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The Effect of Three-Body Interactions on Thermal Desorption Spectra

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Thermal desorption spectra are calculated for a one-dimensional chain and for a two-dimensional square lattice using the transfer-matrix technique and Monte Carlo simulations. Lateral interactions of adsorbed particles cause a splitting of spectra. The repulsive three-body interactions are shown to lead to an inequality of the integral intensities of the thermal desorption peaks.

KEY WORDS: Lattice-gas model; lateral interactions; transfer-matrix technique; Monte Carlo simulation.

1. INTRODUCTION

In the case of chemisorption of atoms and simple molecules on close-packed faces of single crystals, the assumption of surface uniformity is often justified, i.e., it may be assumed that adsorbed particles are distributed among equivalent elementary cells. The nonideality of the adsorbed layer in this case is due to lateral interactions between adsorbed particles. In statistical physics, a system of interacting particles distributed among equivalent cells is called a lattice gas. It turns out that many phenomena occurring on the surfaces of solids (kinetics of adsorption and desorption, kinetics of chemical reactions, surface diffusion, phase diagrams, surface reconstruction induced by adsorption) can be described in the framework of the lattice-gas model.(1)

The general formulas for describing various phenomena in the lattice-gas model have, as a rule, a simple form. However, these formulas are not

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so much a solution as a formulation of the problem, since the main difficulty lies in calculating the various probabilities appearing in these formulas. Indeed, the lattice-gas model is well known to be exactly soluble only in exceptional cases.(2) The kinetics of real surface processes is usually studied at comparatively high temperatures. In this temperature range, the cluster method is suitable for calculating the rates of elementary processes. As a rule, the practical calculations take into account lateral interactions only between nearest neighbors and the mean-field, the quasichemical, or the Bethe–Peierls approximation are used.(3–7) More precise results may be derived using Monte Carlo simulations.(8–10) The Monte Carlo method is still not used widely for describing the kinetics of elementary surface processes, because this method is rather laborious. However, further simulations of the surface rate processes will aparently be linked with more extensive use of the Monte Carlo method.

In a previous paper,(10) we compared thermal desorption spectra calculated using analytical approximations (the quasichemical approximation for the nearest-neighbor interactions and the mean-field approximation for the next-nearest-neighbor interactions) and Monte Carlo simulations. The results were shown to be in good agreement when order–disorder transitions do not occur in the adsorbed overlayer during thermal desorption. The objective of the present paper is to study the effect of three-body lateral interactions on thermal desorption spectra. The paper is organized as follows. General equations for describing the kinetics of monomolecular desorption are presented in Section 2. Desorption from a one-dimensional chain is considered in Section 3; the one-dimensional problem is solved exactly using the transfer-matrix technique. Desorption from a two-dimensional adlayer is analyzed in Section 4 using Monte Carlo simulations.

2. GENERAL EQUATIONS

General equations for describing the kinetics of various surface rate processes are derived in the framework of the lattice-gas model in ref. 5. In particular, the kinetics of monomolecular desorption $A_s \rightarrow A_g$ is described as

$$d\theta/dt = -k_d\theta \tag{1}$$

$$k_d = \nu \sum_i P_{A,i} \exp\{-[E_d(0) + \Delta\varepsilon_i]/T)\} \tag{2}$$

where θ is coverage, ν is the preexponential factor, $E_d(0)$ is the activation energy for desorption at low coverages, $P_{A,i}$ is the probability that an adsorbed particle has the environment marked by index i, $\Delta\varepsilon_i = \varepsilon_i^* - \varepsilon_i$, ε_i is the lateral interaction of molecule A and its environment (repulsive interactions are assigned positive values), and ε_i^* is the lateral interaction of the activated complex A^* with the same environment; the Boltzmann constant is set to unity. Using Eqs. (1) and (2), we assume that the surface is uniform and that a given cell is either vacant or occupied by a single adsorbed particle; the precursor states are neglected.

The interaction ε_i^* is usually believed to be weak compared to other interactions. Neglecting this interaction and assuming the adsorbed overlayer to be in thermodynamic equilibrium, we can rewrite Eq. (2) as(6, 13)

$$k_d = \nu \exp\{-[E_d(0) + \mu]/T\}(1-\theta)/\theta \tag{3}$$

where μ is the chemical potential, known to be related to the energy of the particles. Using Eq. (3), we assume that the energy of a particle equals zero in the case when the sites neighboring to this particle are empty.

Equation (3) is convenient for analytical calculations. On the other hand, Monte Carlo simulations can be carried out using directly Eq. (2), i.e., using the following expression for the probability of a particle at site i to desorb in the interval $(t, t+\Delta t)$:

$$P(\Delta t) = \Delta t\, \nu \exp(-E_d^i/T) \tag{4}$$

with

$$\begin{aligned} E_d^i = E_d(0) - \varepsilon_1 \sum_{j\mathrm{NN}i} n_j \\ - \varepsilon_2 \sum_{j\mathrm{NNN}i} n_j - \varepsilon_t \sum_{j,k\mathrm{N}i} n_j n_k \end{aligned} \tag{5}$$

where n_j and n_k are the occupation numbers of sites j and k, ε_1 and ε_2 are the nearest-neighbor and next-nearest-neighbor lateral interactions, respectively, and ε_t is the three-body interaction defined in detail in the following sections.

3. DESORPTION FROM A ONE-DIMENSIONAL ADLAYER

The one-dimensional problem is of interest from the theoretical standpoint because this problem can be solved exactly using the transfer-matrix technique.(2) Besides, desorption in real systems can be considered as one-dimensional if lateral interactions are strongly anisotropic.

The one-dimensional Hamiltonian can be defined by

$$H=\sum_i (\varepsilon_1 n_i n_{i+1}+\varepsilon_2 n_i n_{i+2}+\varepsilon_t n_i n_{i+1} n_{i+2}) \tag{6}$$

where ε_1, ε_2, and ε_t are lateral interactions explained in Fig. 1.

The grand partition function for the Hamiltonian (6) can be calculated as follows. Let us consider the chain containing n sites and introduce the four-dimensional vector Z_n defined so that its components are the grand partition functions for the chain with fixed occupation numbers of two sites located on the right end of the chain. In particular, $Z_n(1)$, $Z_n(2)$, $Z_n(3)$, and $Z_n(4)$ are the partition functions for occupation numbers (1, 1), (1, 0), (0, 1), and (0, 0), respectively. Adding an additional site to the right end of the chain and examining all possible occupation numbers of sites $n-1$, n, and $n+1$, we have the recursive relationship

$$Z_{n+1}=MZ_n \tag{7}$$

where M is the 4×4 transfer matrix with the following nonzero elements:

$$\begin{aligned}
M_{11}&=\exp[(\mu-\varepsilon_1-\varepsilon_2-\varepsilon_t)/T]\\
M_{12}&=\exp[(\mu-\varepsilon_1)/T]\\
M_{23}&=\exp[(\mu-\varepsilon_2)/T]\\
M_{24}&=\exp(\mu/T)\\
M_{31}&=M_{32}=M_{43}=M_{44}=1
\end{aligned}$$

The matrix M can be represented as

$$M=SDS^{-1} \tag{8}$$

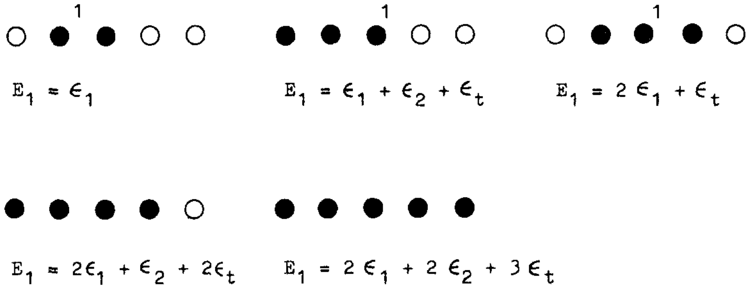


Fig. 1. Particles on the one-dimensional lattice. Occupied sites are indicated by solid circles, empty sites by empty circles. E_1 is the energy of particle 1.

where S is the nonsingular matrix and D is the diagonal matrix with elements that are equal to eigenvalues of the matrix M. Substituting Eq. (8) into Eq. (7), one can easily derive that at $n \to \infty$ the grand partition function Z is expressed as

$$\ln Z = n \ln \lambda \tag{9}$$

where λ is the largest eigenvalue of M. Thus, the calculation of the grand partition function is reduced to the calculation of the largest eigenvalue of

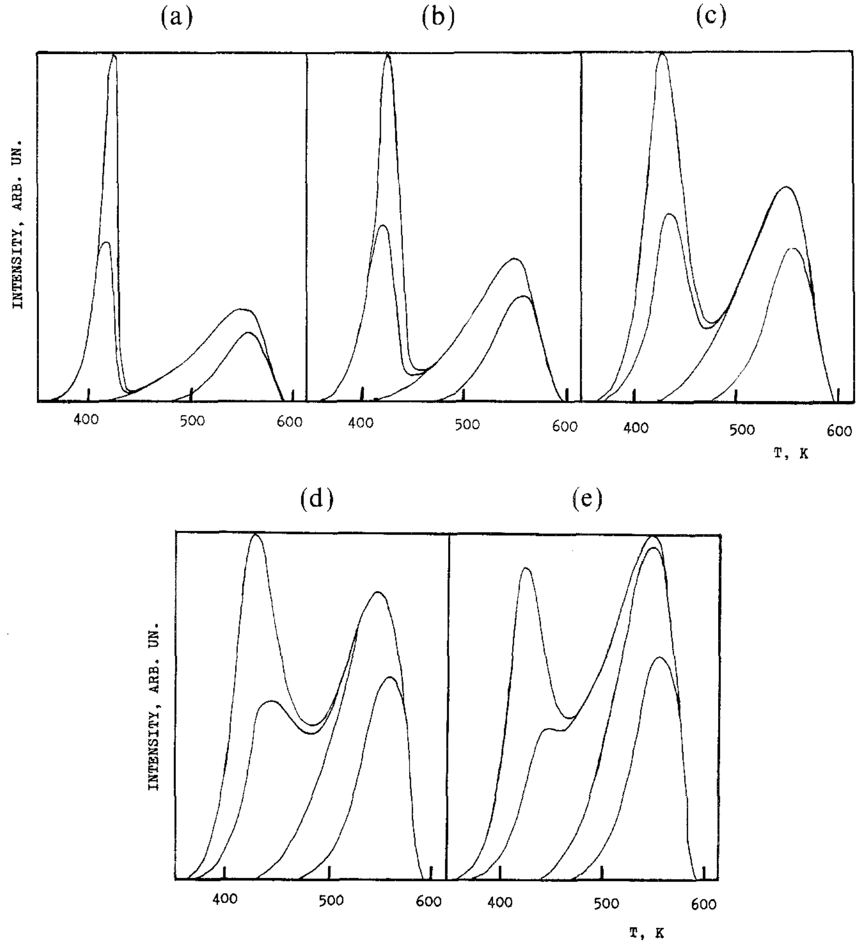


Fig. 2. Thermal desorption spectra for a one-dimensional chain calculated at $\nu = 10^{14}\,\mathrm{sec}^{-1}$, $E_d(0) = 35\,\mathrm{kcal/mole}$, and lateral interactions (in kcal/mole): (a) $\varepsilon_1 = 6$, $\varepsilon_t = -4/3$; (b) $\varepsilon_1 = 5$, $\varepsilon_t = -2/3$; (c) $\varepsilon_1 = 4$, $\varepsilon_t = 0$; (d) $\varepsilon_1 = 3$, $\varepsilon_t = 2/3$; (e) $\varepsilon_1 = 2$, $\varepsilon_t = 4/3$. The initial coverages are $\theta_0 = 0.25$, 0.50, 0.75, and 0.95. The heating rate is $\beta = 50$ K/sec.

the transfer matrix. The latter problem can be solved using standard numerical methods.

The grand canonical distribution yields the following relationship between coverage and the chemical potential:

$$\theta \equiv \frac{T}{n} \frac{\partial \ln Z}{\partial \mu} = T \frac{\partial \ln \lambda}{\partial \mu} \tag{10}$$

Using this relationship, we can calculate the coverage dependence of the chemical potential and then obtain the desorption rate constant [Eq. (3)].

It is also of interest to introduce the desorption activation energy. This value can be defined in various ways. The simplest one is

$$E_d(\theta) = -T \ln(k_d/\nu) \tag{11}$$

Taking into account lateral interactions introduced by Eq. (6), we obviously have

$$E_d(0) - E_d(1) = 2\varepsilon_1 + 2\varepsilon_2 + 3\varepsilon_t \tag{12}$$

Typically, the nearest-neighbor lateral interactions between adsorbed particles are repulsive, while the next-nearest-neighbor interactions are attractive.(1) We restrict our attention to this situation ($\varepsilon_1 > 0$); but to emphasize the effect of three-body forces on thermal desorption spectra, we set $\varepsilon_2 = 0$.

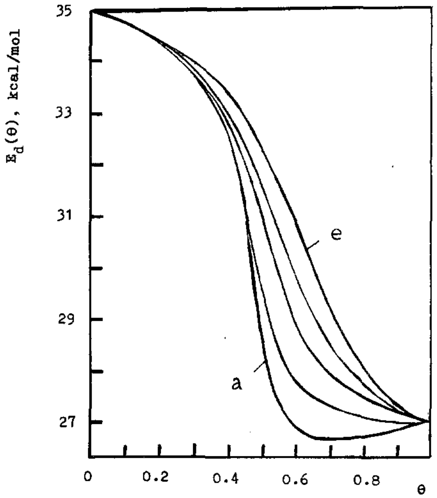


Fig. 3. Activation energy for desorption as a function of coverage. Lateral interactions are the same as in Fig. 2.

Typical thermal desorption spectra calculated using the transfer-matrix method are shown in Fig. 2. The lateral interactions ε_1 and ε_t were chosen so that $E_d(0) - E_d(1) = 8$ kcal/mole. The one-dimensional model is seen to predict two general qualitative features of spectra. First, the splitting of thermal desorption peaks due to repulsive interactions is rather weak (Fig. 2e) and increases as ε_1 becomes more repulsive and ε_t more attractive (Fig. 2a). Second, the integral intensities of the peaks are equal to one another if the three-body forces are absent (this is a consequence of the symmetry of the lattice-gas model with pair interactions relative to the coverage $\theta = 0.5$); the repulsive three-body interactions ($\varepsilon_t > 0$) lead to an increase in the integral intensity of the high-temperature peak (Fig. 2e). These features of spectra are in good agreement with the coverage dependence of the desorption activation energy (Fig. 3).

4. DESORPTION FROM A TWO-DIMENSIONAL ADLAYER

The two-dimensional Hamiltonian can be defined as

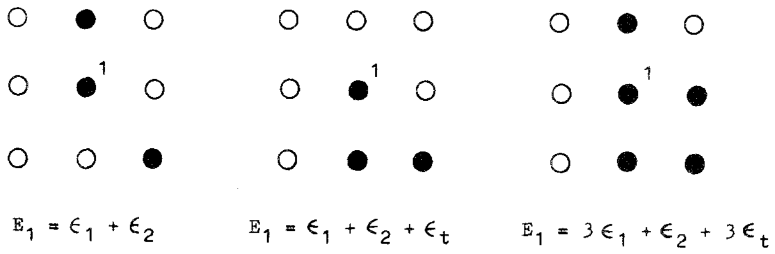
$$H = \sum_{i\mathrm{NN}j} \varepsilon_1 n_i n_j + \sum_{i\mathrm{NNN}j} \varepsilon_2 n_i n_j + \sum_{i \neq j \neq k} \varepsilon_t n_i n_j n_k \tag{13}$$

where ε_1, ε_2, and ε_t are lateral interactions explained in Fig. 4.

Thermal desorption spectra (Fig. 5) have been simulated for a square lattice of $N \times N$ sites ($N = 150$) with periodic boundary conditions following the Monte Carlo method described in ref. 9. The lateral interactions were chosen so that

$$E_d(0) - E_d(1) \equiv 4\varepsilon_1 + 4\varepsilon_2 + 12\varepsilon_t = 8 \text{ kcal/mole} \tag{14}$$

In each temperature interval the coverage dependence of the desorption activation energy has been also obtained (Fig. 5f) by averaging the activation energy over all molecules which actually desorbed in that interval.



$E_1 = \epsilon_1 + \epsilon_2$ $E_1 = \epsilon_1 + \epsilon_2 + \epsilon_t$ $E_1 = 3\epsilon_1 + \epsilon_2 + 3\epsilon_t$

Fig. 4. Particles on a square lattice. Occupied sites are indicated by solid circles, empty sites by empty circles. E_1 is the energy of particle 1.

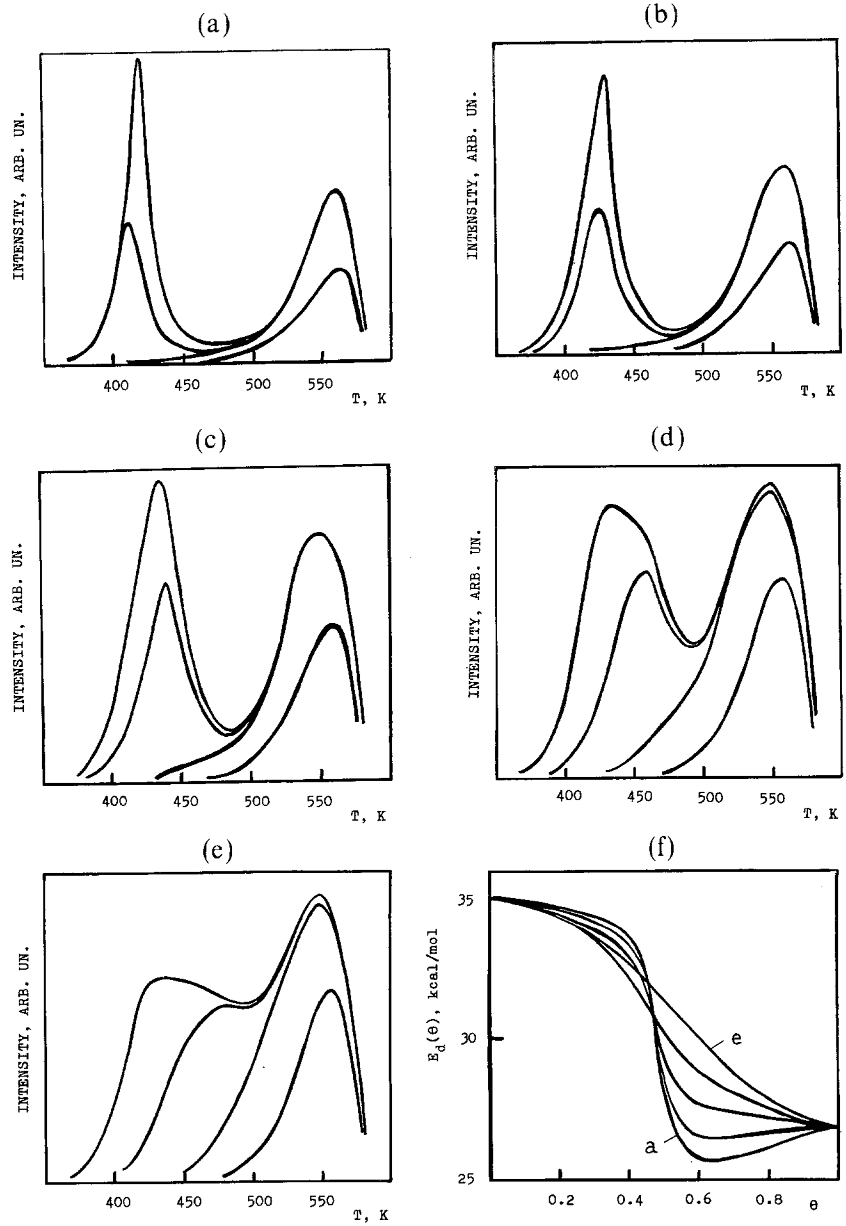


Fig. 5. Thermal desorption spectra for a square lattice calculated at $\nu = 10^{14}\ \mathrm{sec}^{-1}$, $E_d(0) = 35$ kcal/mole, $\beta = 50$ K/sec, and lateral interactions (in kcal/mole): (a) $\varepsilon_1 = 3$, $\varepsilon_t = -1/3$; (b) $\varepsilon_1 = 2.5$, $\varepsilon_t = -1/6$; (c) $\varepsilon_1 = 2$, $\varepsilon_t = 0$; (d) $\varepsilon_1 = 1.5$, $\varepsilon_t = 1/6$; (e) $\varepsilon_1 = 1$, $\varepsilon_t = 1/3$, and $\varepsilon_2 = 0$. The initial coverages are 0.25, 0.50, 0.75, and 0.95. (f) The coverage dependence of the activation energy for desorption.

To calculate thermal desorption spectra for a square lattice, we have also used the transfer-matrix technique. The application of this method to a two-dimensional case is as follows. The lattice is replaced by a strip of finite widths n and N along the X and Y directions. Periodic boundary conditions are used along the Y direction. Adding an additional row of sites to the right end of the strip and examining all possible occupation numbers of sites in rows n and $n+1$, we obtain a relationship similar to Eq. (7). Thus, at $n \to \infty$ the grand partition function is expressed through the largest eigenvalue of a transfer matrix [Eq. (9)], and the coverage is defined by [cf. Eq. (10)]

$$\theta = \frac{T}{N} \frac{\partial \ln \lambda}{\partial \mu}$$

Using this relationship, we can calculate the coverage dependence of the chemical potential. Experience shows that the transfer-matrix technique yields very good results already for small N, such as $N = 4$. In particular, thermal desorption spectra calculated on the basis of this approach are in good agreement with the Monte Carlo spectra (cf. Figs. 5 and 6). There exist, however, some minor differences. For example, the high-temperature peak in Fig. 6a is somewhat wider than the one in Fig. 5a.

Figure 7 shows the phase diagrams of the adsorbed overlayer, as given in ref. 11, and the trajectories followed by the system during thermal desorption. Constructing Fig. 7, we have used the following relationship between the maximum critical temperature (i.e., T_c at $\theta \simeq 0.5$), $T_c^{\max}$, and lateral interactions:

$$T_c^{\max} \simeq 0.567(\varepsilon_1 - \varepsilon_2 + \varepsilon_t) \tag{15}$$

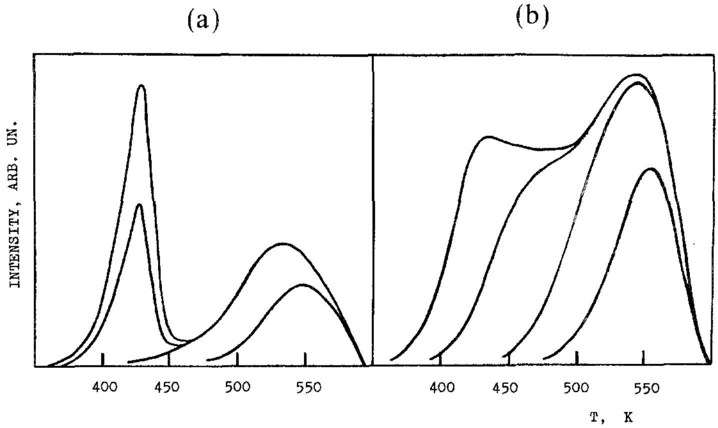


Fig. 6. Thermal desorption spectra for a square lattice calculated by the transfer-matrix technique. All parameters are the same as in Figs. 5a and 5e.

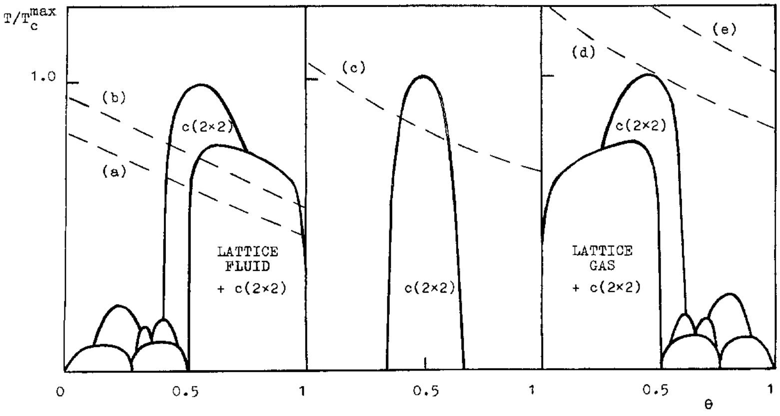


Fig. 7. Schematic phase diagrams of an overlayer on a square lattice.$^{(11)}$ Dashed lines represent the trajectories followed by the system during thermal desorption.

Equation (15) can be easily derived on the basis of arguments presented in ref. 11.

The qualitative features of thermal desorption spectra can be connected with a phase state of the adsorbed overlayer. In case (a), the system enters from the ordered $(1\times1)+c(2\times2)$ phase, passing then the ordered $c(2\times2)$ phase. In this region $(\theta>0.5)$, the desorption activation energy decreases with decreasing coverage (Fig. 6a) due to the attractive interactions ε_t, and desorption is self-accelerating. The presence of the ordered phase at $\theta\gtrsim 0.5$ and the absence of the order at $\theta<0.5$ result in two sharp and well-separated peaks. Case (b) is similar to case (a).

In case (c), the peak widths are much greater than in the former cases due to the fact that the ordered $c(2\times2)$ phase exists only in the narrow range of coverages near $\theta=0.5$, and various configurations contribute to desorption. In cases (d) and (e), desorption occurs at $T>T_c$ and the peaks are wide.

The qualitative features of thermal desorption spectra for a one-dimensional chain and for a two-dimensional square lattice are very similar (cf. Figs. 2 and 5). In particular, the repulsive three-body interactions are seen (Figs. 2e and 5e) to lead to an increase in the integral intensity of the high-temperature peak.

5. CONCLUSION

In our simulations we have used parameters typical for CO desorption from close-packed faces of Ni, Pd, Pt, Rh, and Ru single crystals. The results presented in Figs. 2 and 5 (especially the results for the three-body repulsive interactions) reproduce qualitatively the various features of the real thermal desorption spectra [cf. Fig. 37(i–k) in ref. 12]. However, the experimental data as a whole are somewhat more complex than the theoretical results. This is explained as follows. First, the real lateral interactions and locations of adsorbed particles are more diverse than those considered in this paper. Second, the adsorbate-induced changes in the surface should be apparently incorporated into the theory to interpret experimental thermal desorption spectra.(13)

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