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Temperature-dependent absorption of aromatic molecules on silicon

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We found that the exposure of 85-K cleaved Si substrates to benzene or pyridine vapors produces weakly bound physisorption states rather than the stable chemisorption states obtained by room-temperature exposure. Quite unexpectedly, annealing these states to relatively low temperatures does not simply result in thermal desorption. On the contrary, it results in the conversion of the physisorption states into the stable chemisorption states. This surprising result confirms the unusually high reactivity of aromatic molecules on cleaved silicon, which appears related to the presence of cleavage steps.

I. INTRODUCTION

Recent experiments[1,2] led to the discovery of an unexpectedly stable chemisorption state at room temperature for benzene (C_6H_6) on cleaved Si(111)2×1. A similar state was also found for pyridine (C_5H_5N) on the same surface.[3,4] On the contrary, aromatic molecules do not have stable adsorption states at room temperature on other semiconductor surfaces,[1] including Si(111)7×7. Synchrotron radiation photoemission and high-resolution electron-energy-loss (HREELS) data revealed other unusual features of the above stable adsorption states.[1-4] For example, benzene on Si(111)2×1 forms σ bonds, while on metals it chemisorbs through the donation of π electrons to metal orbitals.

We extended our investigations of C_6H_6 and C_5H_5N chemisorption on Si(111)2×1 to low-temperature substrates. These experiments led to the discovery of another unexpected feature. The annealing of weakly bound adsorption states obtained at low temperatures does *not* simply lead to thermal desorption—but to the formation of the stable chemisorption states. This surprising phenomenon was observed upon annealing to 135 K for two different weakly bound chemisorption states of benzene, obtained for different benzene vapor exposure levels of cleaved Si(111) at 85 K, tentatively attributed to benzene clusters, and benzene multilayers. We also observed a third weakly bound state at very low exposures, consisting of benzene molecules physisorbed with the plane of the aromatic ring parallel to the surface.

For pyridine, only one adsorption state was also observed on 85 K Si(111)2×1, probably consisting of C_5H_5N clusters. This state converts to the stable chemisorption state at an annealing temperature of 275 K. These findings confirm the surprisingly high reactivity of aromatic molecules on cleaved silicon. Ample evidence exists[1-4] that the stable chemisorption states are established by breaking one of the C—H bond of the C_6H_6 or C_5H_5N molecule (or of their deuterated counterparts), and forming C-Si bonds. There is also increasing evidence that this process is stimulated by the cleavage steps.[2]

The following sections will discuss in detail the experimental data demonstrating the existence of the different adsorption states at low temperature, and their conversion to the stable chemisorption states. Specifically, Sec. II will present the experimental procedure, Secs. III and IV will discuss the benzene and pyridine results, and Sec. V will summarize our conclusions.

II. EXPERIMENTAL PROCEDURE

High-resolution electron-energy-loss (HREELS) experiments were performed at the Montana State University Center for Research in Surface Science (CRISS). The experimental system was described in Ref. 2. In particular, the base pressure of the ultrahigh-vacuum chamber was in the 10^{-11} Torr range. The samples were cooled by a circulating liquid nitrogen system, to a temperature ~ 85 K. The HREELS data were first taken on cold, freshly cleaved Si(111), reproducing the well-known spectral features of this surface for reference.

The surfaces, kept at 85 K, were subsequently exposed to benzene or pyridine vapors. The total exposure ranged from 0.5—500 langmuir (1 langmuir$=1\times10^{-6}$ Torr sec) for benzene, and from 2.5—200 langmuir for pyridine. Subsequent annealing was achieved by circulating dc current through a resistive heater close to the sample. After each annealing, the sample was again brought to a temperature of 85 K, to reproduce the previous measurement conditions.

The primary beam energy was 6.5 eV for all the HREELS experiments. A compromise was achieved between energy resolution and signal level. The best resolution on these cleaved samples was 12 meV, and the typical resolution was 14—18 meV. The angle of incidence of the primary electron beam was 30° with respect to normal.

Spectra were taken both in the specular and off-specular detection modes. Data acquisition and processing were controlled by a Tektronix 4051 minicomputer with Transera interfaces. Low-energy electron diffraction (LEED) tests of the stable chemisorption states did not produce any pattern.

III. BENZENE ADSORPTION DATA

The first series of HREELS experiments was performed on cleaved Si(111) substrates kept at 85 K and exposed to benzene vapors. For increasing exposure levels, we obtained three different HREELS spectra, corresponding to different adsorption states. These spectra are shown in Fig. 1, curves *b*, *c*, and *d*, and were all taken in the specular mode.

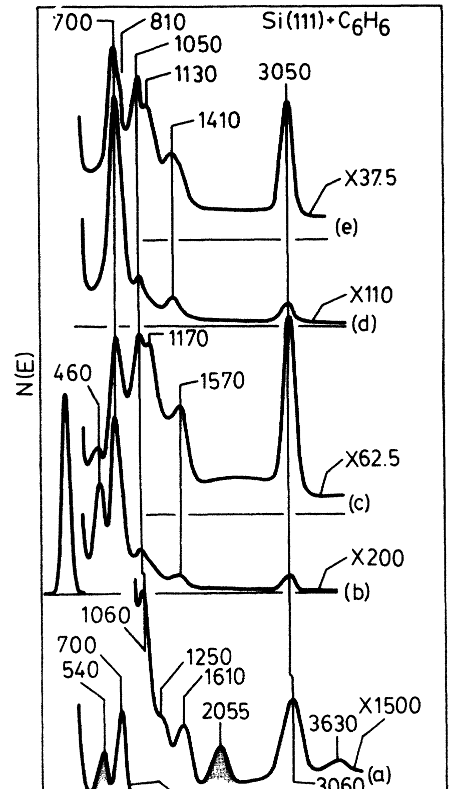

FIG. 1. High-resolution electron-energy-loss spectra of benzene adsorbed on cleaved Si(111)2×1. Curve *a* was taken in the specular mode, and it corresponds to the chemisorption of benzene on room-temperature Si(111)2×1, investigated in Ref. 2. The shaded peaks are the fingerprints of the process leading to a stable chemisorption state. Curves *b*, *c*, and *d* were also taken in the specular mode, and they are representative of different benzene exposure ranges of 85 K substrates. Specifically, the three curves correspond to the 0.5–25, 30–75, and 100–500 langmuirs. Curve *e* is the off-specular counterpart of curve *d*, taken at an angle of 7.5 K. The primary electron energy E_0 was 6.5 eV for all our experiments. [1 langmuir (L) $\equiv 10^{-6}$ Torr sec.]

For comparison, we also show in Fig. 1, curve *a*, the specular-mode HREELS spectrum of room-temperature Si(111)2×1 exposed to benzene.[2] This spectrum characterizes the stable chemisorption state. Notice, in particular, the shaded peaks which are the direct fingerprints of this state. The peak at 540 cm^{-1} corresponds to the stretching mode of Si—C σ bonds. The peak at 2055 cm^{-1} corresponds to a Si—H stretching mode—which is due to the chemisorption of H atoms released upon breaking of benzene C—H bonds. The stable chemisorption state revealed by curve *a* in Fig. 1 was extensively characterized and discussed in Ref. 2. The chemisorption geometry corresponds to a large tilting angle of the aromatic ring plane with respect to the surface.

Figure 1, curve *b*, shows the specular-mode HREELS data for Si(111)2×1 kept at 85 K, after a 25 langmuir exposure to benzene. This spectrum is representative of the exposure range 0.5–25 langmuir. It is characterized by four loss peaks related to benzene modes, at 700, 1050, 1570, and 3050 cm^{-1}, plus a peak at 460 cm^{-1} which corresponds to the well-known Si surface phonon. The last attribution is confirmed by the fact that the relative intensity of the 460-cm^{-1} peak decreases as the exposure to benzene increases. The permanence of the Si surface phonon signal indicates that the surface is not entirely covered by benzene at these exposure levels.

The identification of the adsorption state corresponding to curve *b* in Fig. 1 is best accomplished by comparison with the stable chemisorption state spectrum, curve *a*. Curve *b* exhibits fewer loss peaks than curve *a*. In particular, the features at 540, 1250, and 2055 cm^{-1} are missing. Furthermore, the benzene-related peaks in curve *b* are at lower energies with respect to the corresponding peaks in curve *a*.

The 1250-cm^{-1} peak in curve *a* corresponds to the ν_{17} mode of the free-benzene molecule. This feature could not be detected in curve *b*, and this indicates a higher symmetry of the chemisorption geometry with respect to curve *a*. The other two missing peaks are, as we already mentioned, the fingerprints of the stable chemisorption state. Their absence from curve *a* indicates that the corresponding absorption process does not involve the breaking of C—H molecular bonds and the consequent release and chemisorption of H atoms. The shift to lower energies brings the benzene-related loss peaks in curve *b* closer to the free-molecule values than those of curve *a*. All these facts indicate that the C_6H_6 molecule is much less perturbed by the adsorption process at 85 K than at room temperature—and that it is more weakly bound to the substrate.

Further information on the adsorption state corresponding to curve *b* is provided by the selection rules discussed in Refs. 5 and 6. The weakly bound character of the state suggests van der Waals interactions as the possible adsorption mechanism. This would imply that the ring is parallel or nearly parallel to the substrate, and that the electrostatic interactions take place primarily through the aromatic π system. The chemisorption state would be similar to that usually found for benzene on metals.[6–8]

Table I shows the modes that are dipole active or nondipole active for several possible chemisorption-geometry

TABLE I. Vibrational modes of the free-benzene molecule which are dipole active (A) or nondipole active (N) for the symmetries of the different possible adsorption sites on the Si(111) surface (vibrational energies in cm^{-1}, from Refs. 5—7).

	$C_{3v(\sigma_v)}$	$C_{3v(\sigma_d)}$	$C_{s(\sigma_d)}$	$C_{s(\sigma_v)}$
ν_1(3062)	A	A	A	A
ν_2(992)	A	A	A	A
ν_4(673)	A	A	A	A
ν_5(3068)	A	N	N	A
ν_6(1010)	A	N	N	A
ν_7(995)	A	N	N	A
ν_8(703)	A	N	N	A
ν_9(1309)	N	A	A	N
ν_{10}(1146)	N	A	A	N
ν_{11}(849)	N	N	A	N
ν_{12}(3063)	N	N	A	N
ν_{13}(1486)	N	N	A	N
ν_{14}(1038)	N	N	A	N
ν_{15}(3047)	N	N	A	N
ν_{16}(1596)	N	N	A	N
ν_{17}(1178)	N	N	A	N
ν_{18}(606)	N	N	A	N
ν_{19}(975)	N	N	A	N
ν_{20}(410)	N	N	A	N

symmetries under the above assumptions.[7] The number of peaks in curve *b* immediately suggests a highly symmetric C_{3v} site rather than a low-symmetry site. Table II shows that there is good correspondence between the observed losses in curve *b* and the dipole-active modes for the $C_{3v(\sigma_v)}$ symmetry. No such correspondence is found for the other possible C_{3v} symmetry, $C_{3v(\sigma_d)}$, and for the lower symmetries.

TABLE II. Correspondence between the vibrational modes of the free-benzene molecule which are dipole active for the $C_{3v(\sigma_v)}$ symmetry and spectral features of 85 K Si(111)2×1 exposed to 0.5—0.25 langmuir of benzene.

C_6H_6 on Si (cm^{-1})	Free C_6H_6 (cm^{-1})
700	ν_4(673),ν_8(703)
1050	ν_2(992),ν_6(1010), ν_7(995)
1570	
3050	ν_1(3062),ν_5(3068)

These points suggest $C_{3v(\sigma_v)}$ as a plausible symmetry for the chemisorption site. Sites with such symmetry are shown in Fig. 2. This conclusion, however, is not supported by our data beyond any doubt. Table II shows that the correspondence between the observed peaks and the dipole-active modes for the $C_{3v(\sigma_d)}$ symmetry is not perfect. The weak feature at 1570 cm^{-1} does not correspond to any active mode for such symmetry. It could correspond to the ν_{13} or ν_{16} modes of the free molecule, which are active only for symmetries lower than C_{3v}. A possible explanation is that the screening of parallel vibrational modes by their image dipole is not complete for a semiconductor substrate, thus weakening the energy-loss selection rules. Another explanation is that the spectra could have both dipole and impact contributions even in the specular mode. This last contribution is more important for large-energy-loss peaks such as the one at 1570 cm^{-1} than for small-loss peaks. This suggests that the intense peak at 3050 cm^{-1} contains contributions from modes such as ν_{12} and ν_{15} which are nondipole active for the $C_{3v(\sigma_v)}$ symmetry. Another possible explanation is that the aromatic ring is not perfectly parallel with respect to the surface, but at a small angle.

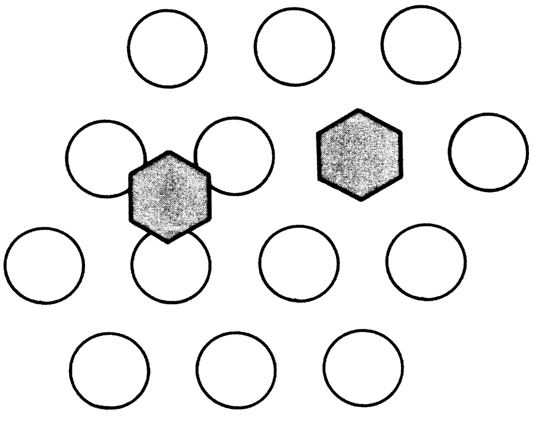

FIG. 2. Chemisorption sites with $C_{3v(\sigma_v)}$ symmetry for benzene on Si(111).

The interpretation in terms of van der Waals interaction is supported by the comparison between the most intense peak in curve *b* and the corresponding features for adsorption on metals. These are found at 730—810 cm^{-1} for benzene on nickel and at 830—920 cm^{-1} for benzene on platinum.[6] Thus the 700-cm^{-1} position in curve *b* is the lowest and the closest to the free-molecule mode. This confirms that the benzene molecule is not much perturbed by the adsorption process, indicating a weak electrostatic interaction rather than donation of π electrons as on metal substrates. We conclude, therefore, that curve *b* corresponds to isolated benzene molecules physisorbed on the Si substrate.

Higher exposure levels to benzene produce different HREELS curves. Curve *c* in Fig. 1 shows the specular-mode spectrum for a 75 langmuir exposure of the 85 K silicon substrate. This spectrum is representative of the exposure range 30—75 langmuir. It exhibits five peaks at 700, 1050, 1170, 1570, and 3050 cm^{-1}, plus the residual 460-cm^{-1} signal from the silicon surface phonon. Thus there are more peaks in this curve than in the spectra obtained for lower exposures, curve *b*. Furthermore, the spectral features in curve *c* are generally broader than those in curve *c*, and the relative intensity of the 700-cm^{-1} peak with respect to the other peaks is lower. The most important contributor to this peak is the ν_4 C—H out-of-plane bending mode, which has a dipole moment

TABLE III. Correspondence between the vibrational modes of the free-benzene molecule which are dipole active for the $C_{s(\sigma_v)}$ symmetry and spectral features of 85 K Si(111)2×1 exposed to 30—75 langmuir of benzene.

C_6H_6 on Si (cm^{-1})	Free C_6H_6 (cm^{-1})
700	$\nu_4(673), \nu_8(703), \nu_{18}(606)$
1050	$\nu_2(992), \nu_6(1010), \nu_7(995), \nu_{14}(1038), \nu_{19}(975)$
1170	$\nu_{17}(1178)$
1570	$\nu_{13}(1486), \nu_{16}(1596)$
3050	$\nu_1(3062), \nu_5(3068), \nu_{12}(3063), \nu_{15}(3047)$

perpendicular to the plane of the aromatic ring. Thus the peak is intense when the plane of the molecule is parallel or nearly parallel to the substrate.

The above observations indicate that curve *c* corresponds to an adsorption state with less short-range order than curve *b*. In particular, the parallel orientation does not appear favored anymore. Table III shows that there is a good correspondence between the observed peaks in curve *c* and the dipole-active modes for the $C_s(\sigma_v)$ symmetry, i.e., a lower symmetry than the one we derived from curve *b*. A possible explanation is that at these exposure levels the adsorbed benzene molecules are interacting with each other and forming clusters, with the aromatic rings at different angles with respect to the surface.

For even larger exposures of the 85-K substrate to benzene, we obtained yet another spectrum, curve *d* in Fig. 1. This curve specifically corresponds to a 100-langmuir exposure, and is representative of the exposure range 100—500 langmuirs. Its peaks are at 700, 1050, 1490, and 3050 cm^{-1}. The absence of the silicon surface phonon indicates that the substrate is entirely covered by the adsorbed benzene.

A reasonable hypothesis for the corresponding adsorption state is the formation of condensed multilayers of benzene. There is, in fact, a close correspondence between number and position of the spectral features in curve *d* and those of the spectra of multiple layers of benzene condensed on nickel or platinum.[6] The number and relative intensity of the peaks in curve *d* suggest again a preferential parallel orientation of the benzene molecules with respect to the substrate. This is supported by the 7.5° off-specular spectrum, curve *e* in Fig. 1. In this curve, we see intense peaks at 810 and 1050 cm^{-1}. The 810-cm^{-1} peak is much weaker in the specular-mode spectrum, curve *d*, and at 1050 cm^{-1} there is only a very weak shoulder. These peaks correspond to the ν_{10} and ν_{11} modes. Their weak intensity in the specular-mode spectrum is consistent with a preferentially parallel orientation of the adsorbed molecules.

We found that the adsorption states corresponding to curves *c* and *d* in Fig. 1 convert to the stable chemisorption state after annealing. In fact, the spectra taken at 85 K after annealing are indistinguishable from those obtained after exposure at room temperature,[2] curve *a* in Fig. 1. This already surprising discovery is even more surprising if one considers the low-annealing temperatures required for conversion to the stable chemisorption state. The conversion begins at temperatures as low as 125—130 K, and is completed at 135 K. No further spectral changes are observed for subsequent annealings up to room temperature. Also, there was no evidence of annealing-induced conversion from the second- and third-physisorption states (clusters and multilayers) to the first physisorption state.

The above results confirm the unusually high-chemical reactivity of aromatic molecules on cleaved silicon. In particular, temperatures as low as 125—135 K are sufficient to stimulate the breaking of C—H bonds which leads to the establishment of stable C—Si σ bonds. We found some evidence that this reactivity is related to the quality of the cleaved surface.[2] Cleaves which appeared very poor from visual inspection gave spectra with traces of the stable chemisorption state even after simple exposure at 85 K. The fingerprint features of the stable chemisorption state appeared at low exposures, and then they merged with the physisorbed-state features at larger exposures. This indicates that some of the chemisorption sites, most likely those at cleavage steps, are more reactive than

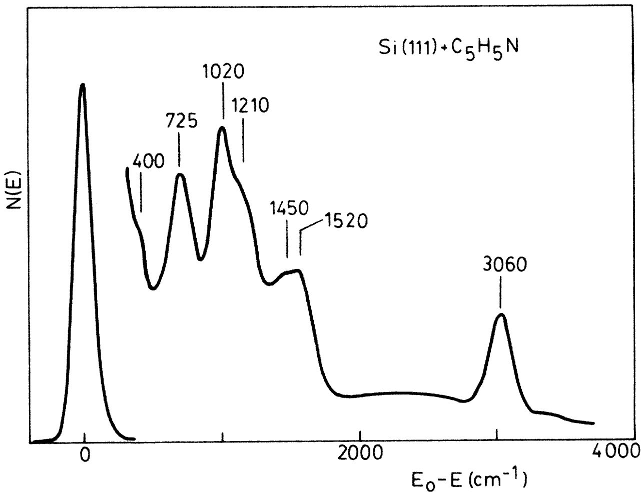

FIG. 3. High-resolution electron-energy-loss spectrum for an 85 K Si(111)2×1 substrate after a 25-langmuir pyridine exposure.

TABLE IV. Correspondence between free-pyridine vibrational modes and spectral features of 85 K Si(111)2×1 exposed to pyridine.

C_6H_6N on Si (cm^{-1})	Free C_6H_6N (cm^{-1})
400	$\nu_{22}(374),\nu_{27}(405)$
725	$\nu_{10}(605),\nu_{19}(652),\nu_{25}(749),\nu_{26}(700)$
1030,1210	$\nu_6(1218),\nu_7(1068),\nu_8(1030),\nu_9(992),\nu_{16}(1218),\nu_{17}(1148)$ $\nu_{18}(1085),\nu_{20}(981),\nu_{21}(886),\nu_{23}(942),\nu_{24}(886)$
1450	$\nu_5(1482),\nu_{14}(1429),\nu_{15}(1375)$
1520	$\nu_4(1583),\nu_{13}(1572)$
3060	$\nu_1(3054),\nu_2(3054),\nu_3(3036),\nu_{11}(3083),\nu_{12}(3036)$

others and promote the formation of stable chemisorption bonds at 85 K even without annealing.

IV. PYRIDINE CHEMISORPTION DATA

Different levels of exposure of 85 K Si(111)2×1 to pyridine did not produce different adsorption states as for benzene. The spectrum observed for 2.5—200 langmuir exposures is shown in Fig. 3. The particular curve shown there was obtained after a 25-langmuir exposure.

In Fig. 3 we see broad loss peaks at 400, 725, 1020, 1210, 1450, and 1570 cm^{-1}. There is a close correspondence between these peaks and the molecular-pyridine spectral features obtained after room-temperature exposure (Ref. 4). The main difference between the two cases is the absence from Fig. 3 of the 520- and 2070-cm^{-1} features, identified in Ref. 4 as Si-C and Si-H stretching modes. Thus the state corresponding to Fig. 3 is not the stable chemisorption state produced at room temperature by the formation of Si—C σ bonds between the substrate and α pyridyl.

As for benzene, a possible interpretation of the spectrum of Fig. 3 is the formation of pyridine clusters. This would explain the broad line shape of the spectral features, and would also correspond to a low symmetry. A low symmetry is indeed suggested by the correspondence between the observed peaks in Fig. 3 and the vibrational modes of free pyridine, shown in Table IV. Notice, in particular, that the peak at 400 cm^{-1} corresponds to the ν_{22} and ν_{27} modes. These modes merge together with the Si—C contribution in the room-temperature exposure spectra of Ref. 4.

The hypothesis of cluster formation for low-temperature exposures is corroborated by several experimental facts. For example, the relative intensity of the low-loss peaks in Fig. 3 relative to the high-loss peaks is lower than for the room-temperature exposures. This suggests the coexistence of several different orientations of the pyridine molecules in the clusters—while room-temperature exposures produce a preferential orientation of α pyridyl, with a large tilt angle possibly close to vertical with respect to the surface.[4] Furthermore, we observed no difference between the specular-mode spectrum of Fig. 3 and a 12° off-specular spectrum.

Thermal annealing eventually converts the state of Fig. 3 to the stable chemisorption state produced by room-temperature exposure. The conversion, however, does not occur for a range of temperatures as narrow as for benzene. The conversion appears completed at a temperature of 275 K.

V. CONCLUSIONS

Our experiments confirm the strong reactivity of aromatic molecules on cleaved Si(111). This reactivity has no counterpart for other cleaved or annealed semiconductor surfaces such as Si(111)7×7, Ge(111), and GaAs(110).[1] Surprisingly low-annealing temperatures are sufficient to convert the weakly bound states obtained by 85° exposure to benzene and pyridine into stable chemisorption states. These states are equal to those produced by room-temperature exposure,[1–4] and they imply the breaking of molecular C—H bonds and the formation of Si—H σ bonds. All these features make the absorption processes of aromatic molecules on this surface different from those on metal surfaces.

Before annealing, benzene exhibits three different physisorption states on 85° Si(111)2×1. These states are achieved for increasing levels of exposure, and can be interpreted in terms of benzene molecules van der Waals bonded parallel to the surface, to benzene clusters, and to benzene multilayers. On the contrary, low-temperature exposures to pyridine only produce the state tentatively attributed to cluster formation.

The unexpectedly high reactivity of aromatic molecules on cleaved Si and the stable states it produces have fundamental interest and possibly applied interest as well. This stimulates further investigations of these phenomena, for other molecules and surfaces and also for other sets of chemisorption parameters.

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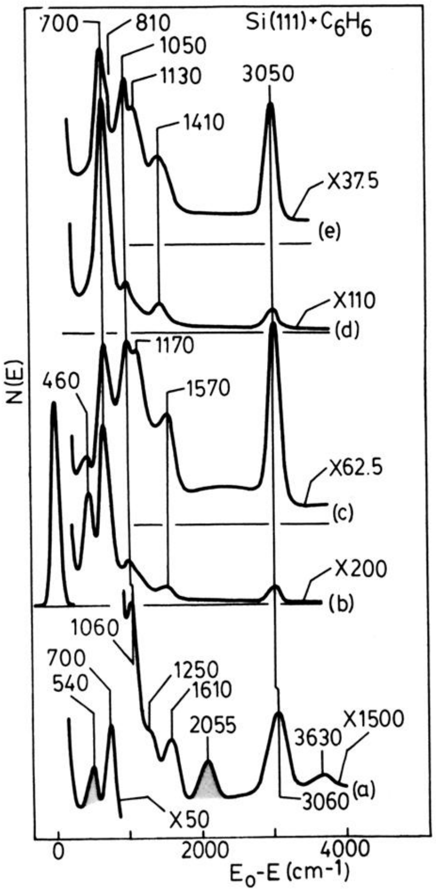

FIG. 1. High-resolution electron-energy-loss spectra of benzene adsorbed on cleaved Si(111)2×1. Curve *a* was taken in the specular mode, and it corresponds to the chemisorption of benzene on room-temperature Si(111)2×1, investigated in Ref. 2. The shaded peaks are the fingerprints of the process leading to a stable chemisorption state. Curves *b*, *c*, and *d* were also taken in the specular mode, and they are representative of different benzene exposure ranges of 85 K substrates. Specifically, the three curves correspond to the 0.5—25, 30—75, and 100—500 langmuirs. Curve *e* is the off-specular counterpart of curve *d*, taken at an angle of 7.5 K. The primary electron energy E_0 was 6.5 eV for all our experiments. [1 langmuir (L)$\equiv 10^{-6}$ Torr sec.]

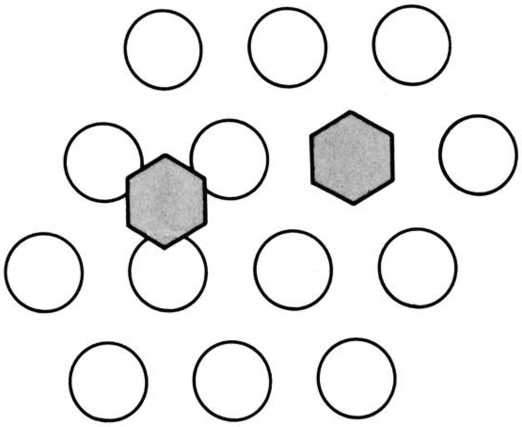

FIG. 2. Chemisorption sites with $C_{3v(\sigma_v)}$ symmetry for benzene on Si(111).