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Atomically Resolved STM study of the Adsorption and Dissociation of Methyl Chloride on Si(001)

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We have studied the room-temperature adsorption and dissociation of methyl chloride (CH_3Cl) on Si(001) using Scanning Tunneling Microscopy (STM). Fragments are identified by the symmetry of their binding on the underlying Si(001) lattice. Methyl chloride adsorbs dissociatively at room temperature, yielding a methyl group and a chlorine atom bound to the surface. Chlorine atoms bind in a variety of geometries, the most common being two chlorine atoms bonded to a single silicon dimer (silicon monochloride dimers). When the surface is heated to 150 °C, all Cl rearranges to this monochloride-type bonding configuration, and images reveal the beginnings of monochloride island formation. The Cl: CH_3 ratio on the surface is found to be approximately 2:1, implying that not all methyl groups are bound to the surface in the reaction. Consideration of the relative bond strengths involved leads us to propose a reaction mechanism in which the surface sometimes abstracts a Cl atom from the CH_3Cl molecule, ejecting a methyl group back into the vacuum.

Introduction

The chemistry of both chlorine and alkyl species on silicon surfaces is important for a number of reasons. Chlorine/silicon reactions are key components of the chemistry of the decomposition of chlorosilanes on silicon in the growth of silicon of precursors molecules such as dichlorosilane, SiH_2Cl_2 . Chlorine is also frequently used as an etching species in reactive ion etching (RIE) processing of silicon. Alkyl species and other carbon-containing compounds on silicon play roles in the chemistry of technologically significant processes ranging from silicon-carbide (SiC) production to diamond thin film growth.

Much previous research has looked at the reactions of these species on silicon. Chlorine-on-silicon chemistry in particular has been extensively explored. It is known that chlorine etches silicon at relatively low temperatures (550 °C), giving primarily silicon chloride species as products¹⁻⁵. Much less is known about the decomposition of organic species on silicon. Several recent studies have explored the chemistry of methyl groups on Si(001) using HREELS^{6, 7}, TPD⁶⁻⁹, AES⁷⁻⁹, UPS and SSIMS⁸. It was found that CH_3 groups are stable up to 600 K. At higher temperatures they react on the surface, releasing hydrogen and decomposing first into CH species and eventually into carbon.

We have used scanning tunneling microscopy (STM) to study the decomposition of methyl chloride on Si(001) in the temperature range of 300 K to 450 K. Our purpose was to elucidate the reaction chemistry of this simple organic chloride on the surface of silicon and

to demonstrate the utility of STM in identifying fragments and in studying surface processes involved in these important surface reactions.

Experimental

Our experimental apparatus has been described in detail previously^{10, 11}. Our STM consists of a chemically etched tungsten tip mounted on a piezoelectric tube scanner (Stavely Sensors, Inc.) which is attached to the end of an Inchworm motor (Burleigh Instruments), contained inside a stainless steel UHV chamber. In tunneling experiments, voltages are applied to the sample in an electrically isolated tunneling stage. Samples can be resistively heated on a separate heating stage by passing current directly through the sample. Methyl chloride was introduced into the chamber through a precision leak valve.

Samples of n-type Si(001) wafers (polished to within 01. degree; Wacker-Chemitronic GmbH) are precleaned with methanol, then exposed to a quartz mercury-vapor lamp to oxidize any organic residues. The samples are loaded into the UHV chamber through a load-lock system, degassed at 630 C, then flashed to 1100 C for approximately one second. After cooling, the sample is exposed to a selected pressure for a selected time interval, typically 1×10^{-8} Torr for 30 s., of methyl chloride (Matheson). The tip is brought into tunneling range and the dosed surface is imaged. Images are recorded with a tunneling current of 0.3 - 0.5 nA and voltage magnitude of 1.5 - 3.0 V. Images can be acquired with either

negative or positive sample bias polarity, giving images of filled or unfilled surface electronic states, respectively.

Results and Discussion

I. Molecular Fragments of Methyl Chloride on Si(001)

STM images of Si(001) surfaces dosed with methyl chloride show a number of features not observed on clean silicon, which we attribute to CH₃Cl fragments. As has been observed by Boland ¹², chlorine atoms bond in a variety of configurations. We find that heating the dosed surfaces slightly causes all Cl atoms to assume a single bonding geometry (making image interpretation easier) without otherwise significantly altering the surface. We therefore begin by considering images of surfaces that have been warmed after dosing, and then move on to the more complex unheated surface.

A) Silicon monochloride dimers and CH₃ groups

Figure 1 shows a large area STM topograph of a Si(001) surface dosed with 0.3 Langmuir of CH₃Cl and heated for two minutes to 150 °C. Figure 2 shows a higher resolution, smaller area image of this same surface. The most notable new features on CH₃Cl-dosed surfaces are what appear to be long line defects; several of these are labeled "Cl₂" in figures 1 and 2. Higher resolution (Figure 2) reveals these features to be columns of silicon dimers, each dimer of which

appears lower than the surrounding dimers and has a minimum in intensity at the center of the dimer, giving it a "split" appearance similar to that observed in ordinary Si dimers at positive bias¹³, or of hydrogenated Si dimers (the silicon monohydride surface) at negative bias¹⁴. Another type of new feature observed in figure 2, labeled "CH3", consists of a low protrusion sitting atop an Si dimer, displaced to one side of the dimer. These features are much less pronounced than the "Cl2" features and are difficult to see in figure 1. Figure 6 illustrates the appearance of these two features.

The "Cl2" features can be readily identified based on their appearance and on previous STM studies. Boland¹² has recently studied the adsorption of molecular chlorine on Si(001) surfaces using STM. He observed chlorine-induced features with the same appearance and symmetry as the "Cl2" features in figures 1 and 2: dark, well-resolved dimer units that were that were only observed after the surfaces had been dosed with Cl₂. Molecular chlorine is known to dissociatively adsorb on Si (001)¹⁵⁻¹⁷, and thus Boland attributed these features to silicon dimers on which chlorine atoms have bonded to both of the silicon atoms, i.e., "silicon monochloride" dimers. Because we see exactly the same features resulting from adsorption of CH₃Cl, one of whose fragments one would expect to be chlorine atoms, we attribute the "Cl2" features we observe to these silicon monochloride dimers. These dimers appear darker in STM images than the surrounding dimers on the terrace because the STM is sensitive to surface states with energies close to the Fermi level. The strongly bound Si-Cl σ -bond orbitals and Cl lone-pair orbitals are much lower in energy than the weakly-binding π -type orbital of the

Si-Si dimers, and so the former appear lower (darker) than the latter. As can be seen in figures 1 and 2, the chlorine atoms have already begun to accumulate into islands of silicon monochloride after heating to 150 °C. Several small islands of monochloride dimers are labeled "I" in these figures.

The features labeled "CH₃" in figure 2 can also be readily identified based on their binding symmetry. Figure 3 shows a high-resolution image of several of these fragments, with horizontal grid lines marking the centers of the dimers rows of the Si(001) dimer lattice. Each "CH₃" feature consists of a small protrusion sitting exactly on top of the position of one silicon atom of a dimer: on top of the dimer, displaced to one side. This is just the bonding symmetry one would expect of a methyl group. A CH₃ group needs only one bond to the Si surface in order for the central carbon atom to achieve 4-fold coordination. This bond can be formed by breaking the weak Si-Si π -bond between two Si atoms of a dimer, and bonding the methyl group to one of the atoms. The feature labeled "CH₃" thus has the symmetry with respect to the silicon lattice that one would expect for a methyl group, as shown in figure 5. In view of our identification of chlorine atoms on the surface, it seems reasonable to expect that CH₃ groups will also be a dominant decomposition fragment from methyl chloride. It is further worth noting that previous investigations by Yates and coworkers^{7, 9} have shown that methyl groups are stable on the Si(001) surface at temperatures up to 600 K. Features with this same appearance and symmetry have been observed in this laboratory in STM investigations of the decomposition of trimethylgallium (Ga(CH₃)₃) on Si(001), and were

identified in that case as methyl groups. We thus conclude that the features labeled "CH₃" in figure 2 are CH₃ groups, products of the dissociation of CH₃Cl on the Si(001) surface.

B) Other Cl-atom configurations

Figure 4 shows STM images of the same Si(001) surface (albiet different areas) before and after dosing with 0.15 L of CH₃Cl at 300 K. This sample was not heated after dosing. Comparison of figures 4a and 4b indicate that dosing with CH₃Cl significantly increases the density of two types of surface features. One type, labeled "H" in figure 4, consists of a bright area next to a dark area on the same dimer, and appears similar to a hydrogen atom on Si(001)¹⁸. The other, labeled "C", consists of bright and dark areas on the same side of two adjacent dimers within a dimer row, and appears similar to certain native defects on Si(001) known as "C-type" defects¹⁹, which are produced during high-temperature annealing. Figure 7 illustrates the appearance of these two types of features. Silicon monochloride dimers are also visible on the dosed surface.

In STM investigations of Si(001) surfaces dosed at 300 K with Cl₂, Boland observed a number bonding configurations for adsorbed individual (non-dimerized) chlorine atoms, including configurations with the same appearance as the "H" and "C" features described above ¹². CH₃Cl dosing thus increases the density of features previously interpreted as adsorbed Cl atoms. While the similarity of these features to certain defects on the pre-dosed surface prevents us from assigning any individual feature as a Cl atom, the increase in

concentration of these features on the dosed surface does allow us to conclude that many such features must correspond to Cl atoms.

The CH_3Cl -dosed surface also exhibits a great deal more dimer row buckling, in which the position of the maximum in intensity of the dimers in a given row alternates between sides of that dimer row. An example of such buckling is labeled "B" in figure 4b. Recent theoretical²⁰ and experimental²¹ results indicate that breaking of the mirror plane symmetry of a $\text{Si}(001)$ dimer row (as by an adsorbate), accompanied by charge transfer between the Si atom and the adsorbate, will induce just such buckling. Because Cl is highly electronegative, we would expect that Cl atom adsorption would lead to increased dimer row buckling. Therefore, our observation of increased buckling on dosed surfaces also suggests the presence of atomic (non-dimerized) chlorine.

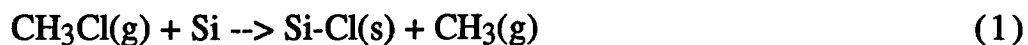
The dosed, unheated silicon surface exhibits more dimer row buckling than the dosed, heated surface (compare figure 4b with figure 1), suggesting that little chlorine remains as undimerized atoms on heated $\text{Si}(001)$ surfaces. Previous work has shown that chlorine does not desorb from $\text{Si}(001)$ below about 800 K^{1-5} . Thus, Cl atoms must be mobile at 420 K and can migrate to their most stable binding site, the monochloride dimer bonding configuration.

Because a buckled dimer appears similar to a dimer with a methyl group bonded to it, it is difficult to count accurately the number of methyl groups on a highly buckled surface. Additionally, the similarity in appearance of undimerized Cl atoms to features seen on pre-dosed silicon makes difficult an accurate counting of the Cl atoms on an unheated surface. Thus, analyses based fragment

counting statistics, as described in the following section, are restricted to surfaces which have been dosed and heated.

II. Fragment Counting Statistics and Reaction Mechanism

The counting statistics of CH₃ groups and Cl atoms on the surface can provide insight into the mechanism of decomposition of methyl chloride on Si(001). On dosed surfaces that have been heated to 420 K, we find that the ratio of chlorine atoms to methyl groups is: $N_{\text{Cl}}:N_{\text{CH}_3} = 2.0 \pm 0.2$. Clearly, there exist substantially more chlorine atoms than methyl groups on the surface. This seems puzzling at first glance because one would expect, based on simple stoichiometry, that the decomposition of methyl chloride should yield one methyl group for every chlorine atom produced. One possible explanation for our observed number density ratios is suggested by the relative bond strengths of the chemical bonds broken and formed in this reaction. The bond energy of a Si-Cl bond is 111 kcal/mole²², whereas the C-Cl bond strength in CH₃Cl is only about 70 kcal/mole²². Thus, the "abstraction" by the silicon surface of a chlorine atom from methyl chloride, leaving behind a (gas phase) methyl group, i.e., the reaction:



is exothermic by approximately 40 kcal/mole. It is thus thermodynamically reasonable to propose that some of the CH₃Cl molecules may react in this way, depositing a chlorine atom on the

surface and creating a methyl radical that rebounds away into the vacuum. This would explain why we see more Cl atoms than CH₃ groups.

A second possible reason for the 2:1 ratio is that perhaps the features which we associate with methyl groups each correspond to *two* methyl groups adsorbed on a single dimer. However, we note that images such as fig. 3 always show that the CH₃-reacted dimers show a protrusion which is significantly off the center of the Si-Si dimer bond; this implies that the inherent mirror-plane symmetry of the Si-Si dimer bond (which leads to symmetric dimers at 300 K in the absence of defects) must be broken, and strongly suggests that each CH₃-reacted dimer corresponds to exactly *one* CH₃ group.

While exothermic, the above reaction is thermodynamically less favorable than the deposition of both Cl atom and CH₃ group onto the Si(001) surface. We suggest that some methyl chloride molecules react via eqn. (4) due to steric constraints. Specifically, if a CH₃Cl molecule impinges upon the surface with the chlorine atom pointed down toward the surface, the reaction may occur by direct linear abstraction of a chlorine atom by the surface, with the CH₃ group rebounding away. In this case, the reaction path is controlled by kinetics rather than thermodynamics: in such an end-on collision the steric bulk of the Cl atom prevents the methyl group from getting close enough to the surface to bind. On the other hand, a side-on collision, with the C-Cl bond approximately parallel to the surface, would allow both Cl atom and CH₃ group to get close enough to the surface to react with the surface. Indeed, our observed Cl:CH₃ ratio

of 2:1 suggests that approximately half of the reacting methyl chloride molecules dissociate in each way.

Conclusions

We have investigated the adsorption and dissociation of methyl chloride on Si(001) using STM and have identified the molecular fragments of this molecule on the surface. CH_3Cl dissociates into CH_3 groups and Cl atoms, both of which can bind to the surface. The chlorine atoms bind at room temperature primarily in the form of silicon monochloride dimers, but also show a variety of other binding geometries as was observed by Boland¹². Upon heating to 420 K the chlorine atoms become mobile, and they migrate so that all Cl atoms occupy monochloride dimer sites. Methyl groups have the same appearance as was observed in the decomposition of trimethylgallium on Si(001)²³. They are mobile at 150 °C and bind preferentially adjacent to rows of Cl-terminated silicon dimers. Detailed counting statistics on Si(001) surfaces dosed with CH_3Cl and warmed to 150 °C suggests that adsorption and decomposition can occur in two different ways at room temperature, one in which both Cl and CH_3 fragments bond to the surface, and the other in which the Cl atom is abstracted from the CH_3Cl molecule by the surface and the methyl group so created rebounds away from the surface.

Acknowledgments

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Figure Captions

Figure 1.

Large-scale STM image of a Si(001) surface dosed with approximately 0.3 Langmuir of methyl chloride, then heated to 150 °C for two minutes. Imaging conditions: Sample Bias = -2.2 V , Tunneling Current = 0.3 nA, 330 Å x 250 Å.

Figure 2.

Small-scale, high-resolution STM image of a Si(001) surface dosed with 0.3 L of methyl chloride, then heated to 150 °C for two minutes, showing "CH3", "Cl2", and "I" features. Imaging conditions: -2.2V, 0.3 nA, 90 Å x 75 Å.

Figure 3.

Small area, high-resolution STM image of several "CH3" features, which are marked with arrows. The horizontal gridlines mark the centers of the Si(001) dimer rows in this image. Imaging conditions: -2.2V, 0.3 nA, 60 Å X 38 Å.

Figure 4.

STM images of a Si(001) surface, (a) before, and (b) after dosing with 0.15 L of CH₃Cl. Features labeled "H", "C", and "B" are described in the text. Imaging conditions: -2.2 V, 0.3 nA, 150 Å x 150 Å.

Figure 5.

Bonding configuration for a CH₃ group on Si(001).

Figure 6.

Diagram showing the appearance and symmetry of the "CH₃" and "Cl₂" features induced by dosing Si(001) with CH₃Cl.

Figure 7.

Diagram showing the appearance and symmetry of the "H" and "C" features induced by dosing Si(001) with CH₃Cl.

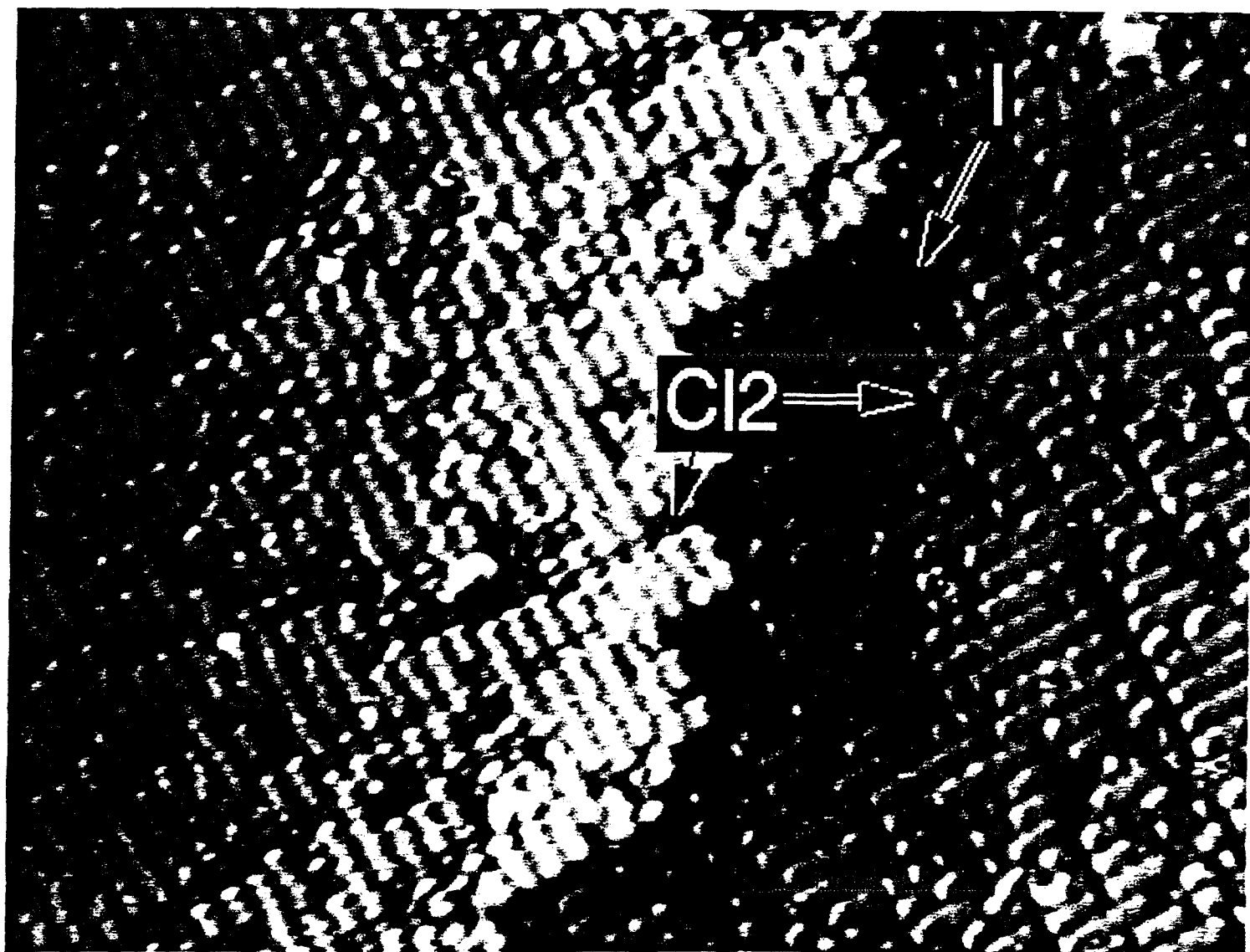


Fig.1

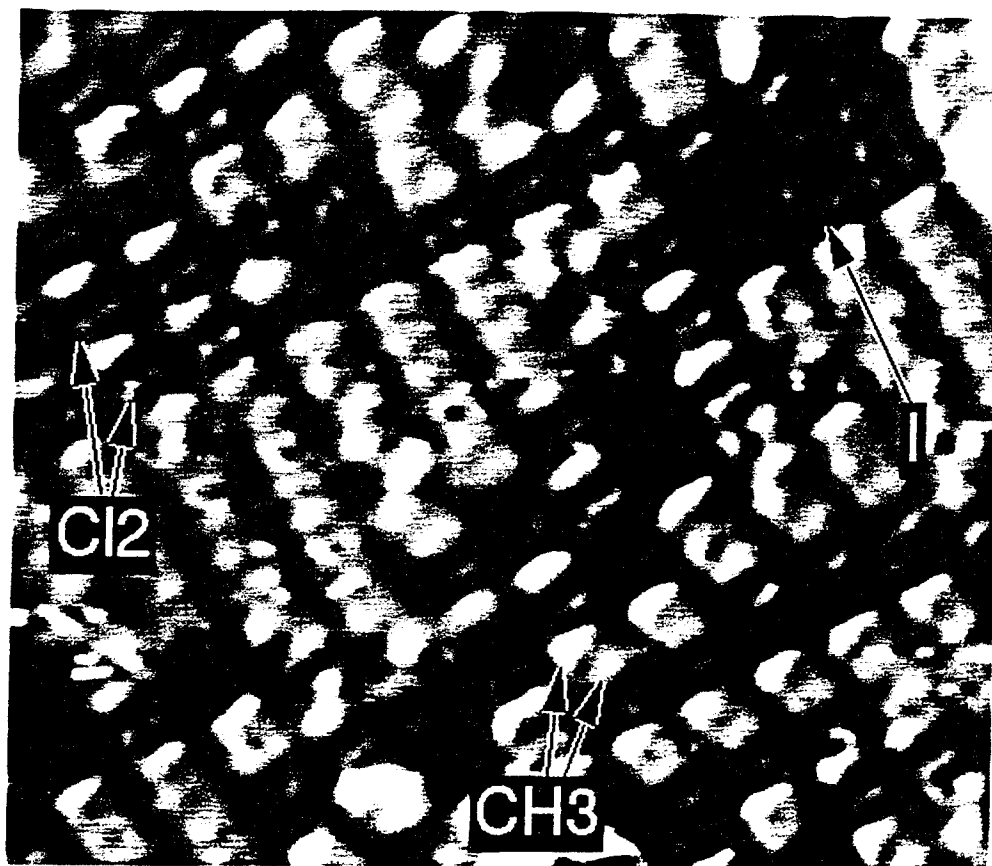


Fig. 2

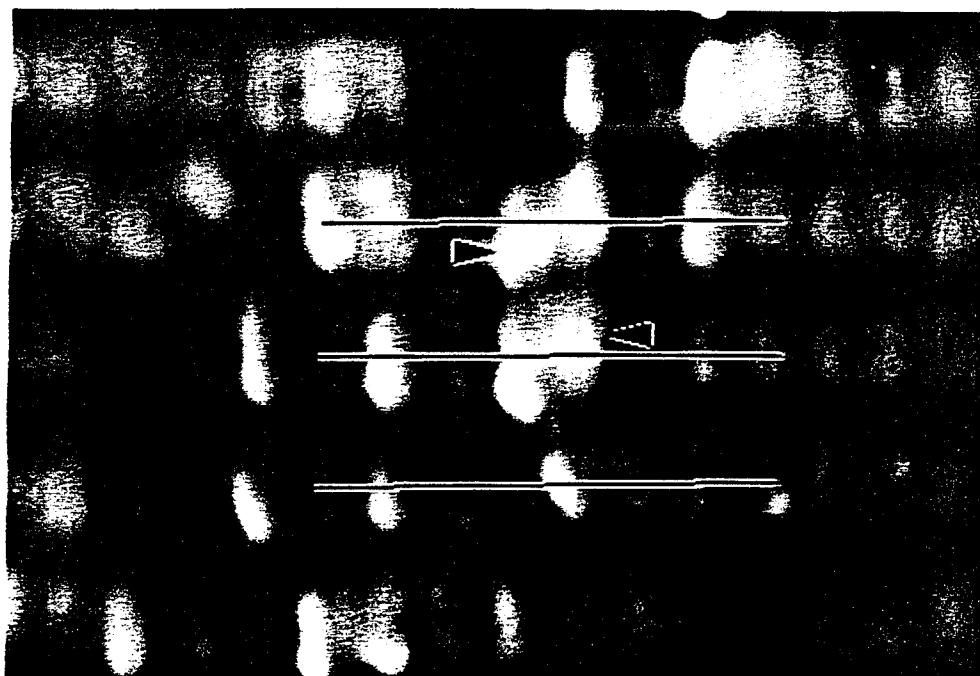


Fig. 3

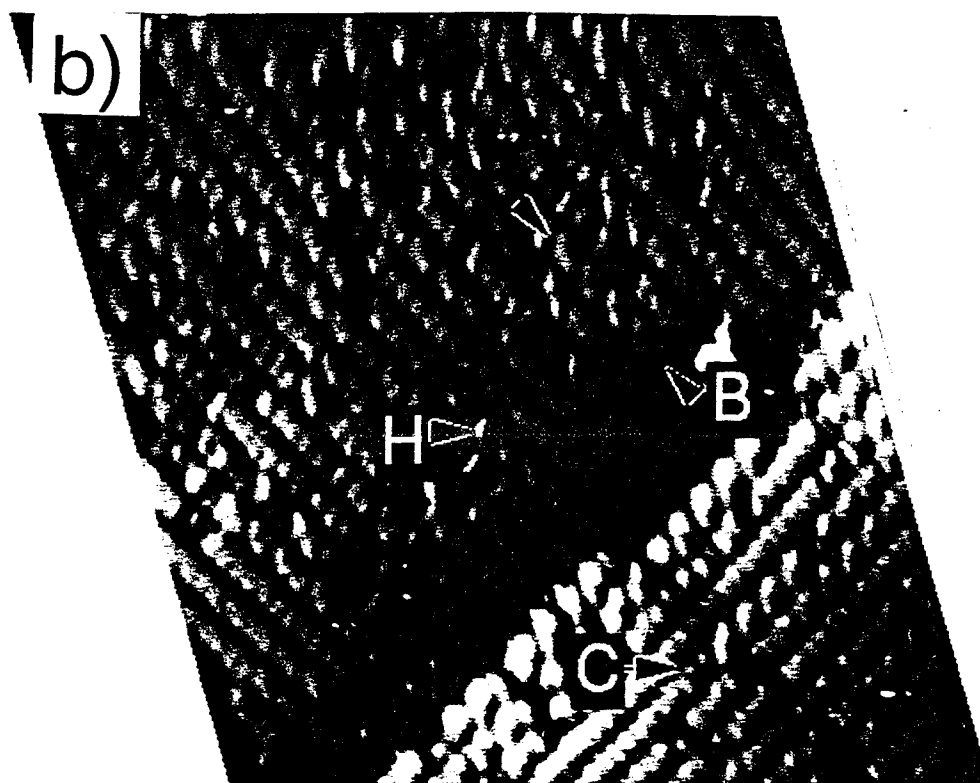
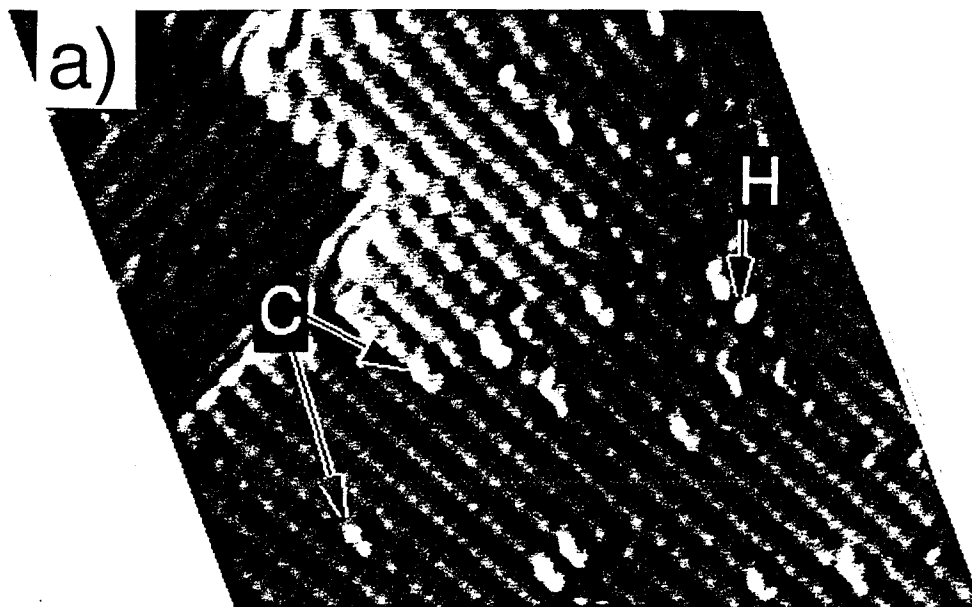


Fig. 4

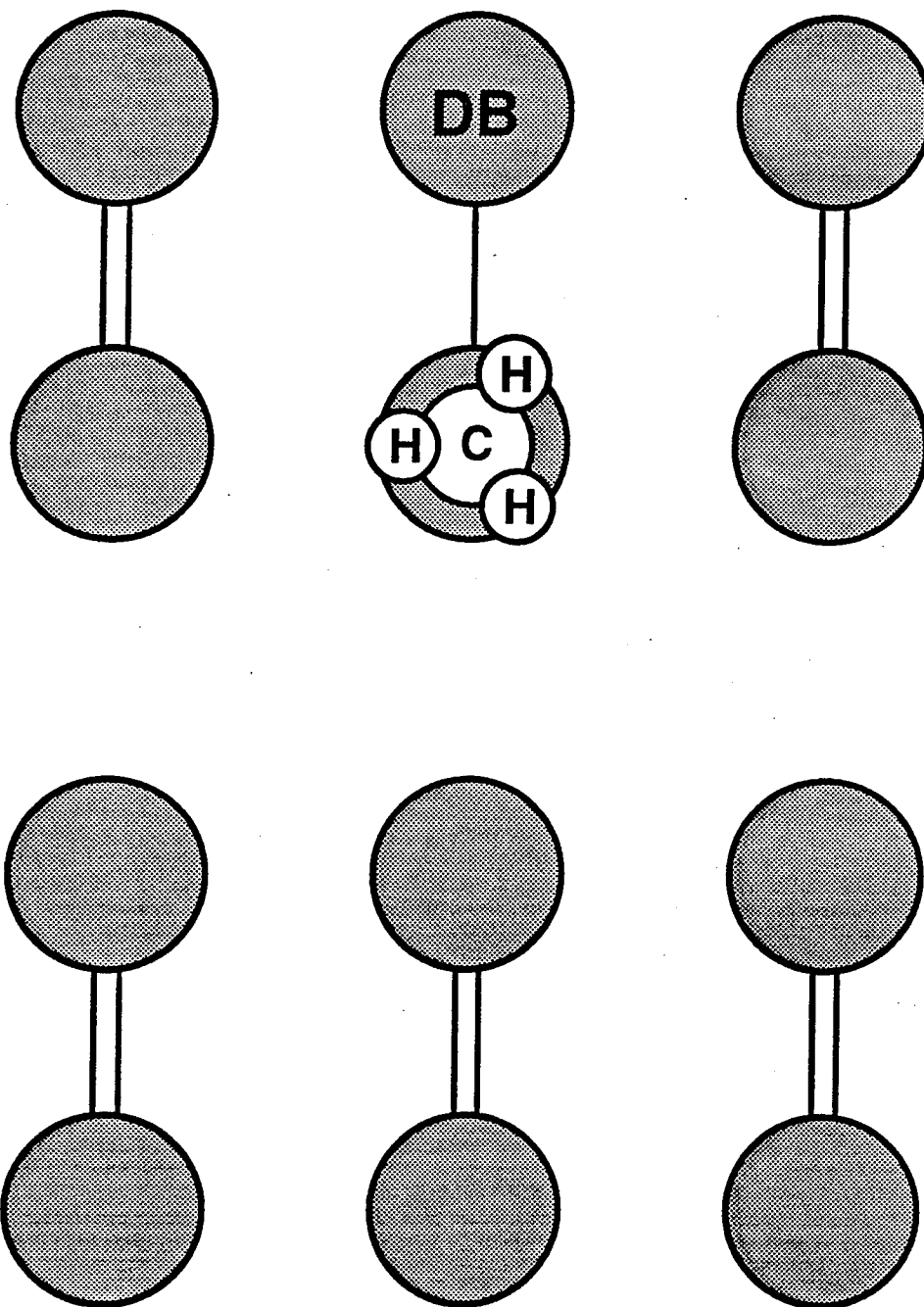


Fig. 5

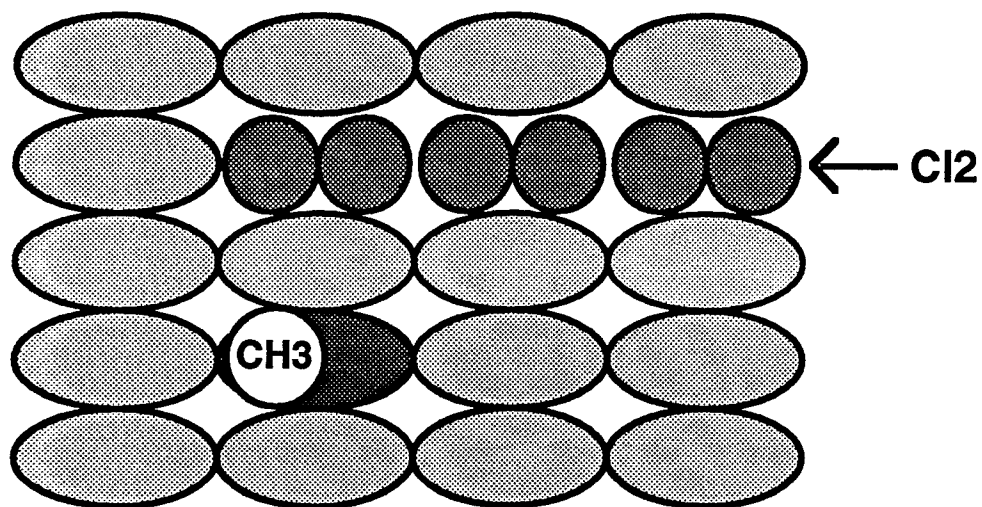


Fig. 6

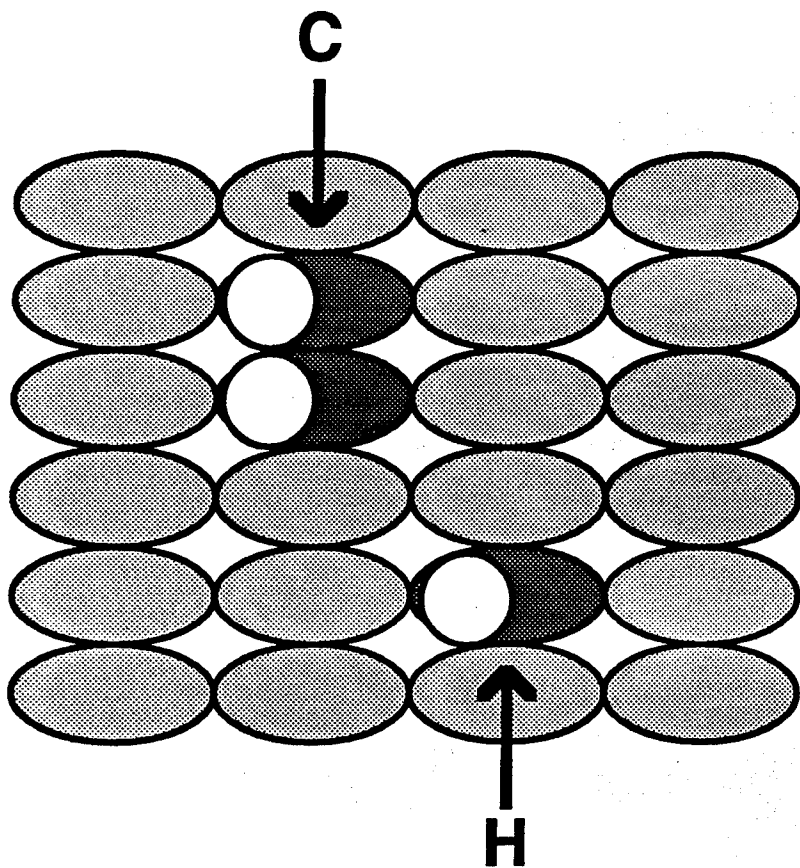


Fig. 7