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Thermodynamic Analysis of the Interaction between Kr Adsorbates on Si(111)-7 × 7 Surface

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Intra-half-unit attractive interactions between Kr adsorbates on Si(111) substrate was investigated on the basis of scanning tunneling microscopy observation at 8 K. A simple thermodynamic model was proposed to extract the interaction energies from the adsorbate distribution. Obtained energies were compared to what is expected from the Lennard-Jones potential and the existence of a considerable degree of additional interaction besides the Van der Waals interaction was suggested.
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KEYWORDS: scanning tunneling microscopy, adsorption, rare gas, Van der Waals interaction

Rare gas adsorbates on substrates have been accepted as a model case of two-dimensional ideal gas systems.[1,2] It was expected that a simple Van der Waals (VdW) interaction between rare gas atoms governs such systems and that a comparison of experimental results with thermodynamic theory would fortify the fundamental understanding of various important phenomena in complicated realistic systems, such as clustering of adsorbates, nucleation of small islands, and phase transition between different surface structures. In reality, however, recent studies utilizing scanning tunneling microscopy (STM) have revealed that weak VdW interaction between rare gas adsorbates can be easily affected by other factors such as dipole-dipole interaction due to a small but finite amount of charge transfer between adsorbates and substrate, and a small deviation of substrate properties due to local structures such as steps, defects, and previously adsorbed rare gas atoms on the surface.[3–12] In particular, rare gas adsorptions beneath step edges showed large deviations from those of the terraces on several metallic substrates.[3–8,11] Importantly, the effect of the local structure can affect the global manner of adsorption processes. For instance, in a Kr/Pt(111) system, it was suggested that islands that grow from step edges have a different packing structure from those in the middle of terraces[8] and this was directly confirmed by atomically resolved STM observation.[11] Here, the first step of island nucleation determines the whole atomic structure of a domain.

When the substrates have a more complicated structure, like the Si(111)-7 × 7 surface, the situation becomes further complicated. Rare gas adsorption onto such surfaces is largely affected by a small difference in the electric structure of the substrate. So far, adsorption of Xe[10] and Kr[12] on to Si(111)-7 × 7 have been investigated at 8 K by STM. These rare gas atoms formed complex adsorption structures and their adsorption processes were different in an unfaulted half unit (UH) and in a faulted half unit (FH) though the atomic structures of the first few layers of the substrate are exactly the same in both half unit cells. The result suggested the adsorption process was not simply determined by substrate corrugations but reflected the small deviation in electronic states of the substrate due to the underlying stacking fault. Understanding the origin of these characteristic adsorbate-adsorbate/adsorbate-substrate interactions and its relationship to the global adsorption processes was desired. In this study, we further investigated the attractive interaction between Kr adsorbates on Si(111) substrate at 8 K. A theoretical model was proposed to describe the interaction, and the interaction energy was retrieved from the adsorbate distribution obtained by STM observation. Finally, the strength of the obtained interaction was compared to the VdW interaction.

The details of the experimental setup are described elsewhere.[10] The Si strip cut from a commercial wafer was prebaked at 1000 K for a night, flashed at 1400 K and cooled to 8 K in an ultrahigh-vacuum chamber with a liquid He cryostat, whose base pressure was 1.0×10^{-8} Pa. Kr dosing was done from a stainless-steel tube at room temperature whose end was ~5 cm from the Si substrate kept at 8 K on the STM stage. The typical measurement condition for STM was tunnel current setting $I_t = 0.3$ nA and sample bias voltage $V_s = +2.0$ V.

As reported,[12] Kr atoms adsorb differently in a UH and in an FH of a Si(111)-7 × 7 unit cell. In a UH, as shown in Fig. 1, Kr atoms, at first, formed an unresolved *base*

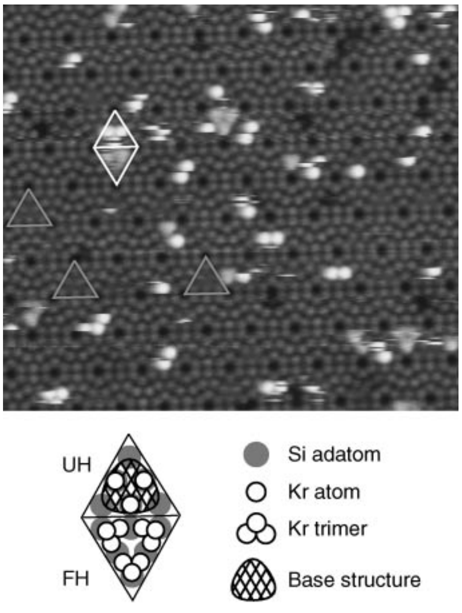

Fig. 1. STM topograph of Kr/Si(111) at 8 K ($V_s = 2.0$ V, $I_t = 0.3$ nA, 28×25 nm^2). The adsorption structure consists of an unresolved base structure and Kr atoms at the center adatom site in UH, and Kr trimers at three corners of the FH. Some UHs with the base structure are indicated by the gray triangles.

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[*] http://dora.ims.tsukuba.ac.jp

structure, which is indicated by a hatched round triangle in the schematic. Note that gaps between adatoms in some UH units, for instance, those indicated by the gray triangles in the figure, look slightly brighter than those in clean UH units. This base structure looks more prominent when observed with $V_s = +3.0\,\mathrm{V}$.[12] On the base structure, successive adsorption occurs at the center adatom sites. Corner adatom sites can also be occupied by Kr atoms. However, these sites are much more unstable so that most Kr atoms on the base structure stay at the center adatom sites. On the other hand, in an FH, Kr atoms always adsorb as trimers without the base structure. Other forms of Kr adsorbate were seldom observed in our experiment. When an FH is fully occupied by three Kr trimers, the atomic structure is identical to that of Xe adsorption in a UH and in an FH, even though the adsorption process is different between them; Xe atoms prefer the dimer form.[10] The reason why Kr atoms prefer the trimer form in an FH remains to be studied. Consequently, both a UH unit cell with the base structure and an FH unit cell have three adsorption sites, each of which can be occupied by one Kr atom or one Kr trimer, respectively.

In order to analyze the intra-half-unit interaction between these Kr adsorbates, all half unit cells were classified by the number of adsorbates inside, and the occurrence of each type is plotted by thick solid lines with square markers in Fig. 2. Note that we neglected UHs without the base structure. In the same figure, the theoretically expected random distribution, that corresponds to the case where no interaction exists between adsorbates, is plotted by dashed lines with circle markers. The random distribution is calculated purely stochastically, i.e.

$$N_k = {}_3\mathrm{C}_k \theta^k (1-\theta)^{3-k} N, \tag{1}$$

with the numbers of half unit cells that have k adsorbate(s) inside $\{N_k\}_{0\le k\le 3}$, the total number of half unit cells N, and the coverage per adsorption site θ.

Compared with random distribution, the experimental results showed larger probabilities for the cases where more adsorbates aggregate in the same half unit cell. Thus, the existence of some attractive interaction between adsorbates is confirmed. However, the magnitude of the interaction can not be directly derived from these plots. In the remainder of this paper, we evaluate the interaction energies by detailed theoretical analysis and discuss the validity of analysis procedures and the origin of the interaction.

First, let us assume there are N unit cells in an adsorbate system at thermal equilibrium with system temperature T. Each of the cells has three adsorption sites. The attractive interaction is characterized by the interaction energies E_2 and E_3. Namely, when two or three adsorbates exist in the same unit cell, the free energy of the system is lowered by E_2 or E_3 per adsorbate, respectively, compared to the cases where each of these adsorbates exists alone in a different unit cell. The situation is illustrated in Fig. 3. Then, the following relationships exist:

$$M = 3\theta N = \sum_{k=0}^{3} k N_k, \tag{2}$$

$$N = \sum_{k=0}^{3} N_k, \tag{3}$$

$$E = -2E_2N_2 - 3E_3N_3, \tag{4}$$

with the number of adsorbates M and the total energy of the system E. To obtain eq. (4), the constant component of ME_1 has been dropped.

A macroscopic state of the system is defined by a series of numbers, $\{N_k\} = \{N_0, N_1, N_2, N_3\}$. Limited by the conditions eqs. (2) and (3), however, this macroscopic state can be identified when only $\{N_2, N_3\}$ are specified. N_0 and N_1 can be derived from $\{N_2, N_3\}$ as

$$\begin{aligned} N_0 &= N - M + N_2 + 2N_3, \\ N_1 &= M - 2N_2 - 3N_3. \end{aligned} \tag{5}$$

Next, we calculate the number of microscopic states that gives the same macroscopic state $\{N_2, N_3\}$, i.e. the partition

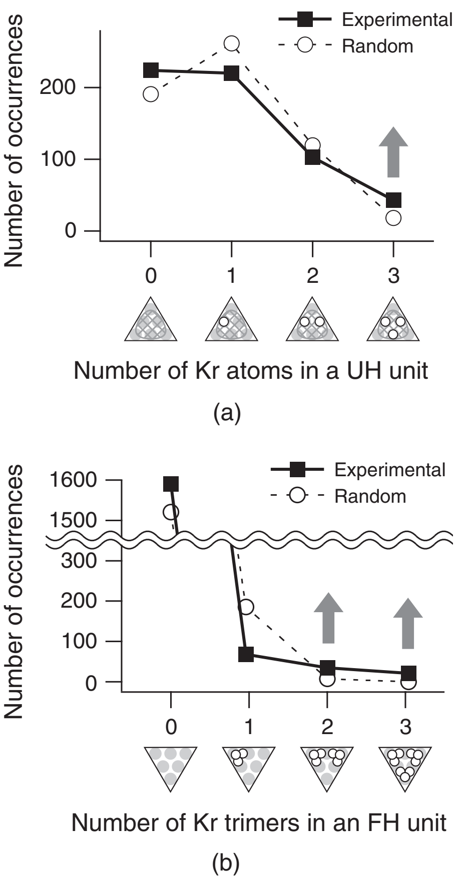


Fig. 2. Distribution of Kr adsorbates. Kr adsorbates tend to be gathered together in the experimental results compared to the theoretically predicted random distribution.

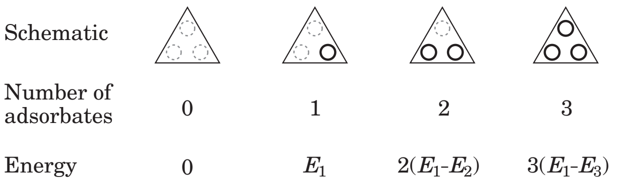


Fig. 3. Definition of interaction energies. Attractive interactions between Kr adsorbates decrease the free energy of the system by E_2 and E_3 per adsorbate when two/three adsorbates exist in the same half unit cell.

function W_{N_2,N_3}. For our purpose, we count the ways of selecting M occupied sites from $3N$ adsorption sites. The number of methods of splitting N unit cells into $\{N_0, N_1, N_2, N_3\}$ is given by $N!/(N_0!N_1!N_2!N_3!)$. In addition, three ways exist to determine occupied sites in a unit cell that contains one or two adsorbates. As a result, the partition function is given as

$$W_{N_2,N_3} = \frac{3^{N_1+N_2}N!}{N_0!N_1!N_2!N_3!}. \tag{6}$$

Assuming a Boltzmann distribution, the probability of finding the system in a macroscopic state $\{N_2, N_3\}$ can be calculated as

$$P(N_2, N_3) = \frac{W_{N_2,N_3}\exp(-E_{N_2,N_3}/k_BT)}{\sum_{N_2',N_3'} W_{N_2',N_3'}\exp(-E_{N_2',N_3'}/k_BT)} \tag{7}$$

with the total energy of the system E_{N_2,N_3} corresponding to the state. The statistical mechanics predicts that the most probable macroscopic state is always realized, where the following conditions hold.

$$\begin{aligned} \partial P(N_2, N_3)/\partial N_2 &= 0 \\ \partial P(N_2, N_3)/\partial N_3 &= 0. \end{aligned} \tag{8}$$

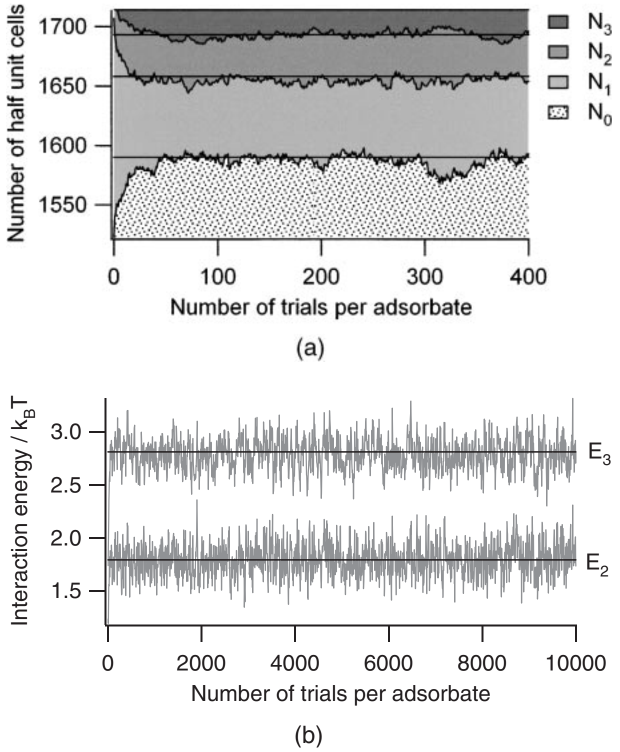
In a specific system, substitution of eq. (7) into this condition results in the following formula.

$$\begin{aligned} E_2 &= -\frac{1}{2}k_BT\ln\frac{N_1^2}{3N_0N_2} \\ E_3 &= -\frac{1}{3}k_BT\ln\frac{N_1^3}{27N_0^2N_3}. \end{aligned} \tag{9}$$

Finally, these equations directly give the magnitude of intraunit interaction energies E_2 and E_3 from the experimentally obtained distribution of adsorbates $\{N_k\}$. In the case of Kr atoms at center adatom sites in a UH, $E_2 = 0.179k_BT$ and $E_3 = 0.566k_BT$ are obtained from $\{N_k\} = \{224, 220, 103, 43\}$, while in the case of Kr trimers at the corners of an FH, $E_2 = 1.79k_BT$ and $E_3 = 2.81k_BT$ are obtained from $\{N_k\} = \{1590, 68, 35, 21\}$.

Before proceeding to the detailed discussion, let us consider the statistical error of the analysis. For this purpose, Monte Carlo simulations were performed. The model systems consisted of approximately 10^4 cells in a triangular lattice with a periodic boundary condition. An appropriate amount of adsorbates were, at first, scattered randomly in this lattice. Note that random distribution corresponds to the infinite temperature of the system. Then, the Monte Carlo trial described below was run repeatedly: 1) picking up an adsorbate randomly, 2) selecting one of the six neighboring cells, 3) selecting one of the three adsorption sites in the cell, 4) quitting the trial if the cell is already occupied, 5) calculating the energy cost ΔE necessary to move the adsorbate to the selected site and 6) accepting the movement with a probability of $\exp(-\Delta E/k_BT)$. The calculation of ΔE is done by using eq. (4) with the substitution of experimentally obtained E_2 and E_3. During repetition of the trials, a selected area with the same size as the experiment is intermittently examined to obtain snap shots of the adsorbate distribution.

A typical result of the simulations for Kr trimers in an FH is shown in Fig. 4. The lateral axes indicate the number of Monte Carlo trials divided by the total number of adsorbates in the system, which gives an arbitrary time scale. The vertical axis of Fig. 4(a) indicates the number of unit cells that contain a specified number of adsorbates and the values obtained by our experiment are indicated by black horizontal lines. As soon as the trials started, the system temperature rapidly cooled down from infinity and reached the equilibrium in ~100 trials per adsorbate. The fluctuation after reaching equilibrium gives the statistical error. Averaging 10^4 trials per adsorbate, we obtained the root mean square amplitude of the fluctuation $\{\Delta N_k\} \sim \{11.5, 11.9, 9.2, 6.1\}$ for a UH and $\{\Delta N_k\} \sim \{8.44, 8.0, 5.1, 3.9\}$ for an FH. Figure 4b indicates the corresponding change in E_2 and E_3 calculated from instantaneous $\{N_k\}$ using eq. (9). The interaction energy including the statistical error level (2σ) is summarized in Table I.



(a)

(b)

Fig. 4. Evaluation of statistical error by a Monte Carlo simulation. (a) Fluctuation of adsorbate distribution for the system of Kr trimers in an FH. (b) Fluctuation of apparent interaction energies calculated using eq. (9). See text for details.

Here we discuss the results in detail. First, so far the interaction energies have been written as multiples of thermal energy k_BT. Then, what are the absolute values? If we simply substitute the measured system temperature $T = 8$ K, $E_2 = 0.123$ meV and $E_3 = 0.391$ meV for Kr

Table I. Intra-half-unit interaction energies between Kr adsorbates calculated from experimentally obtained adsorbate distribution.

	E_2/k_BT	E_3/k_BT
Kr atoms in FH	0.18 ± 0.18	0.57 ± 0.19
Kr trimers in UH	1.79 ± 0.30	2.81 ± 0.29

atoms in a UH, and $E_2 = 1.24$ meV and $E_3 = 1.93$ meV for Kr trimers in an FH are obtained. The stability of rare gas structures on Si(111) is, however, known to depend on the tunnel current setting of STM observations.[10,12] The higher current setting results in less stability. Rare gas adsorbates are not only excited by thermal energy but also by the tunnel current and/or electric field under STM observation. The influence of STM observations on rare gas diffusion on metal substrates has been studied.[13–15] For the simplest interpretation, however, the observation effect increases the effective system temperature. Thus, we should take the values obtained above as the lower limit of interaction energies. In order to improve measurement accuracy, variable temperature experiments and/or variable tunnel current experiments are required. On the other hand, the relative magnitudes of interaction energies are expected to be more reliable. If the interaction between Kr adsorbates is purely additive, the relationship $2E_2 = E_3$ is expected because one adsorbate interacts with one/two neighboring adsorbate(s) when two/three adsorbates are in one half unit cell. In the case of Kr atoms in a UH, $2E_2$ is slightly smaller than E_3, and vice versa in the case of Kr atoms in an FH. The difference is larger in the latter case but is still comparable to the error level. We do not insist, at this moment, on whether these differences are considerable.

Even with the uncertainty due to the disturbance by STM observation, comparison of the obtained interaction energies with the well known Lennard-Jones (*L-J*) potential enforces the argument. Figure 5 illustrates the *L-J* potential for Kr atoms, where $\epsilon = 164$ K and $\sigma = 0.338$ nm were employed. When two center adatom sites in the same unfaulted half unit cell are occupied by Kr atoms, the separation between the adsorbates is 0.77 nm and the expected interaction energy from the *L-J* potential is $E = 0.40$ meV as indicated in the figure. This value is comparable to the obtained interaction energy $2E_2 = 0.24$ meV for Kr atoms at the center adatom site in a UH with system temperature $T = 8$ K. If the Kr atoms only experience the VdW potential, however, they will form close packed clusters to maintain the most stable distance between two atoms, σ. In reality, the potential corrugation due to substrate structure prevents clustering so that the Kr atoms are fixed at specific adsorption sites. Thus, this potential corrugation is, at least as large as ϵ. What is notable is that Kr adsorbates easily hop around this large corrugation under the STM observation. Consequently, the effective system temperature under STM observation should be considerably higher than the measured temperature.

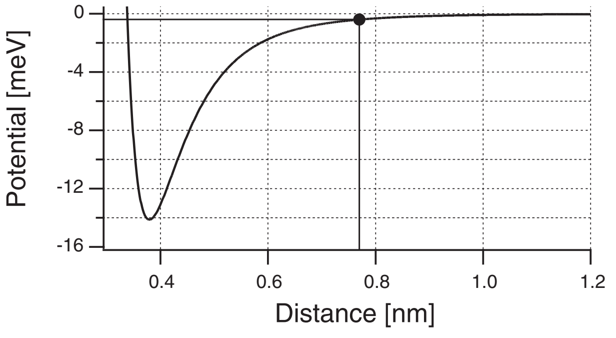


Fig. 5. Lennard-Jones potential for Kr atoms. The black filled circle indicates the distance between two neighboring center adatom sites in the same half unit cell.

The higher effective temperature gives higher interaction energies. If this is the case, there is a considerable amount of additional interaction besides the VdW interaction between Kr adsorbates on Si(111). We suggest that some indirect interaction via the substrate exists even for a rare gas adsorption system. Namely, the previously adsorbed Kr atom or trimer affects the substrate's properties in the surrounding region and increases the adsorption energies slightly. Then, an apparent attractive interaction arises because successively arriving adsorbates effectively probe this small change in the substrate's properties. According to our research for the *inter*-half-unit interaction between Kr adsorption structures,[12] this indirect interaction reaches across half unit boundaries and also increases the probability of Kr adsorption onto the neighboring half unit cells.

In summary, the attractive intra-half-unit interaction between Kr adsorbates on a Si(111)-7 × 7 substrate was investigated using scanning tunneling microscopy at 8 K. A thermodynamic model was proposed for calculating the interaction energies from the distribution of adsorbates and the obtained energy values were compared with that expected from the Van der Waals interaction. The indirect interaction via the substrate was suggested to explain the additional component of attractive interaction.

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