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Long-range-ordered pentacene chains assembled on the Cu(119) vicinal surface

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Pentacene ($C_{22}H_{14}$), deposited on the Cu(119) vicinal surface, forms ordered molecular chains, with the long molecular axis aligned along the step direction. Phase correlation between neighboring chains gives rise to large domains, observed in the low-energy electron-diffraction (LEED) pattern. Scanning tunneling microscopy (STM) images show that the molecules are laying flat on the copper terraces with the molecular axis aligned along the steps, hence, facing the short side of one another. High-resolution STM data suggest that the molecules adsorb, locating the central benzene ring on the hollow site of the Cu(001) surface.

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INTRODUCTION

The comprehension of the detailed mechanism governing the transport of molecular electronic devices[1,2] requires a detailed knowledge of the thin-film molecular structure and of the molecule-substrate interaction at the interface. The control of well-defined and long-range-ordered molecular adlayers on a solid substrate[3–5] is a key issue either in the formation of seed layers for the growth of epitaxial single-domain organic films or to obtain model systems to study low-dimensional molecular architectures.

Among organic molecules suited for applications in molecular electronics, pentacene ($C_{22}H_{14}$) is a linear polycyclic hydrocarbon that generally adsorbs with the molecular plane parallel to the metallic surface.[4–7] Molecular ordering on a surface is controlled by a subtle balance between intermolecular forces and molecule-substrate interactions. Previous investigations of benzene or acenes ($C_{4n+2}H_{2n+4}$), such as naphthalene ($n=2$) or anthracene ($n=3$), deposited on metal surfaces with unfilled d bands, have suggested a slight distortion of the molecule at the adsorption site.[8,9] Pentacene deposited on noble metal surfaces shows local ordering with side by side orientation.[6,10] An ordered layer of pentacene has been measured on Cu(110), with the molecules adopting a close-packed side-by-side orientation,[6] and it has been attributed to the formation of standing waves in the surface state free-electron gas. It was not possible to induce this local ordering in pentacene adlayers on Cu(111) or on Cu(100).[7,11] A local order of one pentacene molecular layer has been observed by scanning tunneling microscopy (STM) on the Au(111) surface, with the flat-lying pentacene molecule arranged in rows, showing different separation distances and several rotational domains.[10] The presence of different rotational domains hampers the growth of long-range-ordered multilayer films, and the use of suitable anisotropical templates can drive the formation of single-domain-ordered seed layers, a prerequisite for the fabrication of epitaxial thin films.[4,12] A long-range ordering, commensurate with the substrate lattice with a (3×6) symmetry, has been observed on the Au(110) surface,[13] where the reconstructed substrate channels drive the ordered pentacene assembling.[14] Vicinal surfaces have been used as templates to direct regular single-domain molecular structures, driven by the step arrays.[4,12] In fact the steps, as other defects, can enhance the local density of empty states, increasing the molecule-surface binding energy at the terraces borders, driving the formation of ordered one-dimensional (1D) and two-dimensional (2D) molecular architectures.

In this paper, we show that a long-range-ordered stable pentacene chain structure can be grown on a copper (119) vicinal surface, where the terrace width is compatible with the molecular size. STM images show unidirectional pentacene chain structures decorating the edges of the monoatomic steps. The long-range row ordering extends in the direction perpendicular to the chains, driven by the substrate temperature.

EXPERIMENTAL DETAILS

The STM experiments have been performed at the INFM Nanoscience Laboratory at the Università Cattolica del Sacro Cuore (Brescia, Italy), on an OMICRON STM/SEM/SAM UHV system, equipped with ancillary facilities for sample preparation and quality control (base pressure better than 1×10^{-11} mbar). Tungsten tips have been prepared by chemical etching method in a 2N NaOH solution and subsequently bombarded in UHV with high-energy electrons (up to 1 keV), to eliminate residual tip contamination.

The Cu(119) surface is obtained by several cycles of sputtering ($\mathrm{Ar}^+, E_p=700$ eV) and annealing at 720 K. The step

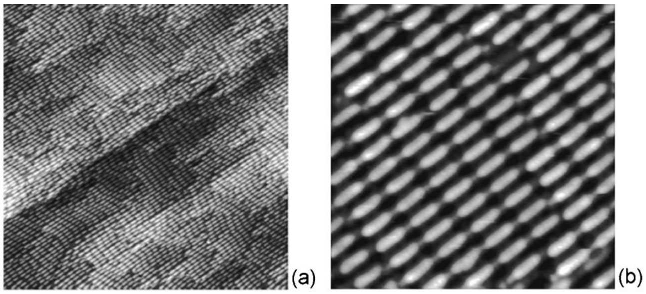

FIG. 1. STM images of the ordered pentacene rows at the completion of the first layer, deposited on the Cu(119) substrate kept at 370 K: (a) 80×80 nm^2 and (b) 15×15 nm^2. Sample-to-tip bias −1.4 V, $I=0.8$ nA.

ordering was checked by low-energy electron-diffraction (LEED) and STM. The pentacene layers were grown by molecular beam deposition from a quartz crucible, taking care of keeping the crucible temperature at 400 K in order to reproduce a constant evaporation rate. A quartz microbalance was used to calibrate the evaporation rate, that was chosen to be about 0.1 nm/min, corresponding to a pressure in the UHV chamber below 3×10^{-10} mbar. In the following, we take as one monolayer (1 ML) the first layer of long-range-ordered molecules adsorbed on the copper step edges. This corresponds to a density of 4.1×10^{13} molecules/cm^2, as deduced from STM images (see Fig. 1).

RESULTS AND DISCUSSION

The clean Cu(119) vicinal surface, obtained by miscutting the (001) surface at an angle of 8.9°, is formed by (001) terraces with the step edges running along the $[1\bar{1}0]$ direction. Figure 2(a) represents an ideal (119) surface with terraces 1.16 nm wide, a monoatomic steps height of 0.18 nm, shifted by half surface lattice constant ($a_0=0.255$ nm) from one step to the adjacent one, reflecting the fcc Cu crystalline structure. The LEED pattern of the clean vicinal (119) surface, shown in Fig. 2(b), presents clear extra spots due to the step ordering. The step-step correlation function presents a high correlation over the entire surface, giving rise to a splitting of the main spots as a function of the impinging electron energy. If we measure the ratio between the step-induced spots separation and the surface reciprocal lattice vector for different LEED patterns, we can estimate the terrace width, obtaining an average value of $L=1.26\pm 0.15$ nm. The terrace width, obtained by averaging over several STM constant current profiles [see Fig. 2(c) and 2(d)], gives an average value of $L=1.17\pm 0.05$ nm. A closer inspection of the STM image of Fig. 2(c) shows that the step edges are not perfectly defined, and the step width is variable along a single terrace. This is in agreement with the expected kink motion along the step direction at room temperature, previously reported for other high-Miller index surfaces.[15]

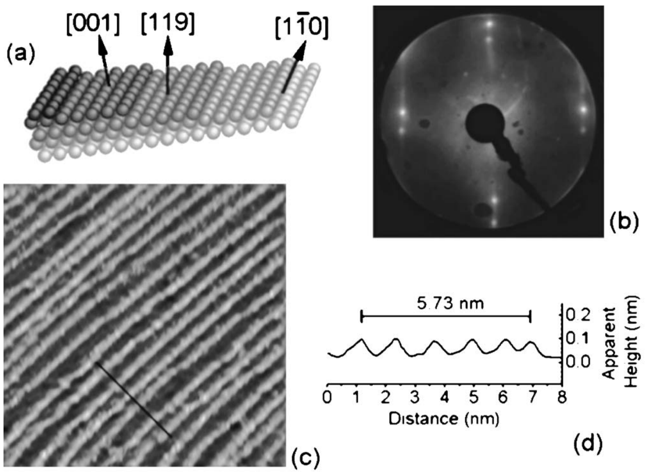

FIG. 2. (a) Schematic draw of the stepped Cu(119) surface, in which the main symmetry directions are indicated by arrows; (b) low-energy electron-diffraction pattern taken at primary electron energy $Ep=55$ eV for the clean Cu(119) surface; (c) typical STM 20×20 nm^2 image of the clean surface. Note that some steps present a larger than the average value; (d) constant current profile taken from the line marked in (c).

The geometrical structure of the Cu(119) vicinal surface is an ideal template to induce the formation of pentacene regular chains along the steps. Deposition of a single layer of pentacene molecules on the substrate kept at 373 K, results in long-range-ordered chain structures, as observed in the typical STM images [Fig. 1(a) and 1(b)]. The molecules are aligned in rows oriented along the steps and separated by the step width (1.1 nm). The measured size of the molecules is 1.62 and 0.73 ± 0.09 nm for the longer and shorter sides, respectively,[16] in good agreement with values obtained from STM images of pentacene molecules lying flat on other copper surfaces.[6,7] The distance between the center of each molecule along a single row is 2.20 ± 0.09 nm, very close to an integer multiple of the underlying Cu(001) surface lattice parameter a_0.

A surprising property of this pentacene single layer is the 2D ordering extending over individual step edges. The images show that adjacent rows present an alignment also in the direction perpendicular to the steps, extending for several terraces. By measuring the position of two molecules lying in parallel rows, we obtain a relative shift of $d=0.12$ ± 0.02 nm, i.e., half of the Cu surface lattice vector. The shift is likely generated by the crystal structure of the underlying vicinal surface, in which a monoatomic step is shifted by 0.125 nm with respect to the underlying atomic plane, as sketched in Fig. 2(a). The chain-chain ordering can extend up to ten consecutive molecular chains, but every domain constituted by regular chains in phase can be shifted with respect to the neighbor domain by an integer multiple of the distance d. The alignment of adjacent rows of pentacene molecules seems controlled by the substrate temperature, since a long-range ordering of parallel rows has never been observed after a deposition with the Cu substrate kept at room temperature. In a surface energetic study of solid pentacene Northrup *et al.* demonstrated that the growth morphology of pentacene could change significantly between 300 and 375 K, when the interaction is purely directed by van der Waals forces.[17] The increased thermal energy available on the surface allows the molecules to form ordered structures, suggesting the presence of a molecule-molecule

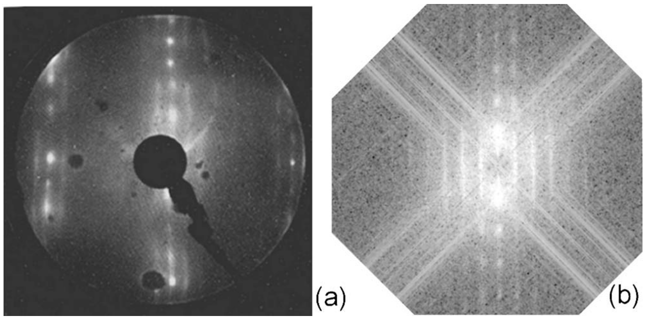

FIG. 3. (a) LEED image of the pentacene layer, deposited on the Cu(119) substrate kept at 370 K. Primary electron energy $Ep = 55$ eV; (b) Fourier transform of the STM image (20×20 nm^2) taken on the same surface. Sample-to-tip bias -1.6 V, $I = 0.4$ nA.

interaction that drives a self-organization process of the pentacene arrays. However, the relative position of two adjacent rows is related to the substrate lattice constant, indicating that the molecule-substrate interaction is playing an important role in the determination of the actual geometric position of the rows. The 2D ordering extending over individual steps observed here is also consistent with previous LEED patterns on smaller acenes, deposited on other copper vicinal surfaces.[4]

The long-range ordering of the pentacene arrays, observed by STM, is reflected by the periodical structure detected in the LEED patterns reported in Fig. 3(a) along with the Fourier transform (FT) of the tens-of-nanometers-wide STM image [Fig. 3(b)]. By measuring the minimum wave vector $\mathbf{k} = 2\pi/\mathbf{a_0}$ ($\mathbf{a_0}$ is the surface cell vector), corresponding to the spots separation of the FT, we can compare the FT with the LEED pattern, considering the corresponding wave vector obtained from the diffraction conditions. The brightest and sharpest spots of the LEED pattern correspond to the clean (119) surface diffraction spots, indicating that the molecular layer is following the same symmetry due to the step ordering on the entire surface, in agreement with the STM images of Fig. 1(a). Although the symmetry of the LEED pattern depends on the entire surface unit cell, whereas STM images depend mostly on the topmost layer,[18] we observe stripes both in the LEED and in the FT-STM image. From Fig. 1(b) we have observed that the distance between the centers of two molecules lying along a single step is a half of the Cu substrate lattice constant, and the corresponding wave vector is an integer fraction of the substrate lattice wave vector, giving rise to a commensurate structure. Large domains, constituted of aligned pentacene rows, can give rise to the stripes in the diffraction pattern because the chains are shifted by an integer multiple of the substrate lattice.

More details on the molecular structure of the pentacene layer can be deduced from inspection of Fig. 4. Isolated molecules appear as rods with an increased charge density located at the ends, a lower intensity extending between two molecules along the step direction, and a weak intensity extending perpendicular to the steps. A careful inspection of the molecular shape in the STM data indicates that there are no observed asymmetries in the charge-density distribution, suggesting that the molecules are laying flat on the terrace and parallel to the step edge. However, this suggestion cannot completely exclude a few degrees tilting of the molecular plane, defined by the benzene rings, with respect to the substrate terrace.

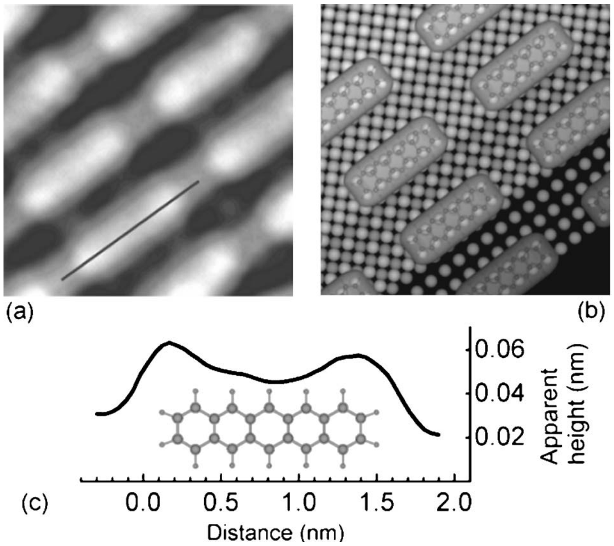

FIG. 4. (a) High-resolution STM image (3.8×3.8 nm^2) of pentacene molecules deposited on the Cu(119) surface kept at 370 K. Sample-to-tip bias -1.6 V, $I = 0.4$ nA. (b) Schematic model for the molecular adsorption on the step edges for the pentacene ordered layer. (c) Constant current profile taken from (a), with the pentacene molecule schematized below.

The charge-density distribution suggests the structural model sketched in Fig. 4(b). On the basis of the present experimental data, it is not possible to quantify structural intramolecular relaxations, and hence the dimensions of the free molecule were drawn considering the geometrical positions of the carbon atoms taken from Ref. 17. The gray shadow represents the electronic cloud measured by STM, which is larger than the geometrical structure of the molecule. In this model, we placed the central ring of the benzene molecule on the hollow site of the Cu(001) surface, which is the lowest-energy adsorption site for the benzene molecule on the same surface.[19] This position seems reasonable, since it can accommodate mostly all benzene rings in the pentacene molecule in or close to the hollow adsorption site. With this hypothesis, we obtain a very good agreement between the expected center-to-center molecular distance (2.23 nm) with the observed value (2.20 nm). Furthermore, only the hollow adsorption site can justify the observed charge density extending between the molecules in the direction parallel and perpendicular to the steps, as demonstrated in the calculation for the hollow adsorption site of benzene adsorbed on Cu(001), reported in Ref. 19. Finally, the model is assuming molecules lying flat on the step terraces, since this geometry would maximize the number of benzene rings close to the most favored adsorption site.

In Fig. 4(c) a typical constant current profile, marked in Fig. 4(a) is plotted. The profile is taken between two neighboring molecules belonging to the same row. Therefore it does not give the total apparent height of the molecule with respect to the substrate, due to the presence of a detectable

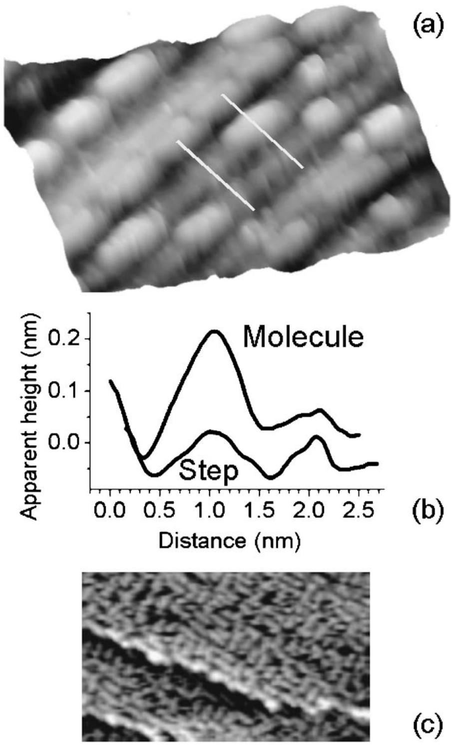

FIG. 5. (a) High-resolution STM image (8×8 nm^2), taken at 0.2 ML pentacene coverage and (b) constant current profiles obtained from the scans marked in (a) that shows the position of the molecule with respect to the step edge. Sample-to-tip bias -1.6 V, I=0.4 nA. (c) STM image (30×18 nm^2) of pentacene molecules on a flat area of the copper surface. Sample-to-tip bias -1.8 V, I =0.3 nA.

charge density linking the molecules in a row [see Fig. 4(a)]. The apparent height of the pentacene molecule, measured with respect to the copper substrate, is 0.17 ± 0.01 nm, which is fairly consistent with previously reported STM results on pentacene adsorbed on other copper substrates.[6,7] The constant current profile also presents two maxima close to the molecule edges, very similar to the case of pentacene deposited on Cu(111).[7] A possible explanation of such profile might be a slight bending of the molecule with respect to the substrate plane, again because of a mismatch between the outer benzene rings (assuming there are negligible distortion and variations of the C—C bonds inside the molecule upon adsorption)[19,20] and the substrate hollow adsorption site. The different position in the plane could induce a tilting of the outer rings, which could induce the observed maxima close to the ends of each molecule in the STM images.

The analysis of pentacene deposition at lower coverage can give useful insights on the formation mechanism and on the energetic considerations on the ordering of molecular layers. Figure 5(a) corresponds to the deposition of 0.2 ML of pentacene at room temperature. The image clearly indicates that all the molecules present the long side aligned with the step edges, and no tendency to molecular clustering has been observed. At this stage we can exclude any intermolecular attractive interaction, while a dominant role is played by the presence of the steps. The position of the molecule on the terrace can be deduced by the constant current profiles taken from Fig. 5(a) and shown in Fig. 5(b). The maximum intensity is very close to the step edge, and the image is showing a clear gap between the step wall and the molecule, independently on the terrace width. The molecule position suggests that the preferred adsorption site is on the step edge, as deduced by LEED studies for other acenes adsorbed on stepped metal substrates,[4,21] and consistent with a charge transfer across the steps leading to an enhanced density of empty Cu electronic states.[21] At this low coverage, the molecules appear to lie flat on the copper surface, but do not form rowlike structures. The molecules appear as fuzzy features indicating high molecular diffusion along the terraces, as observed in the STM images. The average molecular speed, obtained by assuming one directional motion of the molecule, and measuring the displacement of a molecule between two consecutive STM images, is ranging from 8 to 23×10^{-3} nm/s. This, in turn, corresponds to an average resident time for each hollow site of 11–30 s. By increasing the coverage up to the completion of the first layer, the molecules do not form a second layer but rather fill up all the available areas on the steps, preserving the alignment along the terrace edges and the adsorption position at the step kink.

A direct proof that the step edge acts as preferred adsorption sites, and drives the relative orientation of the molecules, is reported in Fig. 5(c). Pentacene molecules, adsorbed on a rather flat region with few step defects and large areas with the (001) surface, are strictly aligned along the equivalent $[1\bar{1}0]$ and [110] symmetry directions, preserving the preferential hollow site of the benzene units. In contrast to the behavior found on homogeneous surface, where there is a random distribution along the main symmetry directions, steps act as effective sites for molecular aggregation. This can be observed in Fig. 5(c) at the border of the large terrace, where all the pentacene molecules are aligned with long molecular axis parallel to the step direction. This behavior has been similarly observed for pentacene molecules on Cu(111),[11] and it is well known for benzene molecules adsorbed on Cu surfaces,[19] ascribed to the presence of the intrinsic step dipoles at a metal surface.[22] The minimum energy of the molecule bound to the copper vicinal surface, is strongly influenced by the presence of defects, but the pentacene molecule minimizes the total energy aligning the long side parallel to step edges and preferring a hollow site for its benzene units.

CONCLUSIONS

In summary, we have investigated how pentacene aligns on the step edges of the Cu(119) vicinal surface, resulting in the formation of a long-range-ordered layer of unidirectional molecular chains. The planar molecule adopts flat adsorption geometry, with the long molecular axis aligned along the steps, and the benzene units centered on the copper hollow site. Phase correlation between pentacene molecules adsorbed at neighboring steps indicates an intermolecular interaction driven by the substrate temperature. The STM informations on the configuration geometry and on the adsorption sites suggest that such a long-range-ordered 2D layer can be a route for creating highly oriented epitaxial multilayers.

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[1] D. J. Gundlach, Y. Y. Lin, T. N. Jackson, S. F. Nelson, and D. G. Schlom, IEEE Electron Device Lett. **18**, 87 (1997).
[2] A. Kahn, N. Koch, and W. Cao, J. Polym. Sci., Part B: Polym. Phys. **B41**, 2529 (2003).
[3] G. Witte and C. Wöll, J. Mater. Res. **19**, 1889 (2004).
[4] S. Lukas, S. Vollmer, G. Witte, and C. Wöll, J. Chem. Phys. **114**, 10123 (2001).
[5] K. Morgenstern, E. Laegsgaard, I. Stensgaard, F. Besenbacher, M. Bohringer, W. D. Schneider, R. Berndt, F. Mauri, A. De Vita, and R. Car, Appl. Phys. A: Mater. Sci. Process. **69**, 559 (1999).
[6] S. Lukas, G. Witte, and C. Wöll, Phys. Rev. Lett. **88**, 028301 (2002).
[7] J. Lagoute, K. Kanisawa, and S. Fölsch, Phys. Rev. B **70**, 245415 (2004).
[8] K. Weiss, S. Gebert, M. Wuhn, H. Wadepohl, and C. Wöll, J. Vac. Sci. Technol. A **16**, 1017 (1998).
[9] C. Mainka, P. S. Bagus, A. Schertel, T. Strunkus, M. Grunze, and C. Wöll, Surf. Sci. **341**, L1055 (1995).
[10] P. G. Schroeder, C. B. France, J. B. Park, and B. A. Parkinson, J. Appl. Phys. **91**, 3010 (2002).
[11] M. Schunack, L. Petersen, A. Kühnle, E. Lægsgaard, I. Stensgaard, I. Johannsen, and F. Besenbacher, Phys. Rev. Lett. **86**, 456 (2001).
[12] V. Marsico, M. Blanc, K. Kuhnke, and K. Kern, Phys. Rev. Lett. **78**, 94 (1997).
[13] V. Corradini, C. Menozzi, M. Cavallini, F. Biscarini, M. G. Betti, and C. Mariani, Surf. Sci. **532**, 249 (2003).
[14] Ph. Guaino, D. Carty, G. Hughes, O. Mc Donald, and A. A. Cafolla, Appl. Phys. Lett. **85**, 2777 (2004).
[15] J. Frohn, M. Giesen, M. Poensgen, J. F. Wolf, and H. Ibach, Phys. Rev. Lett. **67**, 3543 (1991).
[16] L. Gavioli, M. Fanetti, D. Pasca, M. Padovani, M. Sancrotti, and M. G. Betti, Surf. Sci. **566**, 624 (2004).
[17] J. E. Northrup, M. L. Tiago, and S. G. Louie, Phys. Rev. B **66**, 121404(R) (2002).
[18] L. Petersen, Ph. Hoffmann, E. W. Plummer, and F. Besenbacher, J. Electron Spectrosc. Relat. Phenom. **109**, 97 (2000).
[19] N. Lorente, M. F. G. Hedouin, R. E. Palmer, and M. Persson, Phys. Rev. B **68**, 155401 (2003).
[20] S. J. Stranick, M. M. Kamna, and P. S. Weiss, Surf. Sci. **266**, 99 (1994); Surf. Sci. **338**, 41 (1995).
[21] P. S. Weiss, M. M. Kamna, T. M. Graham, and S. J. Stranick, Langmuir **14**, 1284 (1998).
[22] R. Smoluchowsky, Phys. Rev. **60**, 661 (1941).