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Equilibrium structure of 1,4-cyclohexadiene monolayer on Si(001)-(2×1)

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The adsorption layer of 1,4-cyclohexadiene on Si(001)-(2×1) is one of the most studied organic/semiconductor interfaces. To this day the stable structure of the adsorption layer and its dependence on pressure and temperature are hypothetical. In this work, we have developed several lattice models of the adsorption layer of 1,4-cyclohexadiene (1,4-CHD) on Si(001)-(2×1), taking into account the main features of the chemisorbed layer: different types of adsorption complexes and their asymmetry, and repulsive intermolecular interactions. A unique combination of density functional theory methods and the tensor renormalization group within the framework of the developed models allowed us to reveal the equilibrium structure of 1,4-CHD monolayer on the Si(001)-(2×1) surface. We have found four stable phases in the most advanced model. There are two phases consisting of tetra-bound (tetra-σ) complexes only: the phase of mixed composition with tetra-bound and double-bound (di-σ) complexes, and the close-packed phase, where each Si = Si dimer of the Si(001)-(2×1) surface is occupied by a di-σ complex. All the phases differ in the number of 1,4-CHD molecules per Si = Si dimer. Repulsive intermolecular interactions along the row of Si = Si dimers are demonstrated to determine the self-assembly of two phases. Those are the phase of the lowest density that comprises only the tetra-bound complexes and the phase of mixed composition. Repulsion between 1,4-CHD molecules adsorbed on neighboring rows of Si = Si dimers leads to a coordinated filling of these rows. As a result, the existence region of the mixed phase consisting of the tetra-σ and di-σ complexes narrows. The transition from the phase consisting of tetra-bound complexes to the phase of mixed composition is found to occur abruptly through a first-order phase transition.

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I. INTRODUCTION

Today, traditional methods for manufacturing and operating semiconductor devices are approaching an atomistic scale, reaching the fundamental limits of top-down technology. This stimulates the development of alternative methods and materials for creating molecular-scale devices [1]. Using semiconductor surfaces as substrates in such devices has several advantages. The most important is the possibility of covalent binding of organic molecules to the silicon surface. This is a direct path to incorporating molecular functionality into conventional semiconductor technology [2–4]. However, much remains to be done. Specifically, methods for accurate control and tuning of the structural and electronic properties of the organic layer should be developed.

The Si(001)-(2×1) surface is one of the most studied surfaces in materials science [2,5–7]. This surface is ideal for organic functionalization due to its high reactivity resulting from the reconstruction of the surface to form the parallel rows of Si = Si dimers [7]. The most studied class of adsorbates on this surface is unsaturated hydrocarbons, which bind to the silicon surface via Si-C σ bonds [2,7–9]. Since the chemisorption of unsaturated hydrocarbons on the Si(001)-(2×1) surface does not break the σ bonds in the molecule, it is defined as molecular. Small unsaturated molecules such as acetylene and ethylene adsorb on the Si(001)-(2×1) through the [2+2] cycloaddition mechanism to form a four-membered ring with two Si-C bonds. See, for example, Fig. 1(b), where the adsorption complexes of 1,4-cyclohexadiene on the Si(001)-(2×1) surface formed through the [2+2] cycloaddition mechanism are shown. The adsorption of π-conjugated molecules occurs through the [4+2] cycloaddition to form a six-membered ring with two Si-C bonds [2,7,8]. In the case of bi- and polyfunctional molecules, the adsorbed molecule may retain the ability to attach other molecules or functional groups [9–14]. Therefore, this approach seems promising for creating functional organic/semiconductor interfaces [1,4]. Considering several possible ways of chemisorption of bi- and polyfunctional molecules on the Si(001)-(2×1) surface, it becomes important to control not only the adsorption state of each molecule, but also the structure of the entire adsorption layer [1,4,7,15]. The control can be executed either through chemical modification of the molecule structure that prohibits or promotes the formation of specific adsorption complexes, or by tuning external parameters such as pressure and temperature. In the latter case, intermolecular interactions in the adsorption layer play an important role [5,16–18]. From a technological point of view, the goal of this process is to obtain an ordered organic monolayer of high density [4].

The adsorption layer of 1,4-cyclohexadiene on Si(001)-(2×1) is well studied as a prototype of a molecularly modified semiconductor surface and functional organic/semiconductor interface. Comprehensive experimental researches [9,18–22] revealed several adsorption configurations of the 1,4-cyclohexadiene (1,4-CHD) molecule on the

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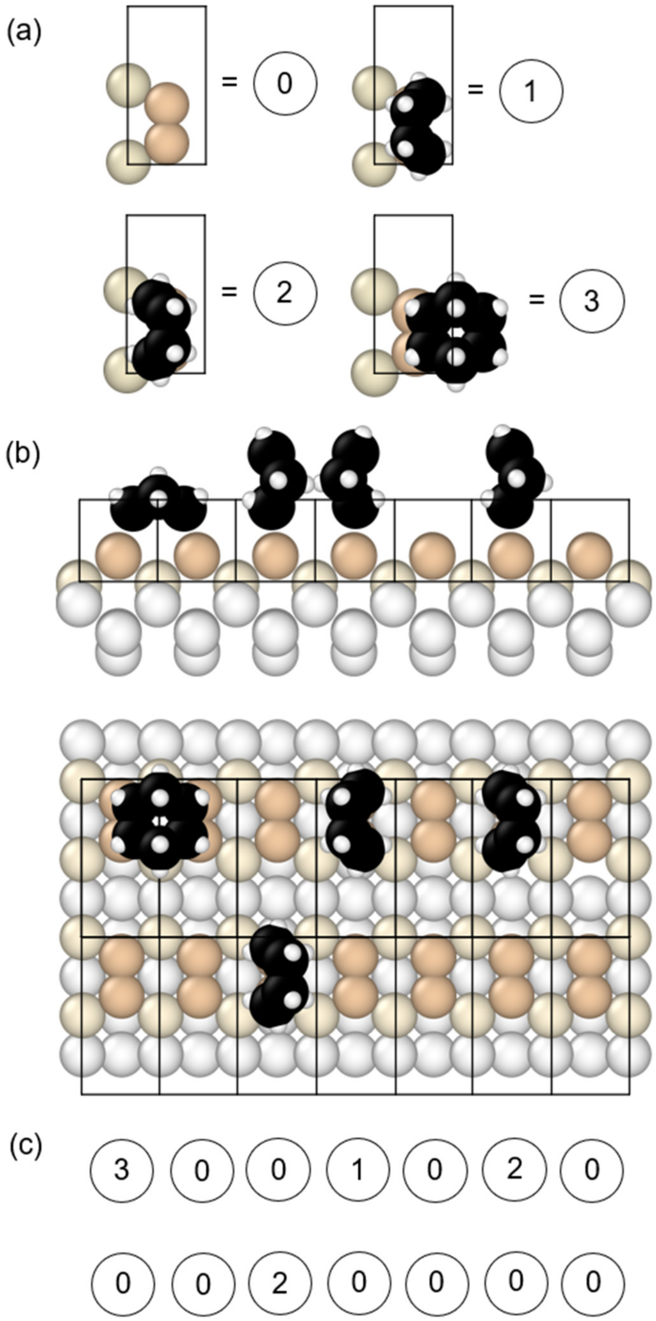

FIG. 1. Adsorption complexes of 1,4-CHD on the Si(001)-(2 × 1) surface. (a) The mapping of the adsorption complexes onto lattice site states: 0, empty site; 1, "left" di-σ complex; 2, "right" di-σ complex; and 3, tetra-σ complex. (b) Mapping of the adsorption layer onto the lattice model. (c) Lattice model of the adsorption layer.

Si(001)-(2 × 1) surface depending on external conditions. When temperature increases, the π complexes on the surface transform to the di-σ configurations and then to the tetra-σ complexes (see Fig. 1). The effect of surface concentration (proportional to the gas phase pressure) has also been investigated. The tetra-σ complexes predominate at low coverage. Increasing partial pressure over the adlayer promotes the appearance of di-σ complexes and the disappearance of the tetra-σ ones. The chemical structures of di-σ and tetra-σ complexes have been established using quantum chemistry methods [23,24]. On the other hand, the structure of a stable adsorption layer and its dependence on external pressure and temperature are still hypothetical. Understanding the phase behavior of the entire adsorption layer requires research with statistical physics methods.

Previously, we developed the simplest lattice model of the 1,4-CHD adsorption layer on Si(001)-(2 × 1) [17]. The model considered all known adsorption complexes as hard-core particles of different sizes. Unfortunately, the simplest model did not describe the formation of a stable phase containing di-σ complexes. This contradicts the experimental observations, where the di-σ complexes of 1,4-CHD on Si(001) are observed most often [9,18,20–22]. The reason for the contradiction is either the influence of kinetic factors or oversimplification of the model. The simplest model [17] did not take into account the finite intermolecular interactions and asymmetry of the di-σ complex. As follows from the experimental and computational research, these factors play a key role in the phase behavior of the adsorption layer [18,24].

In the last two decades, theoretical methods of condensed matter physics have developed significantly. This allowed us to formulate and study here a series of detailed lattice models of the chemisorbed layer of 1,4-CHD on Si(001)-(2 × 1), taking into account more factors. In this work we use density functional theory (DFT) methods to evaluate the parameters of considered lattice models: formation energies of all adsorption complexes and energies of pairwise intermolecular interactions. The lattice models were solved using the transfer-matrix (TM) and tensor renormalization group (TRG) methods [25–27]. One-dimensional (1D) models have been solved numerically exactly, but two-dimensional (2D) models required some approximations. Here we use a combination of quantum chemistry and statistical physics methods to identify the ordered phases of the equilibrium adsorption monolayer of 1,4-CHD on the Si(001)-(2 × 1) surface. It is worth noting that the TRG method was previously applied only to the generalized or abstract models of phase interfaces [25,28–32]. Here, the TRG method has been used to investigate a detailed and chemically specific model of an adsorption layer.

II. LATTICE MODELS

To simulate the phase behavior of 1,4-CHD adsorption monolayer on the Si(001)-(2 × 1) surface we use the lattice gas approximation. In this case, the lattice gas model is a natural approximation due to the specific character of chemisorption. The Si(001)-(2 × 1) surface is reconstructed in such a way that neighboring silicon atoms bond in Si = Si dimers, which are arranged in parallel rows forming the (2 × 1) structure. We considered the monolayer adsorption mode close to room temperature. This allowed us to consider only the chemisorbed states of the 1,4-CHD molecule on the Si(001)-(2 × 1) surface, namely, di-σ and tetra-σ complexes (Fig. 1). A physically adsorbed state of 1,4-CHD on the Si(001)-(2 × 1) surface is known to exist in the form of π complexes below 150 K [9,22]. In the di-σ complex, the 1,4-CHD molecule binds to one Si = Si dimer, and the molecule plane is perpendicular to the direction of the Si = Si dimers row. In other words, the 1,4-CHD molecule in the di-σ complex on the Si(001)-(2 × 1) surface is bound with a single Si = Si dimer, and not with two neighboring Si = Si dimers. The 1,4-CHD molecule in the di-σ complex has an asymmetric structure relative to the Si = Si dimer its bound (Fig. 1). Therefore, it is necessary to distinguish between "right" and "left" di-σ complexes within the row of silicon dimers (Fig. 1). In the symmetric tetra-σ complex, the 1,4-CHD molecule forms four σ bonds with four Si atoms of two neighboring Si = Si dimers of the same row. A 1,4-CHD molecule cannot adsorb on the silicon atoms belonging to different rows of Si = Si dimers [23,24]. Thus, one Si = Si dimer of the reconstructed Si(001)-(2 × 1) surface represents a single adsorption site for the 1,4-CHD molecule. These adsorption sites form a regular two-dimensional lattice of rectangular symmetry. Di-σ and tetra-σ complexes occupy one and two neighboring sites of such lattice, respectively (Fig. 1).

In this work, we considered five models. To a first approximation, we ignore the interactions between the molecules adsorbed on the adjacent rows because the distance between them is large enough. This assumption allows us to consider only one row of the Si = Si dimers in the framework of one-dimensional models. The first model (1D-HC) is a 1D model without any intermolecular interactions, except the hard core of the molecule. The hard-core condition prevents two molecules from being bound to the same Si = Si dimer. The second model is a 1D model with symmetric interactions between the di-σ complexes (1D-SYM model). The third model is also one-dimensional, but it distinguishes between the right and left di-σ complexes (1D model). The fourth (2D-SYM) and fifth (2D) models are two-dimensional analogs of the second and third models, respectively. In two-dimensional models we take into account an interaction between the 1,4-CHD molecules adsorbed on adjacent rows of Si = Si dimers.

The thermodynamic Hamiltonian of the model adsorption layer of 1,4-CHD on the Si(001) surface treated as an open thermodynamic system can be written as follows:

$$\mathcal{H} = \sum_{i} E(n_i) + \sum_{\langle i,j\rangle} \varepsilon(n_i, n_j, \mathbf{r_{ij}}) - \mu \sum_{i} (1 - \delta_{0,n_i}). \quad (1)$$

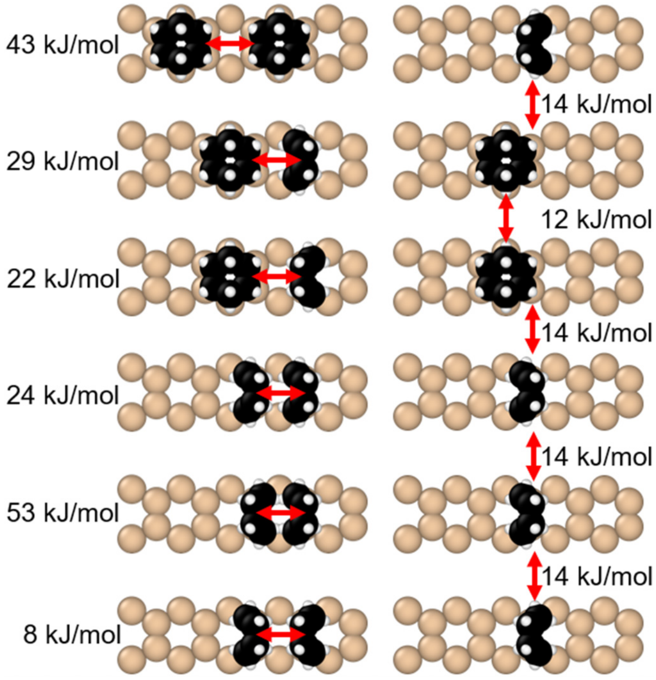

FIG. 2. Intermolecular interactions considered in the lattice models of the adsorption layer of 1,4-CHD on the Si(001)-(2 × 1) surface. Left column: interactions along the row of Si = Si dimers. Right column: interactions between the molecules adsorbed on adjacent rows of Si = Si dimers (not considered in 1D models). The corresponding energies of intermolecular interactions were calculated by DFT (see Sec. III).

Here the first sum runs over all lattice sites, and the second sum runs over all different pairs of the lattice sites. n_i is a state of the ith lattice site, and $\mathbf{r_{ij}}$ is a radius vector from the ith site to the jth site. The set of states is determined by all possible orientations (adsorption complexes) of the 1,4-CHD molecule on the Si(001)-(2 × 1) surface. In this case, there are four different states of the lattice site (Si = Si dimer): empty (0), the left di-σ complex (1), the right di-σ complex (2), and the tetra-σ complex (3) (Fig. 1). In the case of the tetra-σ complex, only the left of two reacted Si = Si dimers is considered to be occupied in the lattice model of the adlayer. $E(n_i)$ is the formation energy of the adsorption complex corresponding to the n_i state in zero coverage limit. $\varepsilon(n_i, n_j, \mathbf{r_{ij}})$ is a function of intermolecular interactions that depends on the state of the interacting site and their relative positions (radius vector). Our models consider only short-ranged interactions between all different pairs of adsorption complexes along the row of Si = Si dimers (Fig. 2). In two-dimensional versions of the model, the interaction between the molecules adsorbed on the nearest sites of neighboring Si = Si rows is additionally taken into account. In the models that have a symmetric interaction function (1D-SYM and 2D-SYM), the states (1) and (2) are assumed to be equivalent. Therefore, the related energies of intermolecular interactions are equal: $\varepsilon(1, 1, \mathbf{r_{ij}}) = \varepsilon(1, 2, \mathbf{r_{ij}}) = \varepsilon(2, 1, \mathbf{r_{ij}}) = \varepsilon(2, 2, \mathbf{r_{ij}})$ and $\varepsilon(1, 3, \mathbf{r_{ij}}) = \varepsilon(3, 1, \mathbf{r_{ij}}) = \varepsilon(2, 3, \mathbf{r_{ij}}) = \varepsilon(3, 2, \mathbf{r_{ij}})$. μ is the chemical potential of the ideal gas phase in equilibrium with the adsorption layer. Under the thermodynamic equilibrium condition, μ is equal to the chemical potential of the adsorption layer and proportional to the pressure in the gas phase. Thus, μ regulates the density of the model adsorption layer. Here δ_{0,n_i} is the Kronecker's delta, therefore $(1 - \delta_{0,n_i})$ is equal to unity for an occupied lattice site and zero for an empty site.

The value of μ can be used to estimate the equilibrium pressure in the ideal gas phase of 1,4-CHD. The conversion of chemical potential values to ideal gas pressures was carried out using the following equation:

$$\mu(p, T) = N_a k_B T \ln\left[\frac{p}{k_B T}\left(\frac{2\pi\hbar^2}{m k_B T}\right)^{3/2}\right] + (A + BT + CT^2). \quad (2)$$

Here k_B, $\hbar$, and N_a are the Boltzmann, Dirac, and Avogadro constants, respectively. m is the mass of the 1,4-CHD molecule equal to 1.33×10^{-25} kg. A, B, and C are the fitting parameters. The chemical potential of the ideal gas phase of 1,4-CHD was calculated using thermochemical algorithms implemented in the ORCA 5.0.3 program [33] at different temperatures and pressures. The calculations were done for the 1,4-CHD molecule optimized with the options described in the next section. The following values of the fitting parameters were found: $A = -12.74$ kJ/mol, $B = -1.75 \times 10^{-3}$ kJ/mol/K, and $C = -3.8 \times 10^{-4}$ kJ/mol/K^2 ($R^2 = 0.99$).

III. DFT CALCULATIONS OF THE MODEL PARAMETERS

The formation energies of adsorption complexes $E(n_i)$ and the energies of intermolecular interactions $\varepsilon(n_i, n_j, \mathbf{r_{ij}})$ were calculated using DFT methods. In this work, we focus on the short-range interactions between 1,4-cyclohexadiene molecules chemisorbed on the neighboring Si = Si dimers of the Si(001)-(2 × 1) surface. To adequately assess such interactions in covalently bonded structures it is sufficient to consider the finite cluster model, as done in most quantum chemical calculations of organic and metal-organic systems. The Si(001)-(2 × 1) surface was represented by two models. The first model consists of four Si = Si dimers arranged in single row with a thickness of four Si atoms. This model was used to calculate the intermolecular interaction energies along the one row of Si = Si dimers. The second model comprises two adjacent rows of Si = Si dimers, four dimers in each row with a thickness of five Si atoms. It is worth noting that the second model of the Si(001)-(2 × 1) slab contains the larger number of silicon atomic layers, since the correct distance between the adjacent rows of Si = Si dimers is important to describe the intermolecular interactions between the molecules adsorbed on these rows. To take this into account, it is necessary to consider a layer of silicon atoms located in the cavity between the adjacent rows of Si = Si dimers. The covalent bonds between these atoms and surrounding silicon atoms define the real geometry of the Si(001)-(2 × 1) slab containing two parallel rows of Si = Si dimers. We used this slab model to determine the interaction energy between two 1,4-CHD molecules on the adjacent rows of Si = Si dimers. All external Si atoms, except for surface Si = Si dimers, were saturated with hydrogen.

The formation energies $E(n_i)$ of adsorption complexes of 1,4-CHD on the Si(001)-(2 × 1) surface were determined as follows:

$$E(n_i) = E_{\mathrm{tot}}(n_i) - E_{\mathrm{Si}} - E_0, \tag{3}$$

where $E_{\mathrm{tot}}(n_i)$ is the total energy of the adsorption complex n_i that contains the Si(100) surface and the adsorbed 1,4-CHD molecule, E_{Si} is the energy of the clean Si(100)-(2 × 1) slab, and E_0 is the energy of the 1,4-CHD molecule isolated in vacuum.

The energies $\varepsilon(n_i, n_j, \mathbf{r_{ij}})$ of intermolecular interactions were evaluated as

$$\varepsilon(n_i, n_j, \mathbf{r_{ij}}) = E_{\mathrm{tot}}(n_i, n_j) - E_{\mathrm{Si}} - 2E_0 - (E(n_i) + E(n_j)), \tag{4}$$

where $E_{\mathrm{tot}}(n_i, n_j)$ is the total energy of adsorption complexes n_i and n_j located at the distance $\mathbf{r_{ij}}$ on the single Si(001)-(2 × 1) slab. Other quantities in expression (4) have the same meaning as in expression (3). These formulas use the energies of the adsorbent and adsorbates in their optimized ground states.

All DFT calculations were carried out using the ORCA 5.0.3 [33]. The B3LYP functional [34,35] with def2-TZVP basis set [36] and DFT-D3(BJ) dispersion correction [37,38] were used. The tolerance of the self-consistent field in all calculations was 3×10^{-5} kJ/mol. Geometric optimizations were done with the following convergence parameters: 0.01 kJ/mol for energy, 0.5 kJ/mol/Å for maximum force acting on each atom, and 0.002 Å for maximum displacement of atoms. All structures were optimized without any geometric restrictions (the *xyz* files provided in the Supplemental Material [39]).

According to our calculations, the formation energies of the tetra-σ and di-σ complexes of 1,4-CHD on the Si(001) surface are −333 and −190 kJ/mol, respectively. Figure 2 demonstrates that energies of intermolecular interactions in all pairs of the adsorption complexes are positive. Thus, the 1,4-CHD molecules adsorbed on the neighboring Si = Si dimers repel each other. This is in good agreement with previous DFT calculations [5,23,24,40]. There is a difference between the interaction energies of neighboring di-σ complexes with different orientations relative to each other. The charge distributions in these pairs of di-σ complexes are similar (see Supplemental Material [39]). We suppose that this difference results from the distances between the nearest hydrogens of the neighboring di-σ complexes. Recall, the (1) and (2) lattice states are assumed to be equivalent in the 1D-SYM and 2D-SYM symmetrical models. The energies of the corresponding intermolecular interactions in the symmetric models were averaged over the (1) and (2) states in all different pair configurations.

IV. METHODS FOR CALCULATING THERMODYNAMIC CHARACTERISTICS

In this section we briefly describe methods for calculating the thermodynamic characteristics of the model adsorption layers as an open system. We consider the grand canonical ensemble of systems, where an explicitly modeled adsorption layer is in contact with an implicit ideal gas reservoir (defined T and μ values). This allows us to reveal how the structure of the adsorption monolayer depends on external pressure. To model the equilibrium state of the adsorption monolayer, it is not necessary to explicitly consider the adsorption kinetics, in particular short-lived intermediate states, even if they exist. The equilibrium state implies infinite time and is thus limiting.

1D-SYM and 1D models are studied by the TM method, since for 1D systems it allows one to obtain a numerically rigorous solution. The TRG was used to solve the 2D-SYM and 2D models. The TRG method allows one to calculate the thermodynamic characteristics for a formally infinite 2D system. The latter is important for a correct comparison of the results obtained for 1D and 2D models by the TM and TRG methods, respectively. To visually identify stable structures of the model adsorption monolayers of 1,4-CHD, the grand canonical Monte Carlo simulation was performed at specified values of T and μ.

A. Tensor renormalization group

The main advantage of studying the 2D models by the TRG method is the ability to calculate thermodynamic characteristics of formally infinite systems. Initially, the lattice model under consideration is represented as a uniform tensor network consisting of interconnected tensors T, where T is a multidimensional linear operator consisting of Boltzmann weights of possible configurations of neighboring nodes. The process of constructing a tensor network is described in detail in [25].

The trace of the constructed tensor network is equal to the partition function of the model $Z = t\ \mathrm{Tr}(\otimes_{i=1}^{N} T)$, where N is the number of tensors in the tensor network. However, direct calculation of the partition function in this way is impossible even for relatively small N. For the system of infinite size, N also tends to infinity. This problem can be solved using some approximations—one of them is TRG [26]. The TRG method is an iterative procedure. At each iteration the tensors T are contracted in the appropriate way, followed by singular value decomposition of the resulting tensor. Further, it is reduced by leaving only χ of the largest singular values corresponding to combinations with the largest Boltzmann weights. Thus, the χ is the main parameter of the TRG methods that controls the accuracy. In this work, $\chi = 84$ was used. An increase in χ above 84 does not lead to noticeable changes in the thermodynamic characteristics of the models under consideration. In practical calculations the χ value is a compromise between the accuracy of the calculations and computational costs. The described process is repeated until the convergence on the resulting value of the partition function per lattice site. Having the value of the partition function, the thermodynamic characteristics of the model adsorption layer can be obtained using the following formulas:

$$\frac{\Omega}{RT} = -\ln(Z), \qquad \rho = -\left(\frac{\partial\Omega}{\partial\mu}\right)_T, \qquad S = -\left(\frac{\partial\Omega}{\partial T}\right)_\mu, \tag{5}$$

$$\frac{H}{RT} = \frac{\Omega}{RT} + \frac{S}{R}, \qquad \frac{U}{RT} = \frac{H}{RT} + \rho\frac{\mu}{RT}, \tag{6}$$

where Ω is the grand thermodynamic potential, T is the thermodynamic temperature, R is the universal gas constant, and ρ is the layer density (the number of molecules per lattice site). H, U, and S are the total energy, potential energy, and entropy of the model adsorption layer, respectively. To calculate ρ and S as the derivatives of the free energy according to the formulas (5), we used the standard numerical differentiation techniques.

B. Tensor network representation of the transfer-matrix method

The TM method is usually used when the two-dimensional lattice under study is limited by a certain value M along one of the dimensions. In the case of the 1D-SYM and 1D models of the adsorption monolayer of 1,4-CHD on the Si(001) surface, $M = 1$. Transition probabilities of a column consisting of M sites (or ring, if periodic boundary conditions are applied) from one state to another are described by the transfer matrix A. Having the transfer matrix constructed, the partition function of the of $M\times\infty$ system can be calculated as $Z = \mathrm{Tr}(A^N)$, where N tends to infinity. In the standard algorithm, the problem is formulated in terms of finding the largest eigenvalue λ_1 of matrix A.

The main problems of the TM method are the exponential growth of the A matrix size with increasing M and poor convergence near the phase transition points due to the degeneracy of eigenvalues. The previously proposed representation of the model as a linear tensor network [25] allows us to partially circumvent these difficulties. Instead of the A matrix, it is enough to store in the computer memory only the T tensor. Due to the linear structure of such tensor network, the eigenvalue can be found by the direct contraction. If necessary, several steps of contraction and reduction of tensors can be carried out in the same way as in the high-order TRG algorithm [41]. This allows one to save computational resources and explore the systems with large M values. However, this is achieved at the expense of increasing the calculation error, which is difficult to estimate.

In this work, all calculations by the TM method for the one-dimensional models were carried out using the above-mentioned algorithms implemented in the SuSMoST library [27].

C. Grand canonical Monte Carlo simulation

To verify the TM and TRG data and visualize the state of the adsorption layer at the specific values of the temperature and chemical potential, we used the grand canonical Monte Carlo method (GCMC) [42,43] as is implemented in the SuSMoST library [27]. The pseudodynamics of the model adsorption layer included the processes of adsorption/desorption, surface diffusion, and the transformation of one adsorption complex into another. As the result of the adsorption process, an adsorption complex n_i is formed on a randomly selected empty site i (Fig. 1). The desorption is a reverse process, when a randomly selected adsorption complex n_i on the ith site is replaced by an empty state $n_i = 0$. When the state of a randomly selected lattice site is replaced by a random nonzero state, the transformation process takes place. Local diffusion is modeled by the permutation of states of a randomly selected pair of nearest-neighboring sites. To improve the convergence to the equilibrium state of the model layer the parallel tempering technique was used [43]. We used the set of 24 temperatures ranging from 100 to 4200 K. The relative probability of all the elementary processes was determined by the Metropolis rule [43]. The GCMC simulation was performed on the lattice comprising 16 rows of Si = Si dimers with 48 Si = Si dimers per row. Therefore, the linear lattice size is 48 × 16. To relax the system and calculate ensemble averages we used 10^6 Monte Carlo steps. One Monte Carlo step corresponds to $48 \times 16 = 768$ attempts to change a state of the lattice model.

V. RESULTS AND DISCUSSION

Here we demonstrate and discuss the calculated thermodynamic characteristics of the one-dimensional and two-dimensional models of 1,4-CHD adsorption monolayer on a Si(001) surface. It allows us to reveal the crucial role of the intermolecular interactions between the adsorbed 1,4-CHD molecules on the phase behavior of the adlayer. Most of the

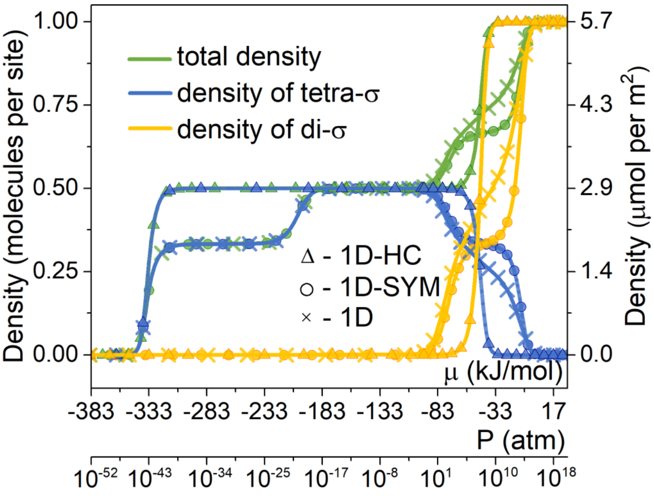

FIG. 3. Adsorption isotherms of 1,4-CHD on the Si(001)-(2 × 1) surface at $T = 300$ K calculated within the one-dimensional models of the adsorption layer by the transfer-matrix method. The 1D-HC model does not take into account any intermolecular interactions except the hard core; the 1D-SYM is a one-dimensional model with symmetrical interactions of the di-σ complexes; the 1D model is also a one-dimensional model in which "right" and "left" di-σ complexes are distinguished.

calculations were carried out at $T = 300$ K, since at higher temperatures (400–600 K) the dehydrogenation of 1,4-CHD with the formation and subsequent desorption of benzene are known to be observed in the experiments [9,18,20]. According to the same experimental data, physically adsorbed π complexes exist on the surface at temperatures below 150 K. At 300 K both chemisorbed di-σ and tetra-σ complexes are observed. Moreover, most of the scanning tunneling microscopy (STM) studies of the 1,4-CHD adsorption layer on Si(001) were performed near room temperature. Thus, we consider the phase behavior of the 1,4-CHD chemisorbed layer on Si(001)-(2 × 1) without taking into account the dehydrogenation of the molecules.

A. 1D models and effect of intermolecular interactions

The total and partial adsorption isotherms $\rho(\mu)$ of 1,4-CHD on the Si(001) surface calculated within the framework of 1D models by the TM method at $T = 300$ K are shown in Fig. 3. Three 1D models of the chemisorbed layer differing in the interactions between the molecules along the row of Si = Si dimers have been investigated. The 1D-HC includes only the hard-core interactions. In this model the adsorption of two molecules onto the same silicon dimer is prohibited. The 1D-SYM model also takes into account the interactions between adsorption complexes on neighboring Si = Si dimers of the same row. In the 1D model we additionally distinguish between the right and left di-σ complexes. Therefore, the intermolecular interactions in the 1D model depend on the relative position of the adsorption complexes.

A horizontal plateau on the adsorption isotherms $\rho(\mu)$ usually indicates the existence of stable phases of the adsorption layer. As can be seen from Fig. 3, the intermolecular interactions significantly affect the set of stable structures observed in the 1D models of the 1,4-CHD adsorption layer on the Si(001)-(2 × 1) surface. The plateaus at $\rho = 0$ and $\rho = 1.0$ on the total adsorption isotherms correspond to the lattice gas and completely covered surface. In addition, we can distinguish horizontal plateaus at $\rho = 0.33$, $\rho = 0.5$, and $\rho = 0.66$. These plateaus determine the μ regions of stability of structures comprising one molecule per three Si = Si dimers, one molecule per two silicon dimers, and two molecules per three dimers, respectively. To understand the composition of these stable structures, we calculated the partial adsorption isotherms $\rho_{4\sigma}(\mu)$ for tetra-σ complexes and $\rho_{2\sigma}(\mu)$ for di-σ complexes. It turned out that structures with $\rho = 0.33$ and $\rho = 0.5$ consist only of the tetra-σ complexes. The structure with density $\rho = 0.66$ contains equal amounts of the tetra-σ and di-σ complexes. Considering the repulsive intermolecular interactions along the row of Si = Si dimers, we can assume that the structure with density $\rho = 0.33$ represents the tetra-σ complexes that alternate with empty sites along the single row of Si = Si dimers. Further, we will denote this structure as "4σ-$p(3 \times 1)$." At $\rho = 0.5$, the repulsive forces are overcome, and all adsorption sites are occupied by the tetra-σ complexes, so that the surface coverage is equal to unity. We will mark this structure as "4σ-$p(2 \times 1)$." In the structure denoted as "$4\sigma/2\sigma$-$c(3 \times 1)$" at $\rho = 0.66$ the surface coverage also equals unity, but here the tetra-σ complexes alternate with di-σ complexes. In the close-packed 2σ-$p(1 \times 1)$ structure, each Si = Si dimer forms the di-σ complex ($\rho = 1.0$).

Due to the absence of any intermolecular interactions except the hard core, a phase behavior of the 1D-HC model is primitive (Fig. 3). Only 4σ-$p(2 \times 1)$ and 2σ-$p(1 \times 1)$ structures are formed in the model adsorption monolayer. Thus, the μ regions of existence of the tetra-σ and di-σ complexes are separated. Accounting for the intermolecular repulsions in the 1D-SYM model leads to a significant complication of the phase behavior. An increase in the partial pressure of 1,4-CHD over the empty surface induces the sequential appearance of 4σ-$p(3 \times 1)$, 4σ-$p(2 \times 1)$, $4\sigma/2\sigma$-$c(3 \times 1)$, and 2σ-$p(1 \times 1)$ structures.

The symmetrical 1D-SYM and asymmetrical 1D models have similar phase behaviors and differ only in the region of existence of the di-σ complexes (Fig. 3). In the 1D-SYM model, the $4\sigma/2\sigma$-$c(3 \times 1)$ structure consisting of both di-σ and tetra-σ complexes is formed. This can be seen from the evident horizontal plateau on the total and partial adsorption isotherms (Fig. 3). The density of the mixed adsorption layer is always higher in the asymmetric 1D model. As follows from the partial isotherms for tetra-σ and di-σ complexes, the reason is different relative amounts of the tetra-σ and di-σ complexes forming the structure. In the asymmetric 1D model, the relative surface concentration of di-σ complexes is higher. The more di-σ complexes on the surface, the greater the difference in potential energy of the model adsorption layers with symmetric and asymmetric interactions (Fig. 4). This is because the intermolecular interactions in the asymmetric 1D model depend on the relative position and orientation of the di-σ complexes. Noteworthy is the drop in the potential energy of intermolecular interactions in the adlayer of mixed composition (Fig. 4). This results from the weaker repulsion between tetra-σ and di-σ complexes than between two di-σ complexes.

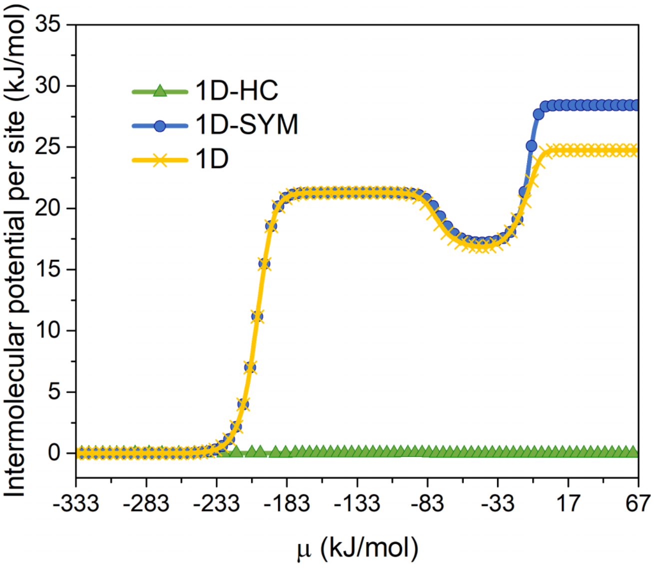

FIG. 4. Potential energy of the intermolecular interactions in the adsorption layer of 1,4-CHD on the Si(001)-(2 × 1) surface vs the chemical potential calculated within the one-dimensional models at $T = 300$ K by the transfer-matrix method. Obviously, the potential energy of intermolecular interactions in the 1D-HC model is independent from the coverage and is equal to zero at any value of the chemical potential.

There is an indistinct plateau at $\rho = 0.75$ on the total adsorption isotherm calculated within the asymmetric 1D model (Fig. 3). At this layer density the number of di-σ complexes is twice as many as tetra-σ complexes in this model. To confirm the presence of such structure, we have calculated the adsorption isotherms in the temperature range from 200 to 600 K (Fig. 5). The plateau at $\rho \approx 0.75$ becomes more evident with decreasing temperature. This plateau is assumed to correspond to an ordered structure where tetra-σ complexes alternate with pairs of di-σ complexes. We will further denote this structure as "$4\sigma/(2\sigma)_2$-$c(4 \times 1)$."

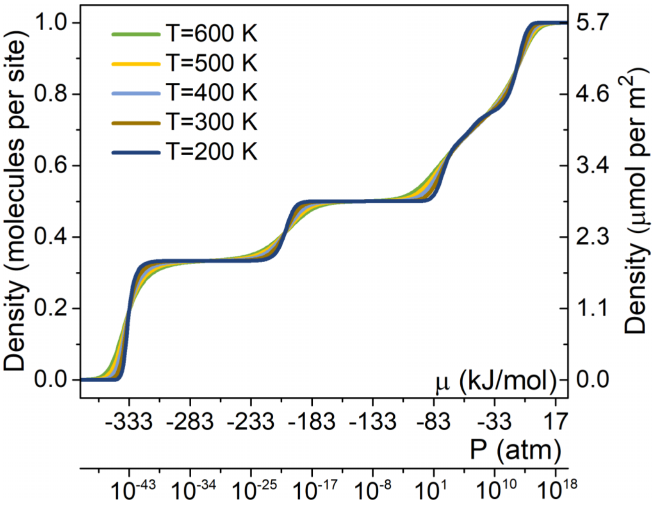

FIG. 5. Adsorption isotherms of 1,4-CHD on the Si(001)-(2 × 1) surface obtained within the asymmetric 1D model by the transfer-matrix method at different temperatures.

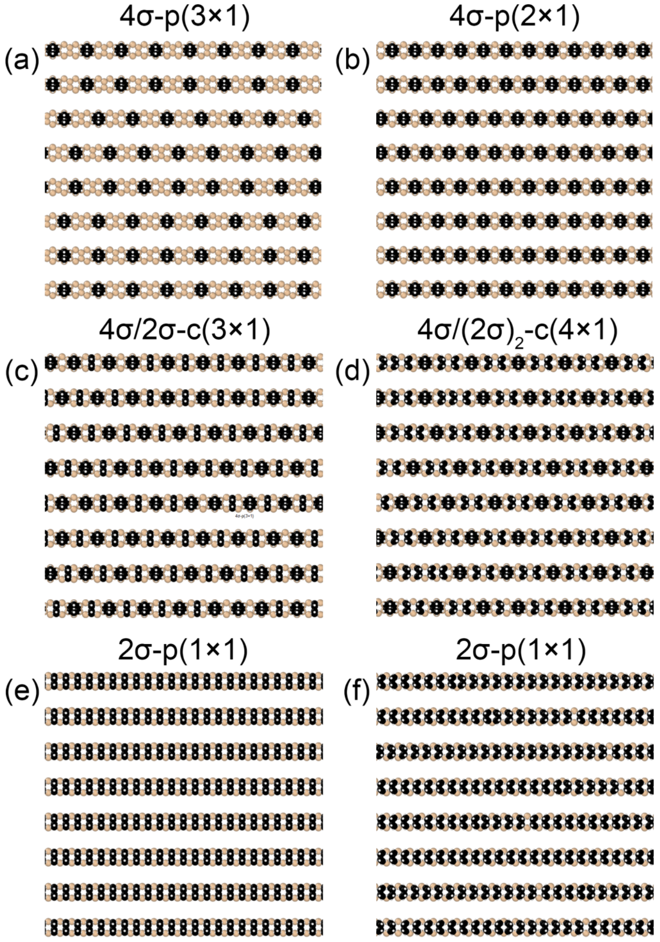

FIG. 6. Snapshots of model adsorption layers of 1,4-CHD on the Si(001)-(2 × 1) surface obtained during the GCMC simulations: (a) 4σ-$p(3 \times 1)$ structure at $\mu = -263$ kJ/mol and $T = 300$ K in the 1D-SYM model; (b) 4σ-$p(2 \times 1)$ structure at $\mu = -133$ kJ/mol and $T = 300$ K in the 1D-SYM model; (c) $4\sigma/2\sigma$-$c(3 \times 1)$ structure at $\mu = -33$ kJ/mol and $T = 300$ K in the 1D-SYM model; (d) $4\sigma/(2\sigma)_2$-$c(4 \times 1)$ structure at $\mu = -33$ kJ/mol and $T = 200$ K in the asymmetric 1D model; (e),(f) 2σ-$p(1 \times 1)$ structure at $\mu = 17$ kJ/mol and $T = 300$ K in the symmetrical 1D-SYM and asymmetrical 1D models, respectively.

The above-mentioned structures in the model adsorption monolayers of 1,4-CHD on the Si(001)-(2 × 1) surface are observed in the GCMC simulation at corresponding values of the temperature and chemical potential. The "snapshots" taken during the GCMC simulation are shown in Fig. 6. One can see that pairs of di-σ complexes in the $4\sigma/(2\sigma)_2$-$c(4 \times 1)$ structure have different orientations (right and left), since the energy of intermolecular repulsions in this pair configuration is the lowest (Fig. 2).

As can be seen in Fig. 3, Fig. 5, and Fig. 6 only the tetra-σ complexes exist on the surface at low pressures. Extremely low equilibrium pressures ($<10^{-12}$ atm) mean that the gas phase is in fact empty. That is, all the molecules entering the "adsorption layer+gas phase" system are instantly adsorbed on the Si(001)-(2 × 1) surface due to the high adsorption energy. In this case, the chemical potential is just a parameter that regulates the density of the adsorption layer. To

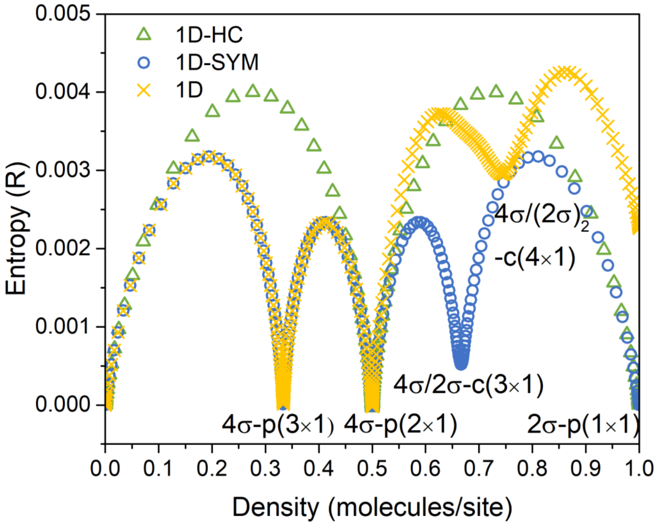

FIG. 7. Entropy vs density of the model adsorption layers of 1,4-CHD on the Si(001)-(2 × 1) surface calculated within the one-dimensional models at T = 300 K by the transfer-matrix method.

make our data useful for planning appropriate experiments and interpreting experimental data, we added another vertical axis to the isotherm graphs. This is the surface coverage axis measured in μmol/m^2.

Using the TM method, we additionally calculated how the entropy of the one-dimensional adsorption layers changes with its density at T = 300 K (Fig. 7). Minima on these dependencies correspond to ordered structures of the adlayer. In the case of the 1D-HC and 1D-SYM models, a self-assembly of all the structures described above is confirmed. The 4σ-$p(3\times1)$ and 4σ-$p(2\times1)$ structures are formed in both symmetric and asymmetric models (Fig. 6). When di-σ complexes appear on the surface, the $S(\rho)$ curves for the 1D-SYM and 1D models are different. There is a characteristic minimum for the $4\sigma/2\sigma$-$c(3\times1)$ structure at $\rho = 0.66$ on the $S(\rho)$ curve for the 1D-SYM. In the asymmetric 1D model, such entropy minimum appears at $\rho{\approx}0.75$. This confirms the self-assembly of the $4\sigma/(2\sigma)_2 - c(4\times1)$ structure comprising two di-σ complexes per tetra-σ complex. Despite that both the density and the entropy of the adsorption layer are the first derivatives of the free energy directly calculated by the TM method, the entropy minimum as a characteristic of the stable ordered structure is more sensitive than the stable density of the adsorption layer.

Thus, the intermolecular interactions in the adsorption monolayer of 1,4-CHD on the Si(001)-(2 × 1) surface along the row of Si = Si dimers determine the self-assembly of the linear 4σ-$p(3\times1)$, $4\sigma/2\sigma$-$c(3\times1)$, and $4\sigma/(2\sigma)_2 - c(4\times1)$ structures. The first one consists only of the tetra-σ complexes alternating with empty Si = Si dimers. The last two have the mixed composition. They are formed by the tetra-σ and di-σ complexes simultaneously. Taking into account the asymmetry of the di-σ complex, the only equilibrium structure of the mixed monolayer of 1,4-CHD on the Si(001) surface is the $4\sigma/(2\sigma)_2$-$c(4\times1)$ structure. In this structure the tetra-σ complexes alternate with pairs of differently oriented di-σ complexes.

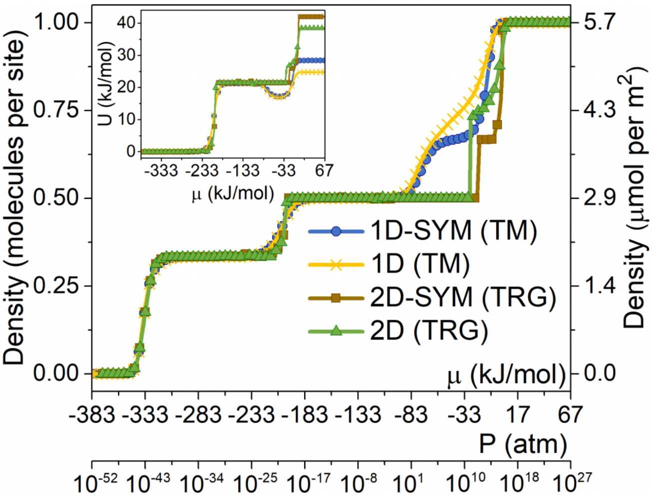

FIG. 8. Adsorption isotherms of 1,4-CHD on the Si(001)-(2 × 1) surface calculated within the 1D and 2D models at T = 300 K by the TM and TRG methods. Inset: potential energy of intermolecular interactions per lattice site vs the chemical potential. Models: 1D-SYM is a one-dimensional model with symmetric interactions of the di-σ complexes; 1D model is a one-dimensional model in which "right" and "left" di-σ complexes are distinguished; 2D-SYM and 2D are two-dimensional models that additionally take into account the interaction between molecules adsorbed on adjacent rows of Si = Si dimers of the Si(001)-(2 × 1) surface.

B. 2D models and phase transitions

In this section, we study how the equilibrium structure of the 1,4-CHD adsorption layer on the Si(001)-(2 × 1) surface depends on the interactions between the molecules adsorbed on neighboring rows of Si = Si dimers. This requires consideration of the 2D-SYM and 2D models described in Sec. II. In the case of two-dimensional lattice models, the TM method is sensitive to the size of the semi-infinite lattice. This can be seen from the adsorption isotherms calculated within the 2D-SYM model at different M values (see Supplemental Material [39]). Therefore, we studied the two-dimensional models by the TRG method, which allows one to calculate the thermodynamic characteristics of systems that are formally infinite in all directions.

Figure 8 demonstrates the comparison of the adsorption isotherms of 1,4-CHD on the Si(001)-(2 × 1) surface calculated within the 1D and 2D models by the TM and TRG methods, respectively. Recall that horizontal plateaus on the isotherms correspond to stable phases. The main differences in the phase behavior of 1D and 2D model adsorption layers arise in the μ region of existence of di-σ complexes, when the 4σ-$p(2\times1)$ phase loses its stability and the tetra-σ complexes transform into the di-σ complexes. The set of ordered structures appearing in the 2D model adsorption layer is preserved. These are 4σ-p(3×1), 4σ-p(2×1), $4\sigma/2\sigma$-$c(3\times1)$, $4\sigma/(2\sigma)_2 - c(4\times1)$, and 2σ-$p(1\times1)$ structures. In the 2D models, the μ regions of existence of the $4\sigma/2\sigma$-c (3×1) and $4\sigma/(2\sigma)_2 - c(4\times1)$ phases in the symmetrical and asymmetrical models are significantly narrower.

In the inset to Fig. 8 the dependences of the intermolecular potential per lattice site on the chemical potential in the 1D and 2D models are shown. The "dip" of potential energy in the

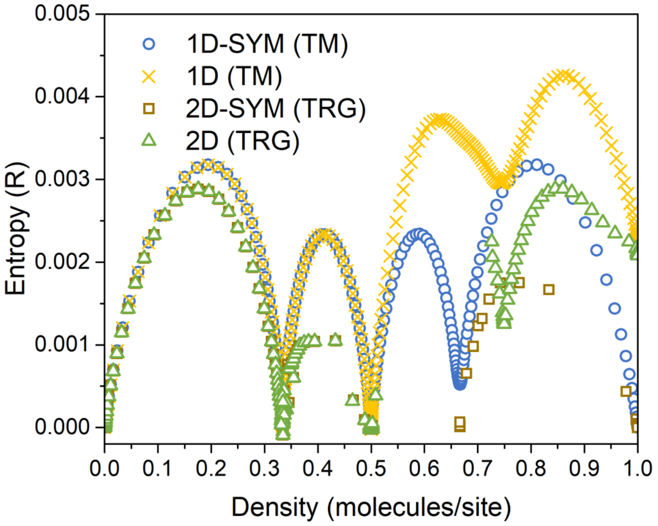

FIG. 9. Entropy vs density of the adsorption layer of 1,4-CHD on the Si(001)-(2×1) surface calculated within the 1D and 2D models at $T = 300$ K by TM and TRG methods.

μ region of the $4\sigma/2\sigma$-$c(3 \times 1)$ and $4\sigma/(2\sigma)_2$-$c(4 \times 1)$ phases observed in the 1D models disappears in the 2D models. It is also seen that the potential energy of the dense monolayer is higher in the 2D models. These observations are explained by additional repulsive interactions between 1,4-CHD molecules adsorbed on the adjacent rows of Si = Si dimers of the Si(001)-(2×1) surface. These interactions are included in the 2D-SYM and 2D models of the adlayer (Fig. 2). Particularly, the contraction of the μ region of the $4\sigma/2\sigma$-$c(3 \times 1)$ and $4\sigma/(2\sigma)_2$-$c(4 \times 1)$ phases and the disappearance of the potential energy dip in the 2D models results from the fact that repulsions between the tetra-σ and di-σ complexes are greater than between two tetra-σ complexes adsorbed on the neighboring Si = Si rows.

Dependences of the entropy on the density of the model adsorption layer at $T = 300$ K confirm the described phase behavior (Fig. 9). The positions of the entropy minima correspond to the density of stable phases and coincide in the 1D and 2D models. However, the entropy of stable phases defined as the depth of the corresponding minima on the $S(\rho)$ curves differs. The entropy of stable phases is always lower in the 2D models than in the corresponding 1D models, especially for the phases of mixed composition appearing at $\rho = 0.66$ and $\rho = 0.75$. The reason for this is the concerted filling of neighboring rows of Si = Si dimers in the 2D models of the 1,4-CHD/Si(001)-(2×1) adlayer. The concerted mechanism of adsorption results from the repulsive interactions between 1,4-CHD molecules adsorbed on adjacent rows of Si = Si dimers of the Si(001) surface. Moreover, the repulsion between two tetra-σ complexes is less than between other pairs of adsorption complexes (Fig. 2). Therefore, the structure of 4σ-$p(3 \times 1)$, 4σ-$p(2 \times 1)$, $4\sigma/2\sigma$-$c(3 \times 1)$, and $4\sigma/(2\sigma)_2$-$c(4 \times 1)$ phases containing tetra-σ complexes are slightly different in the 1D and 2D models (Fig. 6 and Fig. 10). In the 4σ-$p(3 \times 1)$ and 4σ-$p(2 \times 1)$ phases, the tetra-σ complexes on adjacent rows of Si = Si dimers are shifted relative to each other to avoid repulsive interactions. In the $4\sigma/2\sigma$-$c(3 \times 1)$ and $4\sigma/(2\sigma)_2$-$c(4 \times 1)$ phases, the tetra-σ complexes are predominantly formed on neighboring sites of the adjacent rows of Si = Si dimers. Snapshots of the described phases obtained in the GCMC simulations are shown in Fig. 10.

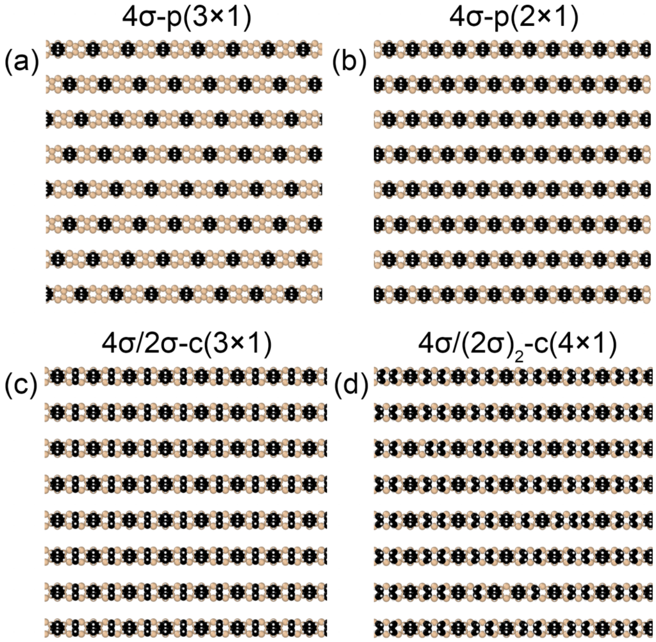

FIG. 10. Snapshots of the adsorption layer of 1,4-CHD on the Si(001)-(2×1) surface obtained in the GCMC simulation of the 2D model at $T = 300$ K: (a) 4σ-$p(3 \times 1)$, (b) 4σ -$p(2 \times 1)$, (c) $4\sigma/2\sigma$-$c(3 \times 1)$, and (d) $4\sigma/(2\sigma)_2 - c(4 \times 1)$ structures.

Discontinuities on the adsorption isotherms $\rho(\mu)$ and $S(\rho)$ curves for the 2D-SYM and 2D models are striking (Figs. 8 and 9). This is not characteristic of the corresponding 1D models. By definition, the presence of discontinuities in the first derivatives of the free energy indicates a first-order phase transition. In the two-dimensional models of the 1,4-CHD/Si(001)-(2×1) adlayer, these are transitions from the 4σ-$p(2 \times 1)$ phase consisting only of the tetra-σ complexes to one of the phases of mixed composition $4\sigma/2\sigma$-$c(3 \times 1)$ or $4\sigma/(2\sigma)_2 - c(4 \times 1)$ depending on the model. The individual process of converting one tetra-σ complex into a di-σ complex is energetically unfavorable. Thus, this transition should be explained by collective effects. Figures 8–10 show that converting of the tetra-σ complexes into the di-σ complexes of 1,4-CHD on the Si(001)-(2×1) surface is an abrupt process occurring at a fixed pressure and is associated with overcoming the intermolecular repulsion forces between the tetra-σ and di-σ complexes. This transition occurs above atmospheric pressures (from 1 to 10^{10} atm depending on the model), and the existence region of the $4\sigma/2\sigma$-$c(3 \times 1)$ or $4\sigma/(2\sigma)_2 - c(4 \times 1)$ phases of mixed composition in 2D models is narrow. The transition to the phase consisting only of the di-σ complexes occurs at extremely high pressures. These are the possible reasons why no superstructure is observed in the low-energy electron diffraction (LEED) experiments at coverages close to 0.6 and higher [9].

The question about the type of other phase transitions remains open and requires additional research beyond the scope of this work.

VI. CONCLUSION

The adsorption layer of 1,4-cyclohexadiene on Si(001)-(2 × 1) is one of the most studied organic/semiconductor interfaces. However, the structure of the stable adsorption layer and its dependence on external pressure and temperature were hypothetical [9,18–22,24]. The experimental data and the results of DFT calculations show that intermolecular interactions and asymmetry of the di-σ complex of 1,4-CHD on the Si(001) surface play a key role. In the mentioned experimental works the dependence of the adlayer structure on its density follows from the LEED, STM, and high-resolution electron-energy-loss spectroscopy studies. It means the structure of the adsorption layer is determined by intermolecular interactions, among other factors. Thus, the structure of the adsorption monolayer is determined by the balance between "molecule-surface" interactions and "molecule-molecule" repulsions. This balance can be controlled using the external pressure. In this work, we have developed and studied a series of detailed lattice models of the 1,4-CHD adsorption layer on the Si(001)-(2 × 1) surface, taking into account more factors including intermolecular interactions. The unique combination of the DFT methods and tensor renormalization group method allowed us to resolve the equilibrium structure of the 1,4-CHD monolayer on the Si(001)-(2 × 1) surface. Summarizing the results obtained, we can draw the following conclusions about the equilibrium structure of the 1,4-CHD/Si(001)-(2 × 1) adlayer and the driving forces of its self-assembly:

(1) There are two phases consisting only of the tetra-σ complexes. These phases differ in density. In the phase with low density, there is one 1,4-CHD molecule per three Si = Si dimers of the Si(001)-(2 × 1) surface. In the denser phase there is one 1,4-CHD molecule per two Si = Si dimers. An increase in the 1,4-CHD partial pressure over these phases leads to the phase of mixed composition, where the tetra-σ complexes alternate with pairs of differently oriented di-σ complexes. In this phase, there are three 1,4-CHD molecules per four Si = Si dimers. In the dense structure of the adsorption layer each Si = Si dimer of the Si(001)-(2 × 1) surface is occupied by the di-σ complex.

(2) Repulsive intermolecular interactions along the row of Si = Si dimers of the Si(001)-(2 × 1) surface drive the self-assembly of the phase containing one tetra-σ complex per three Si = Si dimers, and the phase of mixed composition (tetra-σ and di-σ complexes).

(3) Repulsive interactions between 1,4-CHD molecules adsorbed on neighboring rows of Si = Si dimers of the Si(001) surface lead to the concerted filling of these rows and determine the range of chemical potential (or partial pressure) where the tetra-σ and di-σ complexes coexist.

(4) The transition from the phase consisting only of the tetra-σ complexes to the phase of mixed composition occurs abruptly as the first-order phase transition.

We hope that our results will stimulate further experimental studies, in particular the search for the described phases of the 1,4-CHD/Si(001)-(2 × 1) adsorption layer. The drawn conclusions can be used when interpreting experimental data on the adsorption of bifunctional molecules on the Si(001)-(2 × 1) surface. We also believe that the demonstrated capabilities of the tensor renormalization group in combination with DFT methods will serve to further disseminate this method in theoretical studies of specific adsorption systems.

ACKNOWLEDGMENTS

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