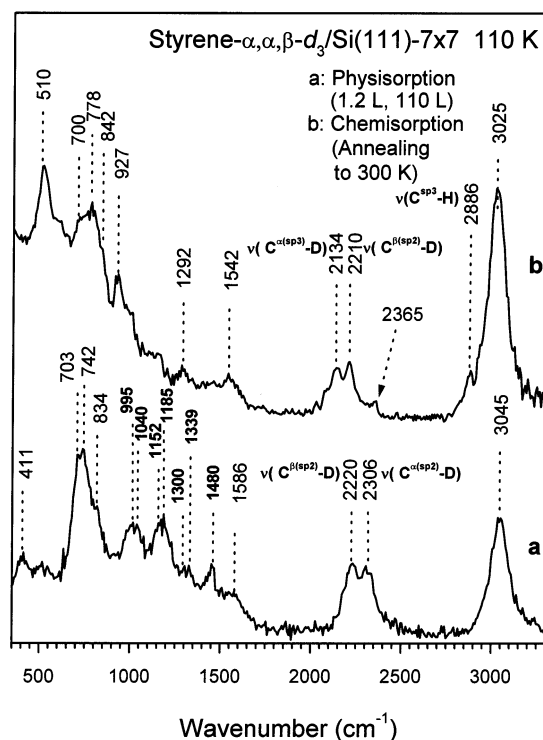**Figure 3.** Schematic diagram of seven possible binding modes for styrene covalently bound to Si(111)-7×7.

Figure 4. HREELS spectra of the physisorbed multilayer (a) and saturated chemsiorption monolayer (b) of styrene-α,α,β-d_3 on Si(111)-7×7.

stretching mode. Another major change is the appearance of a resolvable peak around 2886 cm^{-1} attributed to C^{sp3}H stretching in addition to the 3025 cm^{-1} peak related to C^{sp2}H. This observation clearly shows the rehybridization of one or more C atoms of the phenyl ring from sp^2 to sp^3. Combining the two changes occurring at C–D and C–H stretching regions upon chemisorption, we can conclude that both –CH(D)=CH$_2$(D$_2$) and the phenyl group are directly involved in the covalent attachment to Si surfaces.

Among these possible addition reactions (Figure 3), mode IV involves the cycloaddition between the external –CD=CD$_2$ and the Si dangling bonds, leaving the phenyl ring unreacted. A single C–D stretching peak would be expected to appear around 2134 cm^{-1} due to the rehybridization of both C$^\alpha$ and

C$^\beta$ from sp^2 into sp^3.[30] Moreover, the signature of C–H stretching should be a single peak around 3060 cm^{-1}, similar to chemisorbed benzonitrile on Si(111)-7×7 through the reaction between C≡N and the adatom–rest atom pair.[31] The fact of observing the coexistence of C^{sp2}H, C^{sp3}H, C^{sp2}D, and C ^{sp3}–D stretching vibrations in the above HREELS spectra (Figure 4b) of chemisorbed styrene-α,α,β-d_3 conclusively excludes this possibility.

The main experimental spectra can be well rationalized with the proposed mode VII. In mode VII, both the external –CH=CH$_2$ and its conjugated internal C=C of the phenyl ring take part in the interaction with Si(111)-7×7 through an addition reaction. In the resulting configuration, C$^\alpha$ and one C atom of the phenyl ring rehybridize into sp^3. The characteristic vibrational peaks of the monosubstituted phenyl ring will be absent due to the direct participation of the phenyl ring in the addition reaction.[28,29] This binding mode is consistent with our observation of two separate peaks at 2912 and 3040 cm^{-1} (Figure 2b) assigned to C^{sp3}H and C^{sp2}H, respectively. Moreover, the coexistence of two peaks ascribed to C^{sp3}D and C^{sp2}–D in the spectra of chemisorbed styrene-α,α,β-d_3 (Figure 4b) shows that –C$^\beta$D=C$^\alpha$D$_2$ is involved in the surface reaction, resulting in only the α-carbon atom rehybridizing into sp^3 with the β-carbon atom retaining sp^2.

Noticeably, there is a small intensity at ∼2365 cm^{-1} in Figure 4b. It is probably related to the asymmetrical stretch (ν_a) mode of CO$_2$ condensed on the surface from the background during the acquisition of the HREELS spectrum at 110 K, consistent with the data obtained for physisorbed CO$_2$ on RuO$_2$(110) and K/Mo$_2$C/Mo(100), as well as gaseous CO$_2$.[32–35] However, the possibility of concurrent occurrence of one or more of the reaction channels involving one C=C bond or two conjugated C=C bonds of the phenyl ring (modes I–III, V, and VI) cannot be completely ruled out although the frequency of this small peak is ∼59 cm^{-1} higher than that of ν(C$^{\alpha\,(sp2)}$–D) at 2306 cm^{-1} observed in Figure 4a for physisorbed molecules. Thus, our experimental results strongly support the styrene mainly binding to Si(111)-7×7 through the reaction involving both the ethenyl group and the phenyl ring.

A recent study of styrene on Si(100) showed that styrene selectively chemisorbs on the Si(100) surface.[36] The reaction mainly favors covalent binding through its external C=C bond, leaving the unreacted phenyl ring protruding into the vacuum. This reaction mechanism is significantly different from the binding mode we observed on Si(111)-7×7. This change in reaction pathway is possibly due to the large separation between the adatom and its adjacent rest atom (∼4.5 Å) of Si(111)-7×7 compared to the size of Si=Si dimers (∼2.3 Å) on Si(100).

III.B. Phenylacetylene Binding on Si(111)-7×7. Figure 5 shows the high-resolution electron energy loss spectra of a phenylacetylene-exposed Si(111)-7×7 sample at 110 K as a

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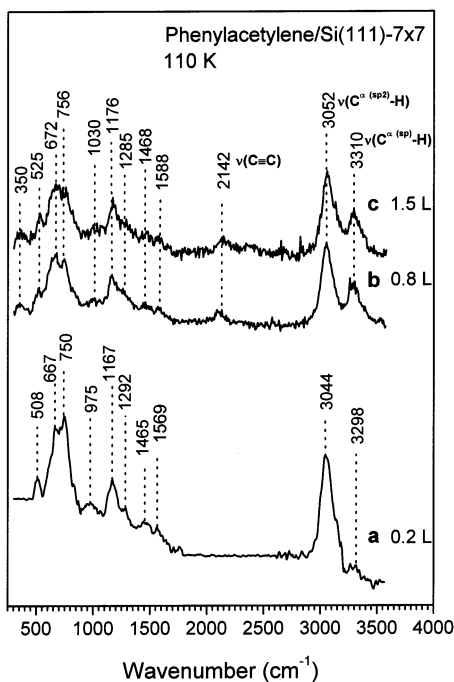
Figure 5. HREELS spectra of phenylacetylene-exposed Si(111)-7×7 at 110 K as a function of exposure.

Figure 6. HREELS spectra of the physisorbed multilayer (a) and saturated chemisorbed monolayer (b) of phenylacetylene on Si(111)-7×7.

function of exposure. The vibrational frequencies and their assignments for physisorbed and chemisorbed molecules are summarized in Table 2. This table shows that the vibrational features of physisorbed phenylacetylene (Figure 5c) are in excellent agreement with the IR spectrum of liquid phenyacetylene.[37] Vibrational signatures at 350, 525, 672, 756, 1030, 1176, 1285, 1468, 1588, 2142, 3052, and 3310 cm^{-1} can be clearly identified in the spectrum of physisorbed molecules. Among these vibrational signatures, the peak at 3310 cm^{-1} is assigned to the C^{sp}–H (−C≡CH) stretching mode; the loss feature at 3052 cm^{-1} is attributable to the stretching mode of C^{sp2}–H on the phenyl ring; the C≡C stretching mode can account for the feature at 2142 cm^{-1}; vibrational features around 1588, 1468, and 1285 cm^{-1} are associated with the characteristic vibrational modes of the monosubstituted phenyl ring.

The vibrational features of chemisorbed phenylacetylene at low exposures (Figures 5a) or obtained by annealing the multilayer phenylacetylene-exposed sample to 300 K to drive away all the physisorbed molecules and only retain the chemisorbed molecules (Figure 6b), however, are significantly different. Losses at 352, 398, 502, 675, 758, 1025, 1167, 1283, 1482, 1595, 1630, and 3060 cm^{-1} can be readily resolved. The absence of observable Si–H stretching around 2000−2100 cm^{-1} suggests the molecular nature of chemisorbed phenylacetylene on the Si(111)-7×7 surface. Compared to the physisorbed molecules, the vibrational peak around 3310 cm^{-1} associated with the C^{sp}–H (−C≡CH) stretching mode is absent in the chemisorbed molecules. This demonstrates the rehybridization of carbon atoms of the C≡C group and their involvement in binding with the Si surface. This is further supported by the absence of a C≡C stretching mode around 2142 cm^{-1} in the vibrational signatures of chemisorbed phenylacetylene. A new peak at 1630 cm^{-1} attributed to the C=C double bond can be identified although its relative intensity is low possibly due to

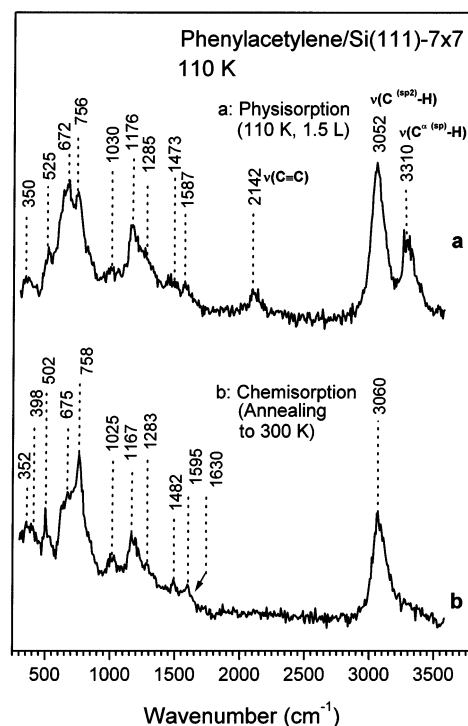(37) King, G. W.; So, S. P. *J. Mol. Spectrosc.* **1970**, *36*, 468−487.

its nearly parallel orientation.[25] Another change is the appearance of a new peak at ∼510−520 cm^{-1}, ascribed to the Si−C stretching mode. Furthermore, the characteristic vibrational modes [ν(C−C)] of a monosubstituted phenyl ring around 1580−1650, 1450−1525, and 1300−1350 cm^{-1} [28,29] are retained in the HREELS spectra of chemisorbed phenylacetylene (Figures 5a and 6b), indicating the preservation of aromaticity of the phenyl ring. The fact that there are no observable intensities around 2900 cm^{-1} suggests that there are no carbon atoms rehybridizing from sp^2 or sp into sp^3 after chemisorption, further supporting the retention of the phenyl ring.

The absence of C^{sp}–H and C≡C stretching modes in the chemisorbed molecules shows the direct involvement of the C≡C group in the reaction with the adatom−rest atom pair. The observation of only a C^{sp2}–H stretching mode at 3060 cm^{-1} together with the characteristic vibrational modes [ν(C−C)] of a monosubstituted phenyl ring rules out the direct involvement of the phenyl ring. Thus, the reaction between the C≡C group and adatom−rest atom pair is the possible binding mode.

For further understanding of the binding mechanism of phenylacetylene on Si(111)-7×7, phenylacetylene-α-d_1 was also employed in our HREELS experiments. Parts a and b of Figure 7 present the vibrational features of physisorbed and saturated chemisorbed phenylacetylene-α-d_1 on Si(111)-7×7, respectively. In Figure 7a, vibrational peaks at 352, 520, 752, 1008, 1176, 1286, 1330, 1464, 1585, 1986, 2590, and 3056 cm^{-1} are clearly resolved. Their assignments listed in Table 2 show that the vibrational features of physisorbed molecules are in good accordance with the IR spectrum of liquid phenylacetylene-α-d_1.[37] Among these vibrational signatures, the two peaks at 2590 and 1986 cm^{-1} are assigned to C$^{α (sp)}$−D (−C≡CD) and C≡C stretching modes, respectively. The peak at 3056 cm^{-1} is ascribed to the C^{sp2}–H stretching of the phenyl ring. For chemisorbed molecules, however, both C$^{α (sp)}$−D and C^α≡C^β

Table 2. Assignments of HREELS Spectra of Physisorbed and Chemisorbed Phenylacetylene on Si(111)-7×7[c]

Designation	Description	Liquid[a]	Phys.	Chem.	Calcu.	Isotope[b]	Phys.	Chem.
ν_1	ν≡C-H(D)	3332	3310	/		2609	2590	/
	ν=C-D						/	2218
ν_{25}	νC-H	3096				3096		
ν_2	νC-H	3078				3078		
ν_3	νC-H	3067	3052	3060	3075	3066	3056	3050
ν_{26}	νC-H	3058				3058		
ν_4	νC-H	3047				3046		
ν_5	νC≡C	2120	2142	/		1984	1986	/
	νC=C		/	1630	1619		/	1635
ν_6	νC-C	1601	1588	1595	1584	1600	1585	1595
ν_{27}	νC-C	1573				1573		
ν_7	νC-C	1488	1468	1482	1462	1488	1464	1458
ν_{28}	νC-C	1447				1447		
ν_{29}	νC-C	1330				1329	1330	
ν_{30}	βC-H	1282	1285	1283	1282	1278	1286	1278
ν_8	νC-CCH	1192				1193		
ν_9	βC-H	1175	1176	1167	1161	1175	1176	1163
ν_{31}	βC-H	1157				1157		
ν_{32}	βC-H	1070				1070		
ν_{10}	βC-H	1028				1025		
ν_{11}	Ring breath	998	1030	1025	978	998		1009
ν_{17}	γC-H	985				985	1008	
ν_{14}	γC-H	968				968		956
ν_{18}	γC-H	915				916		
ν_{15}	γC-H	842				841		
ν_{12}	αC-C-C	760	756	758	728	758	752	760
ν_{19}	γC-H	756			789	758		
ν_{20}	φC-C	689	672	675	700	691		703
ν_{33}	βCC-H(D)	649				482		
ν_{34}	αC-C-C	613				623		
ν_{21}	γCC-H(D)	613				482		
ν_{22}	φC-C	530	525	/		531	520	518
ν_{35}	β(C-C≡C)	513				531		
	νSi-C		/	502	485		/	518*
ν_{13}	αC-C-C	465			475	459		
ν_{16}	φC-C	418		398	394	419		
ν_{23}	γC-CCH	349	350	352		340	352	385
ν_{36}	βC-CCH	349				340		
ν_{24}	γC-C≡C	162				154		

[a] Phenylacetylene in ref 37. [b] Phenylacetylene-α-d_1 in refs 37. [c] All frequencies are in cm⁻¹. Phys. = physisorbed molecules; Chem. = chemisorbed molecules; Calcu. = DFT calculations. Asterisks indicates frequencies used again.

stretching modes are absent. Moreover, a new peak appears around 2218 cm⁻¹, attributable to the C^{sp^2}–D stretching vibration.[24] Indeed, the fact that these changes occurred at the C–D and C–H stretching region upon chemisorption of phenylacetylene-α-d_1 strongly supports the conclusion that only the C≡C bond directly participates in the covalent binding with the surface.

Figure 8 presents all seven possible binding modes of phenylacetylene on Si(111)-7×7. Among them, modes I–III, V, and VI are the possible reaction products between one C=C bond or two conjugated C=C bonds of the phenyl ring and Si surface dangling bonds. Their C–H stretching features would present two separate peaks corresponding to C^{sp^3}–H and C^{sp^2}–H together with C–D stretching remaining at the same frequency as that for physisorbed phenylacetylene-α-d_1. Our experimental results readily exclude the occurrence of these possibilities. In mode VII, both external –C≡CH and its conjugated internal C=C of the phenyl ring take part in the covalent attachment with the Si surface. In the resulting configuration, the C^α rehybridizes from sp into sp² and one carbon atom of the phenyl group changes from sp² to sp³. Thus, the disappearance of both the C^{sp}–H stretching feature and the characteristic vibrational peaks of a monosubstituted phenyl ring would be expected in chemisorbed molecules. In addition, the C^{sp^3}–H stretching at ~2900 cm⁻¹ would be concurrently observed with the C^{sp^2}–H stretching around 3050 cm⁻¹. In fact, our major experimental evidence of (1) the disappearance of both C^{sp}–H and C≡C stretching modes, (2) only a C–H stretching mode around 3050 cm⁻¹ (C^{sp^2}–H stretching), and (3) the preservation of characteristic vibrational modes of a monosubstituted phenyl ring unambiguously excludes the possibilities of modes I–III and V–VII. The experimental spectra can be well interpreted with the proposed mode IV. In this binding mode, due to the rehybridization of C^α and C^β from sp to sp², all the carbon atoms in chemisorbed molecules have an sp² configuration, resulting in a single C–H stretching peak around 3060 cm⁻¹ for
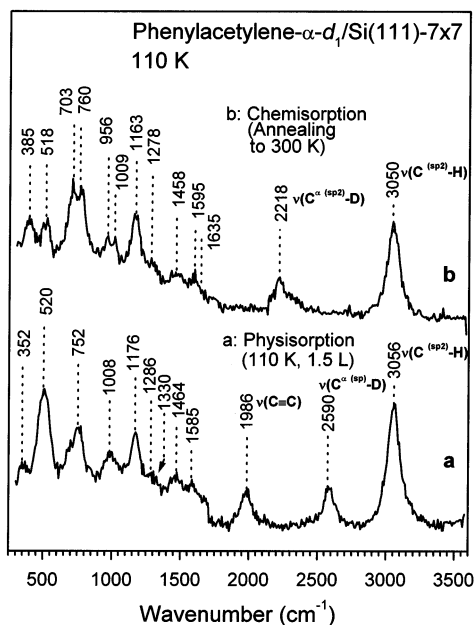
Figure 7. HREELS spectra of the physisorbed multilayer (a) and saturated chemisorbed monolayer (b) of phenylacetylene-α-d_1 on Si(111)-7×7.
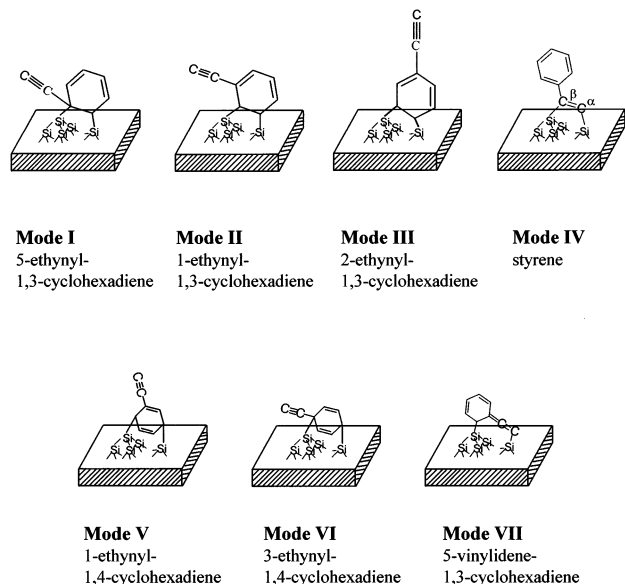

Figure 8. Schematic diagram of seven possible binding modes for phenylacetylene covalently bound to Si(111)-7×7.

chemisorbed phenylacetylene. In the case of chemisorbed phenylacetylene-α-d_1, the $C^α$–D stretching will significantly downshift from 2590 cm^{-1} ascribed to C^{sp}–D observed for physisorbed molecules to 2218 cm^{-1} attributed to the formation of the C^{sp2}–D stretching mode due to the direct involvement of C≡C in the surface reaction on Si(111)-7×7. This binding configuration is further supported by the absence of C≡C stretching modes at 1986 cm^{-1} (Figure 7b). Moreover, the retention of characteristic vibrational features of a monosubstituted phenyl ring upon chemisorption shows that the phenyl ring does not directly interact with the Si surface. On the basis of this experimental evidence, it is reasonable to conclude that phenylacetylene covalently binds to Si(111)-7×7 through the reaction between the C≡C group and adjacent adatom–rest atom pair.
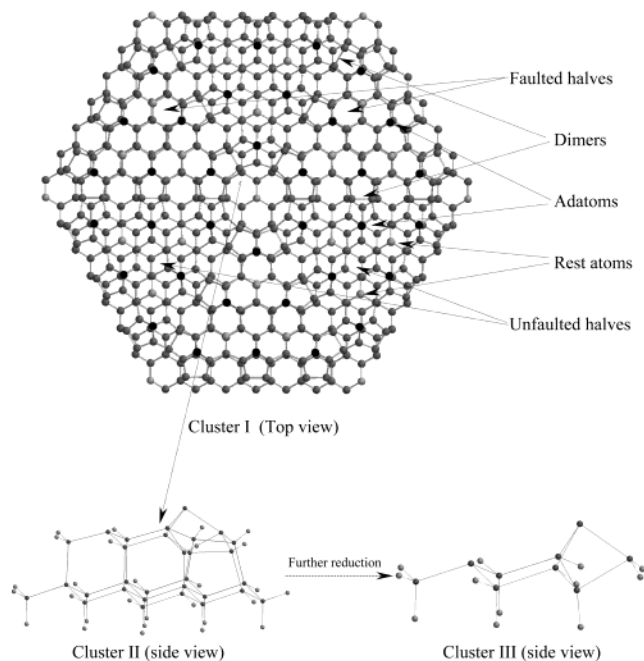
Figure 9. A large cluster of the top five silicon layers constructed on the basis of the DAS model to present three Si(111)-7×7 unit cells surrounding a corner hole. It (cluster I) has 973 atoms including the capping H atoms (not displayed for clarity). Clusters II ($Si_{30}H_{28}$) and III (Si_9H_{12}) are reduced from cluster I.

III.C. DFT Calculations. Both styrene and phenylacetylene have two reactive functional groups. Due to the high reactivity of the phenyl ring, C=C, and C≡C on Si(111)-7×7,[19,22,23] there exist various competitive reaction pathways over the same surface binding sites (the neighboring adatom–rest atom pair) for each molecule. Thus, we have theoretically modeled some of the possible configurations to aid the understanding of the reactivity and selectivity of these π-conjugated systems on Si(111)-7×7.

As shown in the left-bottom panel of Figure 9, cluster model II ($Si_{30}H_{28}$) is cut from the central part of MMFF94[38]-optimized cluster I (the top panel of Figure 9) containing 973 atoms including the capping hydrogen atoms, where the precision of the atomic positions suffers the least from boundary effects. It contains an adatom and an adjacent rest atom from an unfaulted subunit, serving as a "diradical" binding site for the attachment of one styrene or phenylacetylene molecule. Capping H atoms at the cluster boundaries are kept frozen. Silicon atoms in the bottom double layers are placed at bulk lattice positions prior to the geometry optimization process, with each Si–Si bond length set to 2.3517 Å and all bond angles adjusted to 109.4712°. Cluster III (Si_9H_{12}) was obtained from further reduction of cluster II. Similarly, all capping H atoms were frozen during geometric optimization. Clusters I–III were used in successful prediction of the adsorption energy of benzene on Si(111)-7×7[19,39] and the most stable binding configurations of acetonitrile,[40] acrylonitrile,[41] benzonitrile,[31] benzene,[39] pyrrole,[42] and N-methylpyrrole[43] on Si(111)-7×7.

The possible binding modes were constructed by styrene/phenylacetylene adsorption onto the mother cluster (cluster III of Figure 9). Calculations were performed using the SPARTAN

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Table 3. Adsorption Energies of the Local Minima in the Styrene/Si$_9$H$_{12}$ Model System from pBP/DN** [a]

functional group	C$^\alpha$H$_2$=C$^\beta$H−	−C^{5}H=C^{6}H−C^{7}H=C^{8}H−	C$^\alpha$H$_2$=C$^\beta$H−C^3=C^{4}H−
binding mode	IV	V	VII
reaction model	[2 + 2]	[4 + 2]	[4 + 2]
adsorption energy	30.2	28.0	39.8

[a] All energies are in kcal·mol^{-1}. The adsorption energy is calculated by subtracting the total energy of the free substrate cluster (Si$_9$H$_{12}$) and gas-phase styrene (C$_8$H$_8$) from the energy of the cluster (C$_8$H$_8$/Si$_9$H$_{12}$).

Table 4. Adsorption Energies of the Local Minima in the Phenylacetylene/Si$_9$H$_{12}$ Model System from pBP/DN** [a]

functional group	C$^\alpha$H≡C$^\beta$−	−C^{5}H=C^{6}H−C^{7}H=C^{8}H−	C$^\alpha$H≡C$^\beta$−C^3=C^{4}H−
binding mode	IV	V	VII
reaction model	[2 + 2]	[4 + 2]	[4 + 2]
adsorption energy	49.1	26.0	47.6

[a] All energies are in kcal·mol^{-1}. The adsorption energy is calculated by subtracting the total energy of the free substrate cluster (Si$_9$H$_{12}$) and gas-phase phenylacetylene (C$_8$H$_6$) from the energy of the cluster (C$_8$H$_6$/Si$_9$H$_{12}$).

package.[44] The energies of chemisorbed configurations were calculated at the DFT theory level using the perturbative Beck−Perdew functional (pBP86) in conjugation with a basis set of DN** (comparable to 6-31G**).[44] Geometric optimizations were conducted under SPARTAN default criteria. Adsorption energies, synonymous to formation heat, are obtained by subtracting the energy of the adsorbate/substrate complex from the total sum of the energies of the substrate and gaseous molecule. Among the binding modes (I−IV) of both molecules (Figures 3 and 8), mode IV is energetically more favorable due to the retention of the phenyl ring. Compared to mode V, the configuration of mode VI is expected to have a higher energy due to the larger spatial strain and complete breaking down of the π conjugation system. Thus, the optimization mainly focuses on modes IV, V, and VII. Figure 10 presents the optimized geometries of the local minima for the C$_8$H$_8$ (C$_8$H$_6$)/Si$_9$H$_{12}$ model systems. Table 3 reveals that for styrene on Si(111)-7×7 the reaction involving both external C$^\alpha$=C$^\beta$ and its conjugated internal C=C of the phenyl ring is thermodynamically favored compared to other possible reactions. This process is exothermic by 39.8 kcal·mol^{-1}. In addition, the calculated vibrational frequencies (Table 1) for the cluster corresponding to mode VII (Figure 3) are very consistent with the experimental observation. For phenylacetylene on Si(111)-7×7, DFT calculation results are shown in Table 4. The product formed from the addition reaction involving both external C≡C and its conjugated internal C=C of the phenyl ring (mode VII of Figure 8) has an adsorption energy of 47.6 kcal·mol^{-1}, which is slightly lower than the value (49.1 kcal·mol^{-1}) of the reaction product formed through C≡C (mode IV of Figure 8). This can be understood considering the greater structural strain induced by cumulative double bonds (Si−C=C=C$^\beta$−C$^\alpha$−Si) in mode VII. The calculated vibrational frequencies (Table 2) for mode IV are indeed in good agreement with the experimental vibrational spectra of chemisorbed molecules. These calculation results support phenylacetylene covalently binding to Si(111)-7×7 through a reaction between the C≡C group and adjacent adatom−rest atom pair. The present experiments clearly dem-
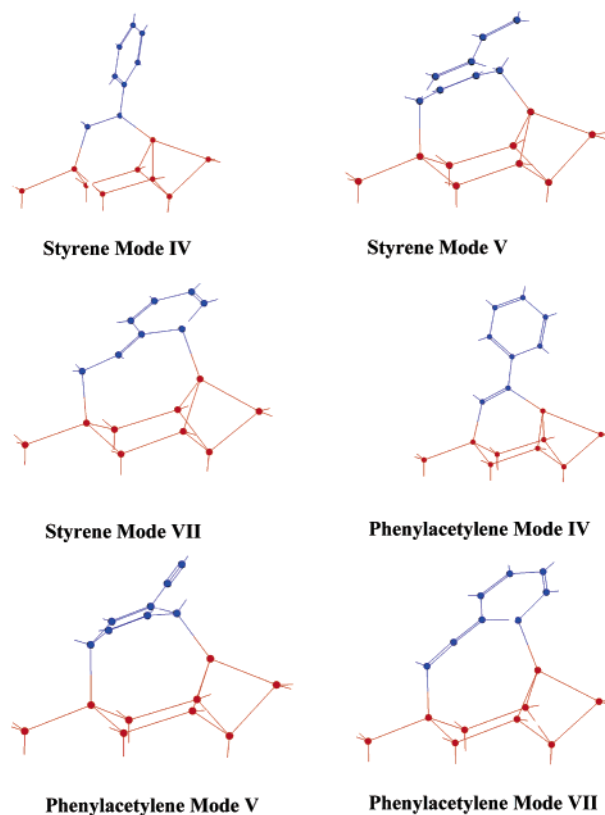
Figure 10. Optimized C$_8$H$_8$/Si$_9$H$_{12}$ and C$_8$H$_6$/Si$_9$H$_{12}$ clusters for reactions involving one C=C bond or two conjugated C=C bonds.

onstrate the strong dependence of the reaction channel on the substitution groups of phenyl rings, providing the necessary chemical flexibility in organic attachment on silicon surfaces.

It is noted that previous investigations[45−48] showed that reactions on silicon surfaces are often kinetically controlled and the route producing the most thermodynamically stable product may be kinetically less favorable. For styrene and phenylacetylene on Si(111)-7×7, although the products with the lowest total energy (Tables 3 and 4) predicted from DFT calculations are consistent with the experimentally observed products, the actual reaction pathway can still be controlled by kinetics.

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Studies on the covalent attachment of conjugated dienes including benzene,[19] chlorobenzene,[20] thiophene,[17,21] furan,[18] and acrylonitrile[41] on Si(111)-7×7 revealed that almost all conjugated dienes covalently bond to the adjacent adatom and rest atom pair involving the two conjugated unsaturated bonds. For styrene on Si(111)-7×7, a binding mechanism through only the external C═C bond, observed on Si(100),[36] may involve a much higher transition state due to the large distance between the adatom and adjacent rest atom. There are three possible addition pathways (modes V−VII of Figure 3) involving two conjugated C═C bonds. However, only the reaction involving the external C═C and its conjugated C═C (mode VII) can form a product containing three conjugated C═C bonds which is expected to have a lower energy than the other two possible products (modes V and VI). In the case of phenylacetylene on Si(111)-7×7, the reaction involving C≡C and its conjugated C═C bond of the phenyl group would result in the formation of a cumulative double bond structure of C═C═C (mode VII in Figure 8) with a great steric strain. On the other hand, the di-σ-bonding through C≡C (mode IV in Figure 8) may involve a transition state with a highly conjugated styrene-like structure. This possibly implies the existence of a lower energy barrier along the reaction coordinate, consistent with our experimental observation.

IV. Conclusions

Our vibrational studies together with DFT calculations have shown the formation of 5-ethylidene-1,3-cyclohexadiene- and styrene-like conjugation structures for styrene and phenylacetylene chemisorption on Si(111)-7×7, respectively. For styrene, the surface reaction mainly occurs through a reaction of both the external C^{α}═C^{β} and its conjugated internal C═C of the phenyl ring with an adjacent adatom−rest atom pair. Phenylacetylene chemically binds to Si(111)-7×7 via the reaction scheme between the external C≡C group and adjacent adatom−rest atom pair. Both the 5-ethylidene-1,3-cyclohexadiene- and styrene-like chemisorption species containing conjugated structures may possibly be employed as precursors for further chemical modification and functionalization of silicon surfaces[49,50] or as intermediates for dry organic syntheses[51,52] and even fabrication of conductive polymer thin films on semiconductors.[11,12,53]

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