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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Henry Eyring Building University of Utah Salt Lake City, Utah 84112			8. PERFORMING ORGANIZATION REPORT NUMBER 29	
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HALOGEN CHEMISORPTION ON SILVER(111). SCANNING  
TUNNELING MICROSCOPY OF COADSORBED HALOGEN ATOMS

by

JOACHIM HOSSICK SCHOTT AND HENRY S. WHITE

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University of Utah  
Department of Chemistry  
Salt Lake City, UT 84112

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# Halogen Chemisorption on Silver(111). Scanning Tunneling Microscopy of Coadsorbed Halogen Atoms

Joachim Hossick Schott  
Department of Chemical Engineering and Materials Science  
University of Minnesota  
Minneapolis, MN 55455

and

Henry S. White  
Department of Chemistry  
University of Utah  
Salt Lake City, UT 84112

**Abstract.** The structures of halogen monolayers (I, Br, Cl, and F) and mixed halogen monolayers on Ag(111) surfaces are measured by scanning tunneling microscopy (STM). Adatom radii determined from nearest-neighbor bond distances are in excellent agreement with literature values of the radii of halides, indicating that the adsorbed halogen atoms have an essentially ionic character and are adsorbed as a surface Ag halide complex. STM images of mixed halogen adlayers, comprised of either coadsorbed I and Cl, I and F, or Cl and F, exhibit several structural features, e.g., a low frequency moire pattern and a large atom vacancy density, that are not observed in single-atom adlayers and that are ascribed to coulombic forces within the ionic adlayer. STM has also been used to monitor variations in adlayer structures following ion exchange of chemically distinct halogen species. STM images and data obtained from Auger electron spectroscopy indicate that the chemical stability of the surface Ag halide complexes in aqueous solutions decreases with increasing halogen electronegativity. The results suggest that the energy of solvation of the halide ions determines the relative stability of the Ag-halide surface bond, similar to that observed for bulk Ag halide crystals.

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## **Introduction.**

Knowledge of the structural and electronic properties of halogen monolayers on Ag surfaces is fundamental to understanding many aspects of silver halide chemistry<sup>1,2,3</sup>. Theoretical studies suggest that halogen atoms adsorb as halide ions on a metal surface at low coverages, due to charge transfer from the metal to the halogen adatom<sup>4</sup>. At higher halogen coverage, epitaxial growth of a silver halide layer is observed in gas-phase reactions<sup>5,6,7</sup>. However, the distribution of electronic charge in a monolayer ensemble of halogen atoms is still subject to speculation.

In recent reports from our laboratory, a relatively simple chemical method of synthesizing halogen (I, Br, Cl, and F) adlayers on Ag(111) surfaces<sup>8,9</sup> has been described that involves immersion of flame-annealed Ag samples in a concentrated solution of the corresponding acid halide. Chemical surface analysis using electron spectroscopy demonstrates that the resulting halogen layers are stable in air for several hours without significant displacement of the halogen atoms by oxygen. The surprising chemical stability of these adlayers makes possible the characterization of their structures using a scanning tunneling microscope (STM) operated in ambient environments.

In the present report, STM and Auger electron spectroscopic examinations of mixed-halogen monolayers, comprised of coadsorbed F and Cl, F and I, or Cl and I atoms on Ag(111) surfaces, are described. In addition to extending the previous studies of the structures of adlayers formed by adsorption of a single halogen species, the results described herein suggest that STM can be used to differentiate between different halogen adlayers, based on significant differences in adatom radii and long-range adlayer structural patterns. Structural features that are unique to adlayers comprised of different halogen species are used to monitor ion-exchange reactions on Ag surfaces, in which a halogen species dissolved in an aqueous solution displaces a previously adsorbed, but chemically different, halogen atom. In addition, comparison of adatom radii (deduced

from nearest-neighbor distances of the halogen adatoms) with the crystallographic ionic radii of the halides, indicates that the halogen adlayer is essentially ionic at high coverages.

### Experimental .

Ag(111) substrates were prepared by melting one end of a ~2 cm piece of Ag wire (Aesar/Johnson Mathey, 0.5 mm diameter, 99.995 % purity) in a hydrogen-oxygen flame to form a ~2 mm diameter sphere<sup>8</sup>. After annealing the sphere in a cooler, hydrogen rich flame at ~1000 K and cooling in air for 10-20 sec, the Ag samples were immersed for 30-300 sec in one of the following solutions: hydrofluoric acid (38 %, Baker) to form F adlayers; hydrochloric acid (38 %, Merck) to form Cl adlayers; hydrobromic acid (48 %) to form bromine adlayers; and hydroiodic acid (1%, Merck) to form I adlayers.

Mixed adlayers comprised of two different halogen adatoms were prepared by successive immersions of the annealed Ag sample in solutions containing different acid halides. Ag samples coated with F/Cl mixed adlayers were formed by immersion of the sample in 38% HF for 300 sec (based on our experience with these systems, this procedure ensured the assembly of a saturated F monolayer on the sample, as is evident from STM images, *vide infra*). The F-saturated samples were then immersed in a 38% HCl for different lengths of time to generate adlayers of different atom percentages of F and Cl. Similarly, F/I and Cl/I mixed layers were formed by immersing the sample in either a HF(38%) or HCl (38%) solution to obtain a saturated F or Cl adlayer, and then immersing the sample into hydroiodic acid (1%). Auger electron spectroscopy and STM indicated that I readily displaces both F and Cl on the Ag surface; thus, a relatively low HI concentration was chosen to obtain mixed adlayers containing a significant atomic percentage of Cl or F.

The formation of the halogen adlayers and their elemental composition, as well as the presence of surface contamination, was monitored by Auger electron spectroscopy

using a PHI 595 SAM, cylindrical mirror analyzer. No measurable oxygen or carbon signal was observed in the Auger electron spectrum for any of the halogen-coated samples after exposure to ambient environment for 2 - 3 hours. A representative set of Auger electron spectra for halogen and mixed halogen adlayers is presented in the Results and Discussion section.

After rinsing with triply distilled water, the Ag spheres were mounted in a home-built specimen holder allowing for orientation of the halogen-coated Ag(111) facets for STM studies. The Ag(111) facets have dimensions typical on the order of 10  $\mu\text{m}$  and are readily recognized on the surface of the Ag sphere using a low magnification optical microscope by the facet boundaries which form 60 and/or 120  $^\circ$  angles<sup>8</sup>.

The surfaces were imaged with a Nanoscope II scanning tunneling microscope<sup>10</sup>, in which the bias voltage is applied to the sample. Experiments were performed in air using mechanically cut Pt(70%)-Ir(30%) tips. All images were recorded in the constant current mode using a scan rate of 8.6 or 19.2 Hz and consist of 400 x 400 data points. Based on our experience with this instrument, we estimate that the reported lateral accuracy is better than or equal to  $\pm 0.3 \text{ \AA}$ .

## **Results and Discussion.**

*Halogen Adlayers.* Atomically-resolved STM images of F, Cl, and Br and I adlayers on Ag(111) are shown in Fig. 1. A detailed structural analysis of the adlayers based on these and similar STM images has been reported elsewhere<sup>8</sup>. A brief description of the adlayers is presented here in order to provide a basis for interpreting STM images of mixed adlayers comprised of different halogen atoms.

Low resolution STM images of the all halogen-coated Ag surfaces show atomically-flat terraces of widths up to 100 nm and separated from neighboring terraces by monoatomic steps of 3.0 $\text{\AA}$  average height. In each case, the saturation coverage of

halogen atoms corresponds to  $\sim 1$  monolayer, as determined by Auger spectroscopy<sup>8</sup> and coulometric measurements<sup>11</sup>.

An systematic progression is observed in the structures of the halogen adlayers, Fig. 1. The F adlayer is characterized by a double-row structure, which is readily apparent in the STM image. The interatomic dimensions are 2.8, 3.0, and  $4.2 \pm 0.3$  Å. The structure of the Cl adlayer is qualitatively similar to that of F, with interatomic dimensions of 3.3, 3.8, and  $4.1 \pm 0.3$  Å. For Br adlayers, the double-row structure is noticeably less pronounced (interatomic spacings of 5.3, 5.1, and  $4.1 \pm 0.3$  Å). For I adlayers, the double-row structure is entirely absent, and the monolayer closely resembles the well-known, but slightly distorted  $\sqrt{3} \times \sqrt{3}/R30$  adlayer structure (interatomic spacings of 4.9 and  $4.6 \pm 0.2$  Å).

The above images suggest that the relative degree of symmetry within the halogen adlayer increases with decreasing adatom electronegativity and increasing atom size. The double row atomic arrangements of the F and Cl atoms, which extends without interruption over the surface of large terraces, Fig. 2, likely reflect asymmetric lateral coulombic forces between localized charges. For I, the relative degree of charge localization is expected to be lower, resulting in a more symmetrical adlayer structure.

STM images are in excellent agreement with previous LEED<sup>12,13,14</sup> and SEXAFS<sup>15,16</sup> studies of halogen monolayers on Ag(111) synthesized from the gas phase. Our previous analysis also provides evidence for a slight expansion of the topmost Ag(111) atomic layer under the influence of Cl adsorption<sup>8</sup>, supporting earlier studies that an epitaxial AgCl layer may form at monolayer Cl coverages<sup>5,6,7</sup>.

All STM images reported in this article are obtained with a negative bias voltage applied to the sample, with electron tunneling occurring from the filled portion of the halogen p-level into the empty tip-metal states. Therefore, both the occupation of the p-level and its energetic position relative to the tip Fermi level determine the apparent brightness of the halogen adatoms in the STM images. Positive sample biases can not be

used to image any halogen-silver adsorption system because tunnel current instabilities, which result from a strong nonlinear resonance tunneling effect, do not allow the feedback loop of the instrument to stabilize. These effects are discussed in detail in a separate paper describing tunneling spectroscopic measurements of each of the Ag halogen systems<sup>9</sup>.

*Measurement of the Radii of Halogen Adatoms.* The series of STM images of the halogen adlayers show that the relative *apparent* dimensions of the adatoms are consistent with expectations based on the relative sizes of halogen atoms (or ions), i.e., the apparent size of I adatoms is roughly twice that of F adatoms, with Cl and Br having intermediate values. The trend in adatom dimensions, which is visually apparent in Fig. 1(a)-(d), suggests a method of identifying chemically different halogen atoms in mixed adlayers. In addition, since there is a comparatively large difference between the radius of a halogen atom and the corresponding halogen ion, measurements of the adatom radii provide an indirect method of determining the degree of charge-transfer in the adlayer. With these goals in mind, we attempted to obtain the adatom radii directly from measurement of the variation in the tunnel current density measured along a line drawn through the center of the atom. This method is appealing because the data correspond directly to the apparent size of the atoms as defined by the image contrast. However, this measurement suffers from a number of intrinsic and instrumental effects. First, there is a significant variation in the apparent dimensions of neighboring adatoms, as is clearly evident in the images of Cl adlayers, Fig. 1. The apparent differences in adatom dimensions may reflect variations in the degree of charge transfer between the metal and adatoms, resulting from coulombic forces within the film and reminiscent the depolarization of alkali species on metals at high coverages<sup>17</sup>. In addition, the model of the Cl adlayer deduced from previous STM studies indicates that the halogen atoms occupy different sites on the Ag surface, which would likely have a pronounced effect on

the magnitude of the tunneling current through individual adatoms. Second, the tunneling current distribution around individual adatoms often appears distorted, resulting in a non-spherical atom geometry (for instance, Fig. 1c). The extent of this distortion is also tip-dependent as apparent from images obtained using different tips. Third, without an appropriate theoretical model to describe the relationship between the tunneling current density and the adatom geometry, the choice of a cut-off in the tunneling current density at which the atom boundary is defined is subjective. The combined effects of these limitations make this method of estimating the adatom radii seemingly unreliable and, indeed, statistical analyses of experimental data show that there are no significant differences in the adatom size.

A more precise and reliable method of determining radii is based on the fact that the shortest possible nearest-neighbor bond distances observed in each of the adlayer structures corresponds to twice the theoretical maximum value of the adatom radius, assuming a hard-core repulsion between roughly spherical electron distributions. Using the shortest nearest-neighbor bond distance measured for each adlayer reported above, the corresponding radii were calculated to be 2.30 Å for I, 2.05 Å for Br, 1.65 Å for Cl, and  $1.40 \pm 0.3$  Å for F (based on approximately 25 determinations for each halogen species using different samples and tips). These distances are plotted in Fig. 3 as a function of literature values of halide radii<sup>18</sup>: I(2.20 Å); Br(1.96 Å); Cl(1.81 Å); F(1.33 Å). Before discussing these data, we note that measurement of the nearest-neighbor adatom bond distances does not suffer from the same inherent limitations as discussed above, and that the values obtained are very reproducible using different STM tips (better than  $\pm 0.3$  Å). The radii of any two halogen species based on this method are statistically different.

The radii of halogen adatoms, measured from the nearest-neighbor bond distance are in excellent agreement with the radii of the corresponding halide ion, as evident from comparison of the data with the solid line which has unity slope and a zero intercept<sup>19</sup>.

As noted above, we interpret these values of STM-measured radii as representing the theoretical *maximum* value of the adatom radius, since it is probable that the separation of the adatoms is not due solely to hard core interactions, but is affected by interactions with the substrate lattice. Indeed, it is most likely that some combination of the two interactions are responsible for the spatial arrangements of the atoms. However, the data in Fig. 3 clearly suggest that each of the halogen adatoms are chemisorbed on the Ag substrate as ionic species, rather than as halogen atoms. In particular, the radius measured for each halogen adatom is at least 50% larger than anticipated if the chemisorbed species were not ionized, but rather existed as neutral atoms (atomic radius<sup>20</sup>: I(1.28 Å); Br(1.11 Å); Cl(0.99 Å); F(0.64 Å)). Based on these findings, we conclude that the structures we have imaged are best described as Ag halide monolayers.

Our finding that the adlayer is essentially ionic indicates that the outermost layer of the Ag surface is partially oxidized, as required by electroneutrality. Thus, the synthesis of the halogen layers, by immersion of Ag in an acid halide solution, is accompanied by oxidation of the Ag surface by a mechanism that is not apparent. However, we note that the electrochemical oxidation of Ag electrodes in the presence of halides (yielding a multilayer Ag halide film) is preceded by several tenths of a volt by the formation of a Ag halide monolayer<sup>11, 2</sup>. Thus, since the Ag halide monolayers are thermodynamically more stable than the corresponding bulk Ag halide, it is not altogether surprising that oxidation of the Ag sample when immersed in an acid halide solution (without an applied potential) is limited to the outermost metal atoms.

#### *Mixed Halogen Adlayers*

It is also possible to image adlayers comprised of mixtures of two different types of halogen atoms. Fig. 4 shows STM images of a Ag(111) surface, which was first saturated with F and then exposed to 38 % HCl. The double row structure characteristic of individually adsorbed F or Cl atoms is completely absent after an exposure to the HCl

solution for 30 sec (Fig. 4a, b). The structure of the mixed layer is, in fact, quite distinct from that of films comprised of only Cl or F. In addition to the atomic corrugation, STM images of the F/Cl adlayer show a longer range periodicity ( $\sim 33$  Å wavelength) that is reminiscent of Moire patterns often observed in STM images of highly-ordered pyrolytic graphite. The long range periodic fluctuation in the tunneling current has a quasi-hexagonal structure that we tentatively assign to a lattice mismatch between the Ag and halogen adlayer. The peak-to-valley atomic corrugation varies in the image between 0.3 and 0.8 Å, as is apparent by the changing contrast in different surface areas. It is interesting to note that the mixed layers also display a larger number of atomic vacancies defects (22 atom vacancies in the in the 17.5 x 17.5 nm image of the adlayer shown in Fig 4a). We speculate that these defects result from stresses in the film that occur as the result of the lattice mismatch between adsorbate and substrate.

In contrast to individual F and Cl adlayers, the interatomic spacings in the F/Cl mixed layer are highly irregular. The shortest nearest-neighbor interatomic distance is 3.1, close to the value measured for F (2.8 Å).

Images of mixed I/Cl adlayers are shown in Fig. 5. These adlayers were synthesized by first saturating the Ag surface with Cl for 300 sec in a 38 % HCl solution and then exposing the surface to HI (1%). Similar to the results obtained for the Cl/F adlayer, the mixed I/Cl adlayer is characterized by numerous atomic vacancies and varying atomic contrast. The nearest-neighbor interatomic distances in Fig. 5 range from 3.6 to 4.6 Å. Longer exposure to HI resulted in complete exchange of Cl by I. The image in Fig. 5c, for example, is of a sample saturated with Cl and then exposed to 1% HI for 60 sec. The nearest neighbor distances in the upper portion of this image are 4.6 and 4.9 Å, identical to the distances measured when I is adsorbed individually (Fig. 1). A small surface cluster of I is also apparent in the left part of the image shown in Fig. 5a, marked by the arrow. The exchange of Cl by I is confirmed by Auger electron spectroscopy. Fig. 6 shows the Auger spectra corresponding to the above STM

experiments. The Cl signal for a Ag sample initially saturated with Cl diminishes when the sample is immersed in weakly concentrated HI (1 %). After an HI exposure of only 60 sec, essentially no Cl signal is observed in the Auger spectrum, while the I signal is markedly increased (Fig. 6). Conversely, when the experiment is performed by initially exposing the Ag to a 1% HI solution and then to a 38% HCl solution, no Cl signal whatsoever is detected in the Auger spectrum, indicating that Cl does not adsorb on the iodine-covered Ag surface. This result is consistent with STM results which show that the I adlayer is essentially undisturbed by immersion in HCl solutions.

In separate experiments, a Ag sample was immersed in a solution containing HI (0.5%) and HCl (19%). As anticipated from the above results, both STM and Auger electron spectroscopy indicate that only I is adsorbed from this mixed solution. Specifically, the STM image is essentially identical to that shown for I in Fig. 1.

F adatoms are also rapidly exchanged by I. STM images of a Ag sample which was first saturated with F in 38% HF (300 sec exposure) and then immersed in 1% HI for only 30 sec, display an adlayer structure that is similar to that shown in Fig. 1 for a Ag surface coated with only I. The most prominent nearest neighbor interatomic distances are 4.6 and 4.9 Å, in quantitative agreement with nearest neighbor distances measured for individually adsorbed I. Occasionally, nearest neighbor distances as low as 3.0 Å are found on the F/I mixed adlayer. Since 2.8 Å is the nearest neighbor distance observed on F-covered Ag surfaces, we assume that such small nearest neighbor distances in F/I mixed adlayer are indicative of a small amount of F that is not exchanged by I during immersion of the sample in the HI solution.

### Conclusions.

The tendency of I to displace Cl and F adatoms is consistent with the ionic nature of the halogen adlayers. Because the adlayers are synthesized in aqueous environments, the solvation of the chemisorbed anions by water molecules plays an key role in the ion

exchange process, lowering the Ag-halogen surface bond strength relative to values in vacuum. The rapid and irreversible exchange of either F or Cl adatoms by I is thus clearly related to the expectation, derived from gas-phase studies of solvated halogen ions<sup>21</sup>, that the smaller halogen anions (F<sup>-</sup> or Cl<sup>-</sup>) are more highly solvated in the chemisorbed state than the larger anion (I<sup>-</sup>). A similar relationship between anion size and hydration number appears to hold also for specifically adsorbed anions<sup>22</sup>. We conclude that the stability of the Ag halide monolayers parallels the behavior of bulk Ag halide crystals in aqueous environments, where the solubility increases with increasing anion electronegativity (solubility product: AgI ( $8.51 \times 10^{-17}$ ); AgBr( $5.35 \times 10^{-13}$ ); AgCl( $1.77 \times 10^{-10}$ )).

The same argument may also explain why the original double row structure of F (Fig. 1) is apparently completely destroyed and slowly replaced by the Cl double row structure upon exposure of the F-saturated sample to HCl solutions. The desorption of F in the HCl solution, and its subsequent replacement by Cl most likely depends on the Ag-F and Ag-Cl binding energies, which in turn depend on the surface-adsorption site and on the anion solvation. Since the Ag-halogen chemisorption system is essentially ionic in nature, strong coulombic forces between neighboring adatoms are likely to occur. Even in the case of a homogenous adlayer comprised of only one halogen species, these forces are apparently highly anisotropic (Fig. 1). In case of a heterogeneous adlayer comprised of two different adatoms, this force anisotropy may be expected to increase, leading to the frequent occurrence of atom vacancies and varying nearest neighbor interatomic distances in the mixed monolayers, as observed in the STM images.

There is considerable variations in the contrast and size of adatoms in mixed adlayers, as imaged by STM (Figs. 4 and 5). While it is tempting to identify different atomic species in the mixed layer based on their apparent sizes, image analyses of the homogenous adlayers shows that these differences are not significant. Therefore,

different atomic species can not be discerned on the basis of the apparent dimensions in the STM image. However, we have shown that significant differences exist in halogen adatom radii as determined from nearest-neighbor bond distances. Absolute values of the adatom radii strongly suggest that the adlayer is essentially ionic, and have proven useful in qualitative STM-image analyses of mixed adlayers.

A more detailed understanding of the complex desorption-adsorption processes at the Ag/solution interface can only come from future in-situ STM experiments, where both tip and sample are immersed in the aqueous halide solution. These experiments promise exciting insights in the ion-exchange mechanism and may allow important conclusions concerning the solvation of halogen adatoms on Ag(111) electrodes immersed in electrolyte solutions.

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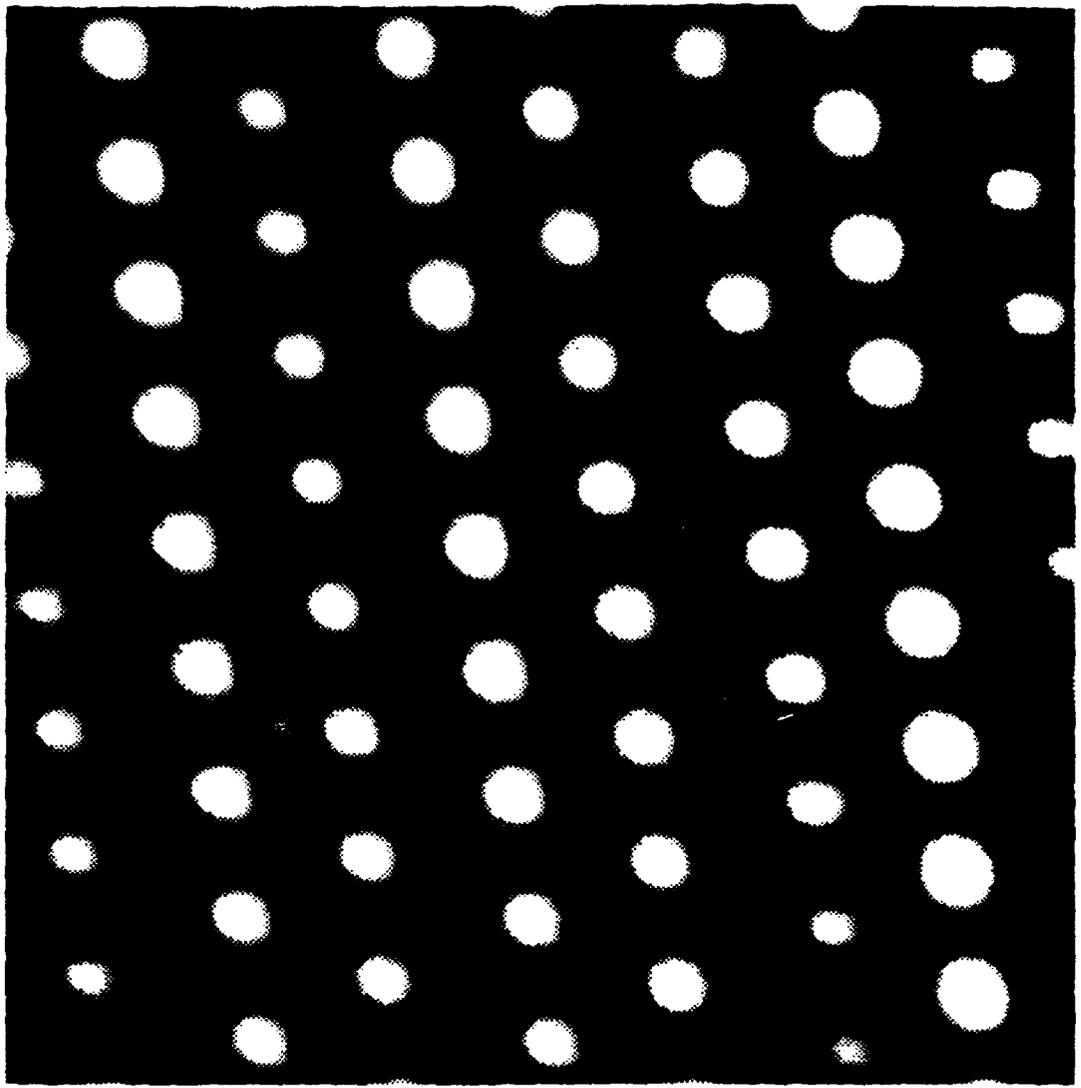
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## Figure Captions

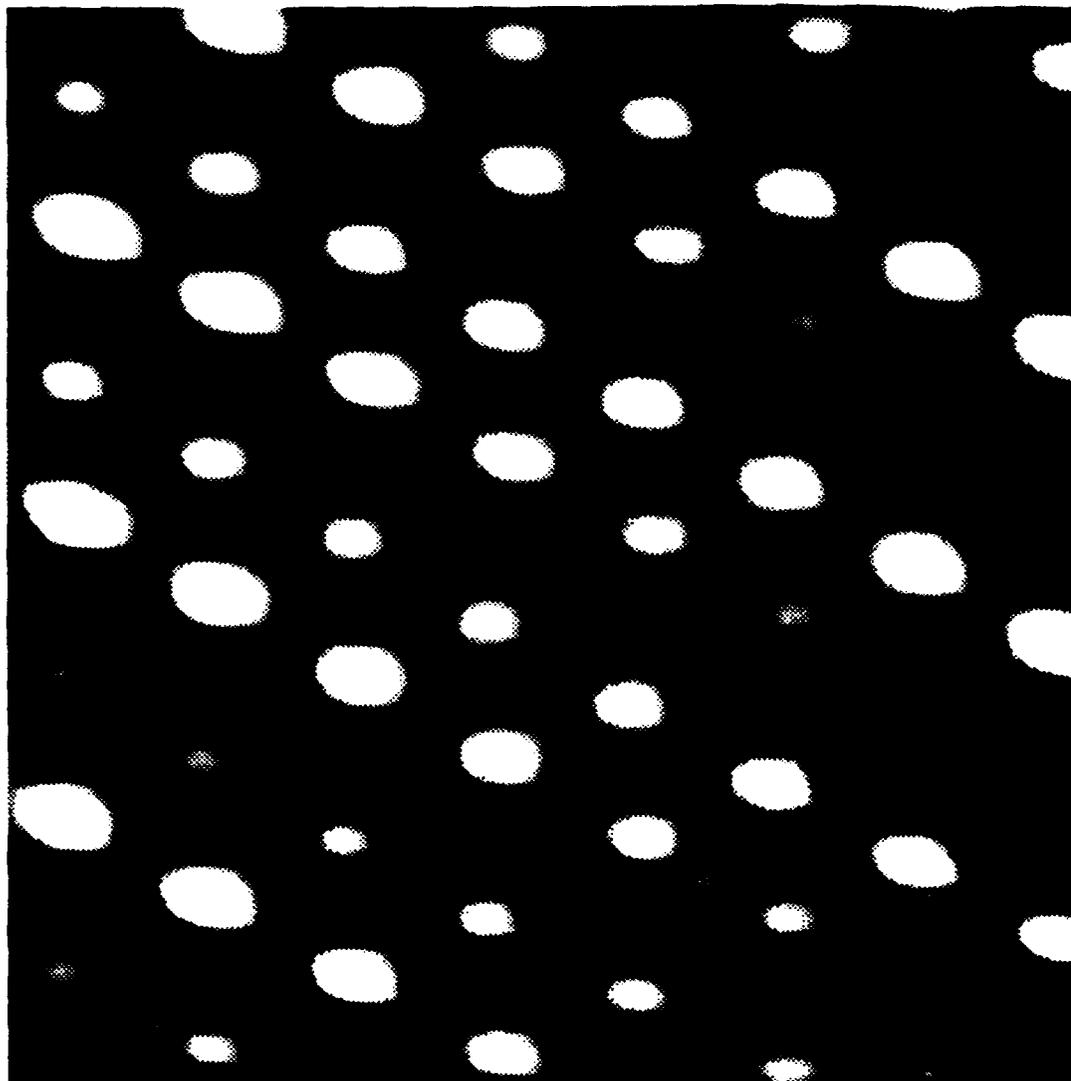
- Fig. 1 Atomically-resolved STM images (each  $2.5 \times 2.5 \text{ nm}^2$ ) of halogen adlayers on Ag(111). (a) F monolayer ( $V_b = -1135 \text{ mV}$ ,  $i_t = 2.2 \text{ nA}$ ; band pass filtered); (b) Cl monolayer ( $V_b = -1085 \text{ mV}$ ,  $i_t = 4.3 \text{ nA}$ ; unfiltered); (c) Br monolayer ( $V_b = -550 \text{ mV}$ ,  $i_t = 5.7 \text{ nA}$ ; band pass filtered); (d) I monolayer ( $V_b = -358 \text{ mV}$ ,  $i_t = 4.9 \text{ nA}$ ; band pass filtered).
- Fig. 2 STM image ( $10 \times 10 \text{ nm}^2$ ) of a Cl adlayer showing the distinctive double row atomic structure characteristic of both Cl and F adlayers.
- Fig. 3 Plot of STM-measured adatom radius vs. the radius of halogen ions. The solid line has unity slope and zero intercept.
- Fig. 4 Atomically-resolved STM images of Ag(111) surfaces initially immersed in a 38% HF solution (300 sec), and then immersed in a 38 % HCl solution. Image (c) shows the surface after a 60-sec exposure to the HCl solution ( $V_b = -575 \text{ mV}$ ,  $i_t = 3.1 \text{ nA}$ ; unfiltered).
- Fig. 5 Atomically-resolved STM images of Ag(111) surfaces immersed initially a 38% HCl solution (300 sec), and then exposed to 1% HI. Images (a) and (b) show the surface after a 30-sec exposure to the HCl solution. The arrow indicates what we speculate is a small iodine surface cluster. Image (c) shows the surface after a 60-sec exposure to the HI solution ( $V_b = -525 \text{ mV}$ ,  $i_t = 3.9 \text{ nA}$ ). All images were low pass filtered once.
- Fig. 6 Auger electron spectra of Ag samples immersed in a 38 % HCl solution for 300 sec, and then exposed to a 1% HI solution for various times: (a)  $t = 0$ , (b)  $t = 30 \text{ sec}$ , (c)  $60 \text{ sec}$ . Note that the Cl signal decreases and the I signal increases as a function of exposure time to HI. No oxygen peak can be discerned in the Auger spectra of halogen or mixed halogen adlayers.



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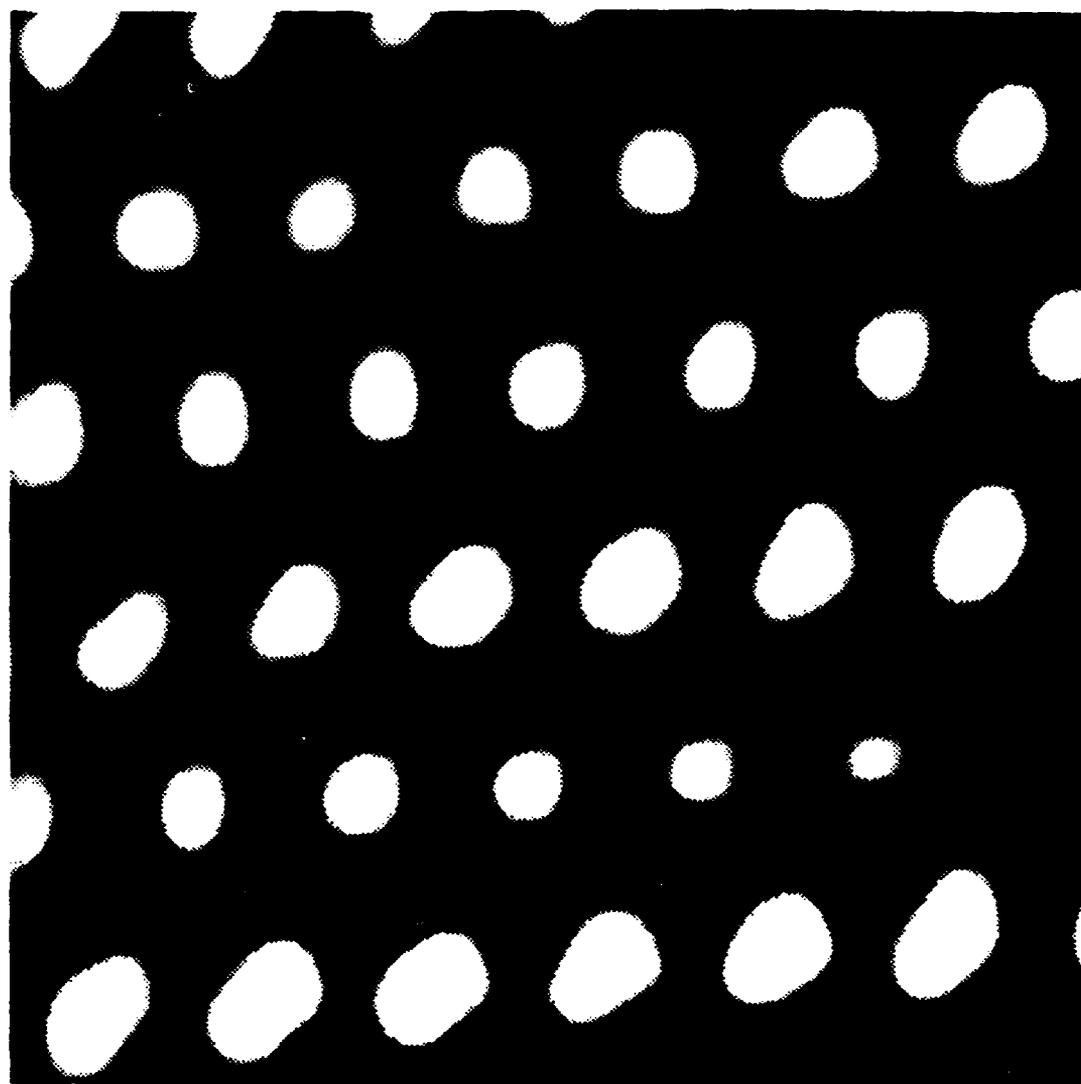
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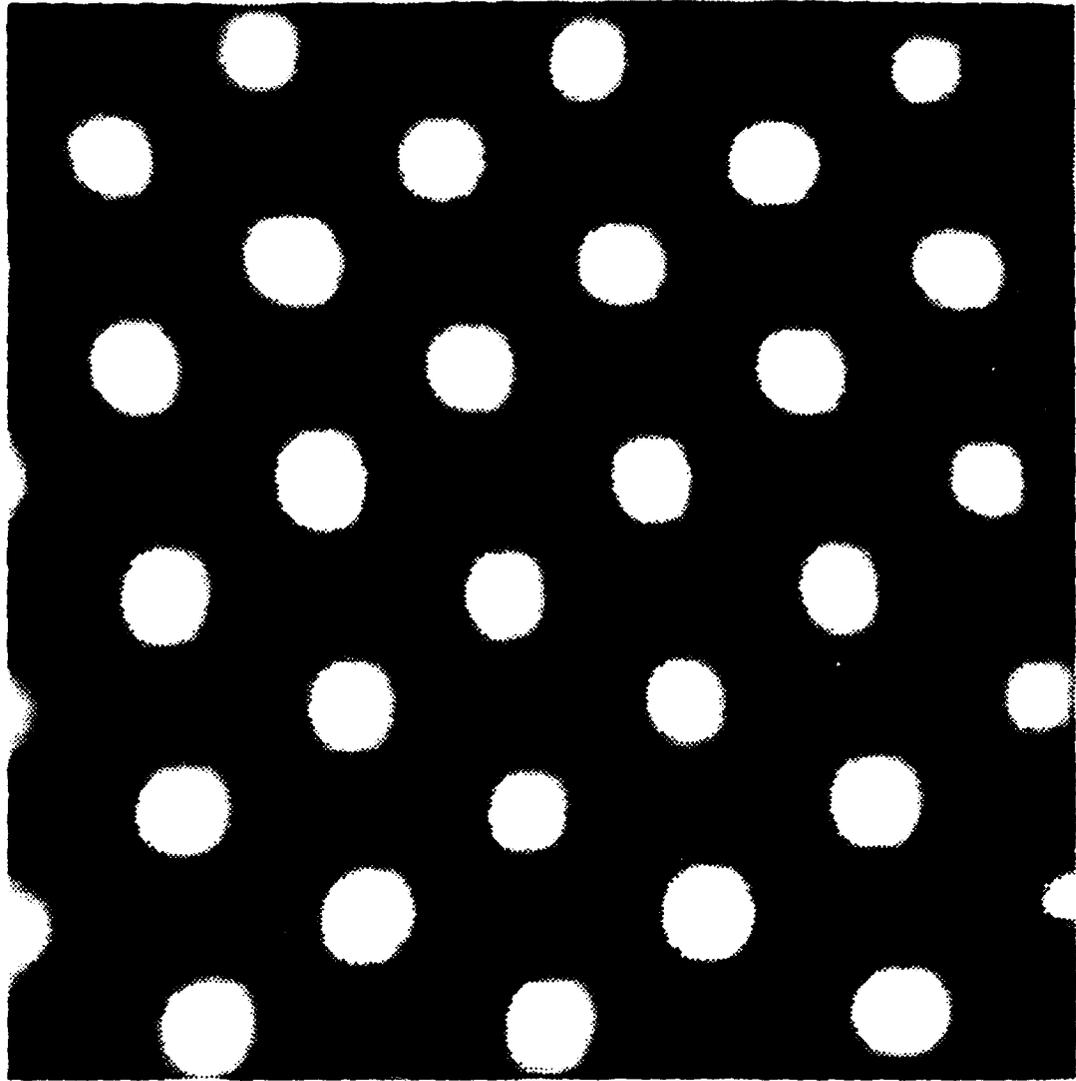
C1

1 nm



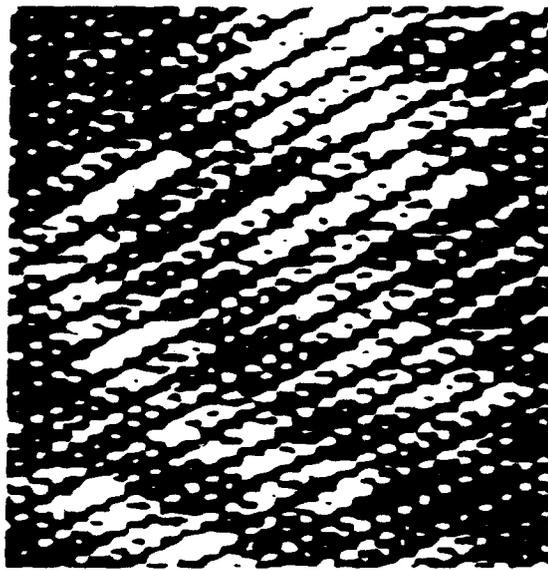
Br

1 nm



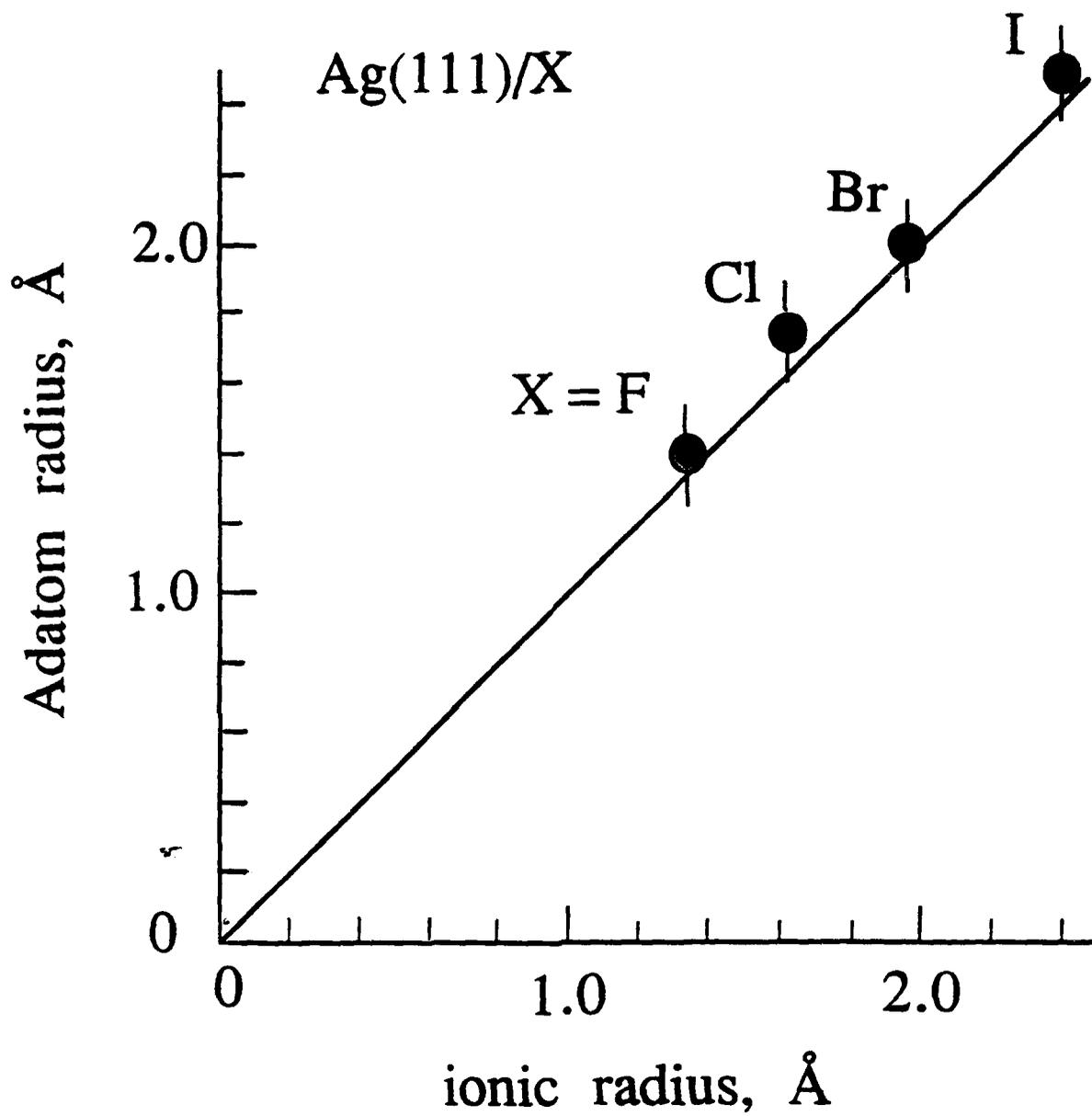
I

1 nm



4 nm

Fig 2  
1



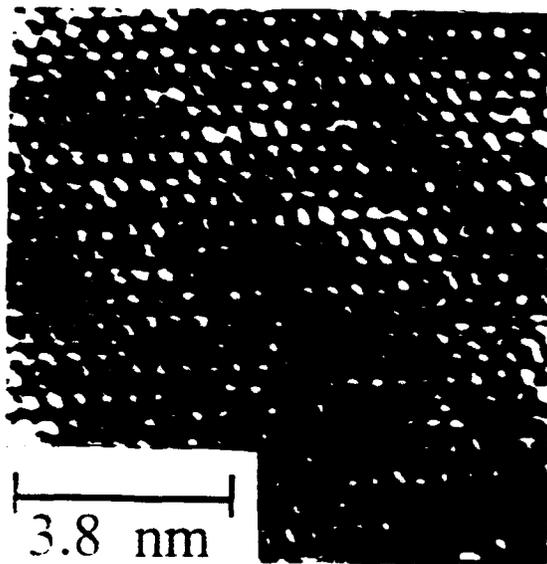
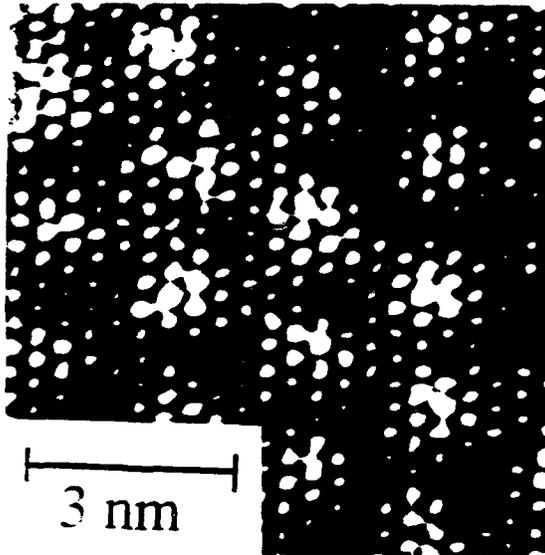
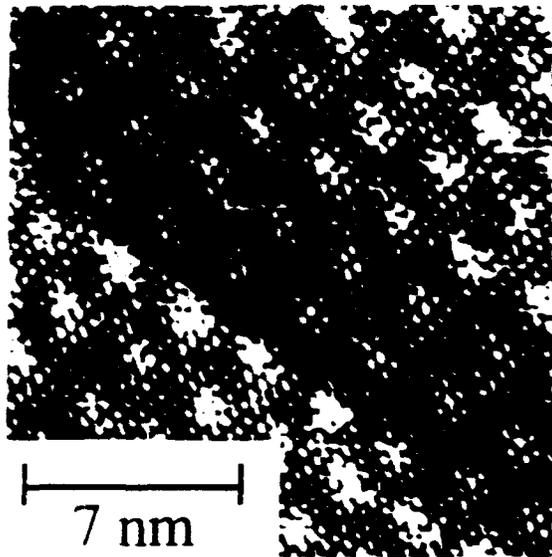
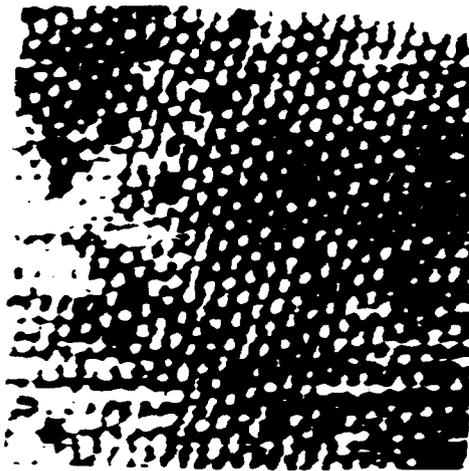
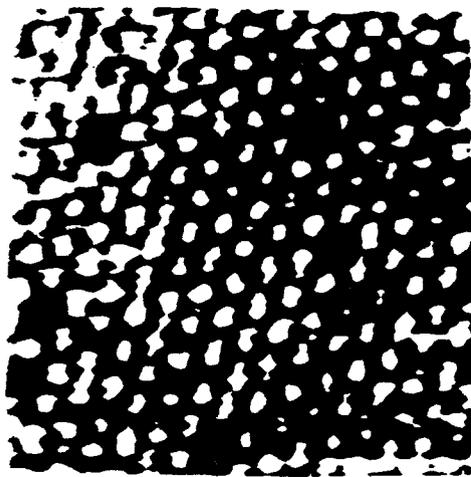


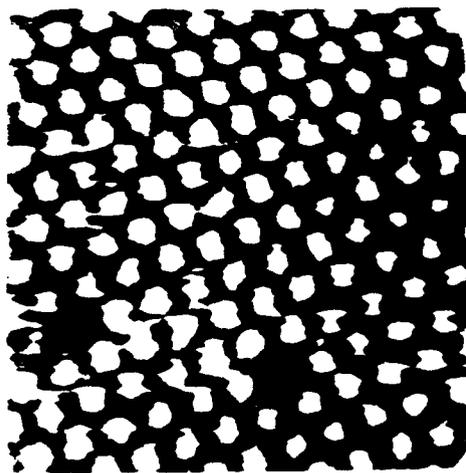
FIG 4



1000



1000



1000

