PHYSICAL REVIEW B VOLUME 32, NUMBER 4 15 AUGUST 1985

Pyridine on cleaved Si(111): Analysis of the vibrational modes and nature of the chemisorption process

M. N. Piancastelli*
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

M. K. Kelly and G. Margaritondo†
Department of Physics and Synchrotron Radiation Center, University of Wisconsin, Madison, Wisconsin 53706

J. Anderson, D. J. Frankel, and G. J. Lapeyre
Department of Physics, Montana State University, Bozeman, Montana 59717

(Received 11 January 1985; revised manuscript received 3 April 1985)

We present evidence that the chemisorption mechanism for pyridine on cleaved Si(111) is similar to that of benzene on the same surface. The mechanism involves the breaking of C—H bonds and formation of C—Si bonds. Similar processes could give rise to an exceptionally high reactivity of other aromatic molecules on room-temperature cleaved Si(111).

I. INTRODUCTION

Recent experiments[1–3] revealed interesting properties of the chemisorption processes of aromatic molecules on silicon. For benzene molecules, synchrotron-radiation photoemission spectroscopy and high-resolution electron-energy-loss spectroscopy (HREELS) have lead to the discovery of a unique strongly bound chemisorption state on room-temperature cleaved Si(111)2×1 while no benzene chemisorption has been observed on any other room-temperature semiconducting substrate.[2,3] The mechanism leading to this state is also unique for benzene on single-crystal surfaces. It involves the breaking of a C—H bond and formation of a σ bond between C and Si. The experiments also suggested a fundamental role of the cleavage steps in stimulating this mechanism.[3]

We present here evidence that a similar mechanism is responsible for the achievement of a stable chemisorption state at room temperature for pyridine on cleaved silicon. HREELS experiments revealed fingerprints of the breaking of C—H bonds and of the formation of C—Si bonds similar to those found[3] for C_6H_6 and for C_6D_6. Similar mechanisms could lead other aromatic molecules to have a uniquely high reactivity on cleaved silicon at room temperature.

Combined with the results of synchrotron-radiation photoemission experiments,[1] our HREELS data also demonstrate that the chemisorption of C_5H_5N involves σ bonding between Si and α-pyridyl, i.e., the formation of bonds between Si and C adatoms adjacent to the N atom. This results in a nonflat chemisorption geometry. The chemisorption bonding process affects not only the pyridine π system, but also the nitrogen lone-pair electrons.

II. DETAILS OF THE EXPERIMENTAL PROCEDURE

The chemisorption of pyridine on cleaved Si was first investigated with photoemission spectroscopy at the University of Wisconsin Synchrotron Radiation Center, and then at the Montana State University Center for Research in Surface Science (CRISS) by HREELS. Both series of experiments were performed in ultrahigh-vacuum chambers with base pressure in the mid 10^{-11}-Torr range. The photoemission experiments were described in a preliminary report,[1] and therefore we shall not repeat here their details. The experimental system used in these HREELS experiments was also described elsewhere.[3]

HREELS data were taken first on freshly cleaved, ultraclean Si(111)2×1, reproducing the well-known spectra of this surface for reference. Then the surfaces were exposed at room temperature to pyridine vapors. The total exposures ranged from a few langmuirs ($1\ \text{L}=1\times10^{-6}$ Torr sec) to 100 L. In a second series of experiments we investigated Si(111)-C_5D_5N surfaces obtained by cleavage in a deuterated-pyridine atmosphere. Our experiments on aromatic molecules on cleaved Si consistently show that the two methods—sequential and simultaneous cleavage and exposure—give results indistinguishable from each other. In the present case, we found a complete correspondence between the results for pyridine and deuterated pyridine, as discussed below. All the HREELS data were taken with a primary energy $E_0=6.5$ eV. The resolution of the CRISS HREELS system (Leybold-Heraeus ELS-22) reaches 5 meV [full width at half-maximum (FWHM)] under optimal experimental conditions. The practical resolution used in the present experiment was 15—20 meV. The angular width of the specular beam was not anomalously larger for these cleaved substrates than for other samples, ruling out extremely large step densities. The angle of incidence of the primary electron beam was 45°, and scattered electrons were collected and analyzed both in specular and off-specular directions. The signal-to-noise ratio was improved by data accumulation controlled by a Tektronix 4051 minicomputer with Transera interfaces.

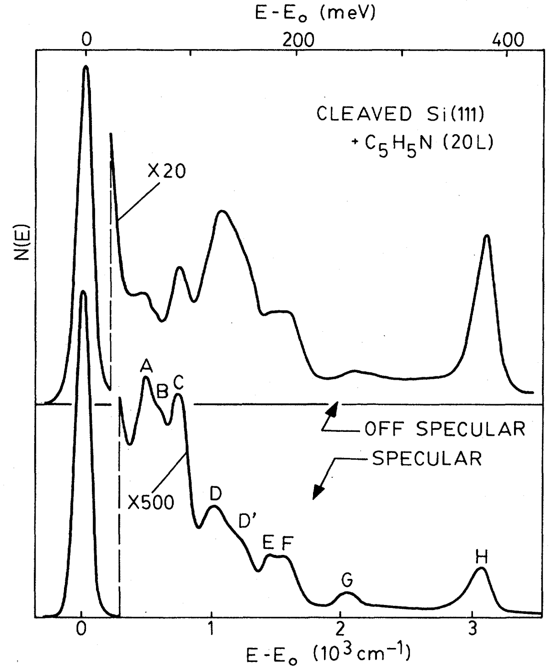

FIG. 1. Bottom: High-resolution electron-energy-loss spectra taken in a specular geometry on cleaved Si(111) after a 20-L exposure to pyridine vapors. The primary energy was $E_0 = 6.5$ eV. Top: Corresponding curve taken at an angle of 26° off specular.

III. PRESENTATION AND DISCUSSION OF THE SURFACE VIBRATIONAL SPECTRA

Figure 1 shows typical HREELS curves obtained for a Si(111)2×1 surface after a 20-L exposure to pyridine vapors. The bottom curve was recorded in the specular scattering geometry while the top spectrum was taken at an angle of 26° off the specular direction. Similar spectra were obtained for different pyridine exposures in the range 5—100 L. The labels in Fig. 1 identify the nine spectral features *A*, *B*, *C*, *D*, *D'*, *E*, *F*, *G*. The corresponding positions are listed in Table I.

TABLE I. Correspondence between electron-energy-loss spectral features for pyridine and deuterated pyridine chemisorbed on cleaved Si(111).

Pyridine Peak	 (cm^{-1})	Deuterated pyridine Peak	 (cm^{-1})
A	520		
B	640	*A*	515
C	770		
D	1050	*B*	840
D'	1200	(shoulder)	970
E	1480	*C*	1210
F	1570		
G	2070	*D*	1555
H	3060	*E*	2300

There are two likely chemisorption states for pyridine on single-crystal surfaces.[4–6] In the first state the chemisorption bonding occurs through the π aromatic system, and the molecule has the aromatic ring parallel to the substrate. In the second state the ring is tilted with respect to the substrate, and the bonding process affects the nitrogen lone-pair electrons. One must also consider the possibility of dissociative adsorption at room temperature.[7,8] Our synchrotron-radiation photoemission spectra—and in particular their independence of the photon polarization—ruled out the "flat" chemisorption geometry corresponding to the first state.[1,9] They also demonstrated that both the π system and the nitrogen lone-pair states are affected by the chemisorption bonding process. However, the photoemission results could not clarify the nature of the chemisorption bonds and therefore the chemisorption mechanism.

The spectra of Fig. 1 are consistent with the evidence against a flat chemisorption geometry provided by photoemission. Furthermore, they show that the chemisorption process for pyridine on Si(111)2×1 is much similar to that of benzene on the same surface,[2,3] which probably occurs at cleavage steps. Table II shows that each spectral feature except peaks *A* and *G* corresponds to a subgroup of the 27 vibrational modes of the pyridine molecule.[10] The features appear broader than expected from the primary-peak FWHM, and also broader than the corresponding features for pyridine on Ag(111), (Ref. 6) or Ni(100) (Refs. 7 and 8). This broadening could be explained, for example, by assuming dipole excitation selection rules,[11] and a low-symmetry chemisorption geometry. This suggests that cleavage steps play a role in this chemisorption process as they do for benzene on cleaved Si(111). Another possible explanation for the broadening is the coexistence of different low-symmetry chemisorption geometries involving, e.g., steps and other kinds of surface defects or terraces.

Table II shows that there are only a few exceptions to the direct correspondence between our spectral features and the vibrational modes of the pyridine molecule. The vibrational modes ν_{22} and ν_{27} are not observed as separate peaks [the same was true[6] for ν_{27} in the case of Ag(111)-C_5H_5N]. These modes probably contribute to the low-energy side of peak *A* causing its asymmetric shape. We already mentioned the absence of peaks *A* and *G* from Table II. These features are extremely important, since they are the fingerprints of the chemisorption mechanism.[3] No spectral features corresponding to peaks *A* and *G* can be found in the spectra of pyridine on Ni(100) at room temperature.[8] These peaks, however, appear at energies very similar to two spectral features of benzene on cleaved Si(111), 540 and 2055 cm^{-1}, and are likely to have the same origin.[3] In particular, peak *A* is in the typical energy range of the molecular infrared absorption peaks due to stretching modes of the Si—phenyl σ bonds.[12] Therefore, it indicates the formation of Si—C bonds.[3] The presence of Si—C σ bonds implies the breaking of pyridine C—H bonds. The H released stays on the surface and gives rise to peak *G*, whose energy is similar[13] to that of the Si-H stretching mode of atomic H on cleaved Si, 2015 cm^{-1}. In conclusion, the presence of peaks *A* and *G*

TABLE II. Correspondence between the vibrational modes of molecular pyridine and the electron-energy-loss spectral features for pyridine on Si(111)2×1.

	Molecular pyridine[a]		C_5H_5N on Si	
Mode	Character	(cm^{-1})	Peak	(cm^{-1})
ν_{22}	Out of plane	374		
ν_{27}	Out of plane	405		
ν_{10}	In plane (ring mode)	605	*B*	640
ν_{19}	In plane (ring mode)	652		
ν_{26}	Out of plane	700	*C*	770
ν_{25}	Out of plane	749		
ν_{21}, ν_{24}	Out of plane	886(2)	*D* *D'*	1050 1200
ν_{23}	Out of plane	942		
ν_{20}	Out of plane	981		
ν_9	In plane (ring mode)	992		
ν_8	In plane (ring mode)	1030		
ν_7	In plane	1068		
ν_{18}	In plane	1085		
ν_{17}	In plane	1148		
ν_6, ν_{16}	In plane	1218(2)		
ν_{15}	In plane	1375	*E*	1480
ν_{14}	In plane (ring mode)	1439		
ν_5	In plane (ring mode)	1482		
ν_{13}	In plane (ring mode)	1572	*F*	1570
ν_4	In plane (ring mode)	1583		
ν_3, ν_{12}	C-H stretching	3036(2)	*H*	3060
ν_1, ν_2	C-H stretching	3054(2)		
ν_{11}	C-H stretching	3083		

[a] Reference 10.

and of the corresponding peaks for Si(111)-C_6H_6 indicates breaking of C—H bonds and formation of C—Si bonds.

The above analysis completes and clarifies the preliminary information provided by photoemission spectra[1] about the chemisorption bonding process. Photoemission shows that *both* the π system and the nitrogen lone-pair states are affected by this process. Thus, the Si—C σ bonds must involve C atoms close to N atoms, so that both kinds of electronic states are at a sufficiently short distance from the surface. The radical adsorbed on Si(111) upon exposure to pyridine vapors is, therefore, α-pyridyl. This result is in agreement with the experimental findings[7] for pyridine on Ni(100), and with studies of pyridine—transition-metal coordination chemistry.[14]

The interaction between Si and the N lone pair is probably a σ donation of electrons to Si states, with a stabilizing effect for the N lone pair. This is a known donor-acceptor mechanism for pyridine chemisorption on metals.[4–6,8] The interaction is likely to be weaker for Si than for metal substrates, and the corresponding Si-N modes are probably at frequencies too low to be observed in our experiments. The absence of identifiable Si-N modes in our spectra could also suggest another, indirect interaction mechanism. This is the intermolecular interaction between the N lone pair of one ring and the π system of another.[6] Our data cannot identify which one among these two interaction mechanisms is active in our systems.

Our analysis is corroborated by the off-specular data of Fig. 1 and by the specular and off-specular HREELS curves obtained from Si(111)2×1 after exposure to deuterated pyridine. The off-specular spectrum of Fig. 1 does not exhibit additional features with respect to the specular spectrum, and this is consistent[11] with our conclusions about the low symmetry of the chemisorption geometry (although it would not be sufficient *per se* to prove that the symmetry is low, due to the role of nondipole excitation). The high-loss peak *H* is enhanced in the off-specular spectrum due to the increased contribution of electron impact scattering.[11] We also see that peak *D* is enhanced in the off-specular geometry with respect to the other features. This behavior was already observed for the Ni(100)-C_5H_5N spectral feature corresponding to peak

A,[8] with a relative intensity change much more pronounced than in our case. This indicates a reduced role of impact scattering in our case, consistent with large deviations from a vertical or nearly vertical position of the aromatic ring as found on Ni(100). Once again, therefore, our data suggest a very-low-symmetry chemisorption geometry on cleaved Si, or a combination of low-symmetry geometries.

Our experiments on deuterated pyridine produced some evidence of water contamination. This problem, however, did not affect our main goal—testing the above spectral analysis of C_5H_5N on cleaved Si(111). We see in Fig. 2 five spectral features, peaks A, B, C, D, and E—their frequencies are also listed in Table I. Peak A is due to a superposition of the modes that give rise to peaks A, B, and C in Fig. 1. This implies that the Si-C stretching peak does not shift much when the "normal" adsorbate is replaced by the deuterated adsorbate, as expected in this case and as indeed observed[3] for benzene on Si(111). The merging of peaks B and C of Fig. 1 into peak A in Fig. 2 is in agreement with the expected shifts on going from C_5H_5N to C_5D_5N.[3] Peaks B, C, D, and E in Fig. 2 correspond to peaks D, $(E+F)$, G and H in Fig. 1—and they all exhibit the expected shifts due to the substitution of H with D.[3,13] Notice in particular that peak D is attributed by this analysis to the Si-D stretching mode, in agreement with the experimental results for Si(111)2×1 exposed to atomic deuterium.[13] The changes between specular and off-specular data in Fig. 2 are entirely similar to those seen in Fig. 1. In particular, the strongest relative enhancement occurs for peak B in Fig. 2, similar to that of the corresponding peak D in Fig. 1.

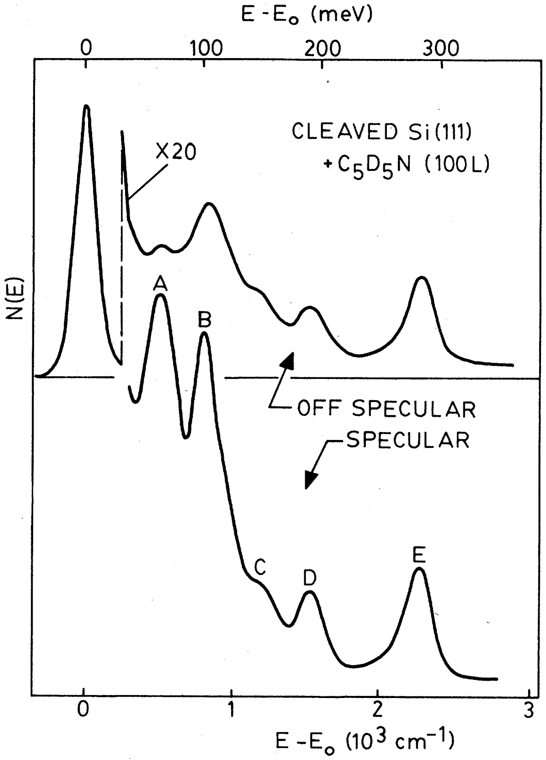

FIG. 2. Specular and off-specular HREELS curves taken on Si(111) cleaved in deuterated-pyridine atmosphere. The total exposure corresponds to 100 L.

IV. CONCLUSIONS

We found striking similarities between the mechanisms responsible for the creation of stable chemisorption states at room temperature for benzene and pyridine on cleaved Si(111). In both cases, the process involves the formation of σ bonds between Si and C. Also in both cases, the formation of these σ bonds is preceded by the breaking of C—H bonds and by the chemisorption of H atoms on the Si surface. Off-specular data and data taken on silicon cleaved in the presence of deuterated pyridine confirm the above conclusions.

Our results raise the possibility that the unusually high reactivity observed for benzene on cleaved Si(111) is not confined to that molecule, but is a general feature of other aromatic molecules. Experiments are in progress to test this intriguing possibility.

ACKNOWLEDGMENTS

This research was supported in part by the NSF, Grants Nos. DMR-82-00518 and DMR-82-05581. We are also grateful to the staff members of the Montana State University Center for Research in Surface Science (supported by the NSF, Grant No. DMR-83-09460) and of the University of Wisconsin Synchrotron Radiation Center (supported by the NSF, Grant No. DMR-80-20164) for their excellent technical support. One of the authors (M.N.P.) received financial support from the Fulbright Foundation during this project, and another author (G.M.) from the Romnes Foundation.

---

[*] On leave from the Dipartimento di Chimica, Università di Roma "La Sapienza," Italy.

[†] Author to whom all correspondence should be addressed.

[1] M. N. Piancastelli, G. Margaritondo, and J. E. Rowe, Solid State Commun. **45**, 219 (1983).

[2] M. N. Piancastelli, F. Cerrina, G. Margaritondo, A. Franciosi, and J. H. Weaver, Appl. Phys. Lett. **42**, 990 (1983).

[3] M. N. Piancastelli, G. Margaritondo, J. Anderson, D. J. Frankel, and G. J. Lapeyre, Phys. Rev. B **30**, 1945 (1984).

[4] B. J. Bandy, D. R. Lloyd, and N. V. Richardson, Surf. Sci. **89**, 344 (1979).

[5] S. R. Kelemen and A. Kaldor, Chem. Phys. Lett. **73**, 205 (1980).

[6] J. E. Demuth, K. Christmann, and P. N. Sanda, Chem. Phys. Lett. **76**, 201 (1980).

[7] R. M. Wexler, M.-C. Tsai, C. M. Friend, and E. L. Muetterties, J. Am. Chem. Soc. **104**, 2034 (1982).

[8] N. J. DiNardo, Ph. Avouris, and J. E. Demuth, J. Chem. Phys. **81**, 2169 (1984).

[9] M. Schluter, J. E. Rowe, G. Margaritondo, K. M. Ho, and M. L. Cohen, Phys. Rev. Lett. **37**, 1632 (1976).

[10] D. A. Long and E. L. Thomas, Trans. Faraday Soc. **59**, 783 (1963).

[11] H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy*

and Surface Vibrations (Academic, New York, 1982).

[12] F. F. Bentley, L. D. Smithson, and A. Rosek, *Infrared Spectra and Characteristic Frequencies* (Wiley, New York, 1968).

[13] H. Froitzheim, H. Lammering, and H.-L. Grunther, Phys. Rev. B **27**, 2278 (1983).

[14] E. Klei and J. H. Teuben, J. Organomet. Chem. **214**, 53 (1981).