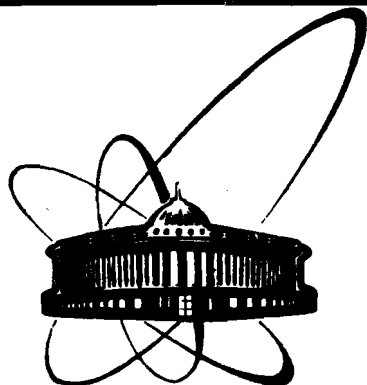


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NONEQUILIBRIUM THERMAL DESORPTION SPECTRA  
OF DISSOCIATIVELY ADSORBED MOLECULES:  
CO/W(100)

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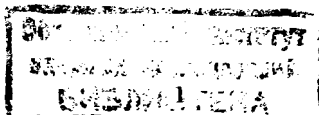
## 1. Introduction

The subject of this paper is a theoretical study of thermal desorption spectra of dissociatively adsorbed diatomic molecules consisting of two different atoms. If the binding energy of the molecule is high enough the desorption energy of the molecule may be comparable with diffusion activation energy or, at least, one of the adsorbed atoms of the dissociated molecule. Then, after adsorption at low temperature the thermal equilibrium in the system of interacting molecules is not established. Further, we show that the nonequilibrium properties of the adsorbate may affect substantially the resulting thermal desorption spectra. For such systems, we expect that the desorption would be sensitive to the history of the system and the thermal desorption spectra would be changed after thermal treatment and following readsorption of desorbed molecules.

CO gas adsorbed on a tungsten surface may serve as an example of a system with above described properties. CO molecules on clean tungsten surfaces are adsorbed mostly dissociatively [1,2,3] and the binding energy of carbon is very high [4,14]. The dissociative adsorption is found on a number of transition metal surfaces [5], as well.

Anders and Hansen [16] have observed extensive isotope exchange in the adsorption peaks above 800 K ( $\beta$ -peaks) what has confirmed the Gouy-King [1] model, according to which  $\beta$ -states arise from dissociatively adsorbed CO. Anderson and Estrup have found that C atoms on W is immobile up to 1000 K. This is also the conclusion of Anders and Hansen interpreting the flash desorption spectra of CO/W with preadsorbed or postadsorbed  $O_2$  isotopes. They find, that the chemisorbed CO is immobile prior to desorption.

Thermal desorption spectra of CO on W(100) [6] and on the polycrystalline tungsten display interesting features. Wang and Gomer [6] have obtained a three-peak spectrum (not taking into account low temperature  $\alpha$ -peaks) where the the first  $\beta_1$  peak disappears after heating to 950 K (to the minimum after the  $\beta_1$  peak) and subsequent readsorption.



The molecules originally adsorbed in  $\beta_1$  and  $\beta_2$  peaks after the thermal treatment are desorbed in the  $\beta_2$  peak only. The third peak  $\beta_3$  is not influenced by the partial desorption and readsorption.

In the following, we try to explain qualitatively the above described behaviour and investigate the properties of nonequilibrium systems by a simple model of dissociatively adsorbed molecules with low surface mobility of one or both species. It is assumed that the desorption takes place only if two nearest neighbouring sites are occupied by different species and the diffusion is represented by nearest neighbour hops. The lateral interactions play an important role in our considerations. They are responsible for the formation of peaks in thermal desorption spectra. To get well separated peaks, the lateral interactions should exceed 5% of the energy of desorption.

The thermal desorption spectra of adsorbed species with lateral interaction were calculated from lattice gas models by many authors, e.g. [8]. Most of these approaches treated equilibrated adsorbates. Recently, there appeared works studying the opposite extreme - desorption from an immobile adlayer. In some cases of one-dimensional lattice gas models they solved the problem exactly [9,10,11,12]. We study here a more general case of the intermediate mobility ranging from immobile adspecies to the adsorbate at thermal equilibrium. The paper is an extension of the previous analysis of desorption of nondissociatively adsorbed molecules [13]. But here, instead of the Kirkwood-type decoupling of a hierarchy of master equations, the requirement of maximum information entropy is used. This procedure ensures unambiguity of the decoupling procedure and homogeneity of the resulting cluster probabilities.

## 2. Model and method

The processes of desorption and diffusion of dissociated diatomic gas will be described by a master equation for cluster configuration probabilities of both types of atoms.

We introduce occupation numbers  $n_i$  which describe the presence of an atom at the site  $i$  of a square lattice. The occupation number  $n_i=0,1,2$  if the site  $i$  is vacant, occupied by an atom of the first kind, occupied by an atom of the second kind, respectively.

We assume homogeneous adsorbate in which the short range order is

characterized by the probabilities  $P(n_1, \dots, n_8)$  for all configurations of the eight site cluster shown in Fig.1. To make further expressions more transparent, we shall write the argument of the function  $P$  in a semigraphical way

$$P(n_1, \dots, n_8) \equiv P \left( \begin{array}{cccc} & n_2 & n_5 & \\ n_1 & n_3 & n_6 & n_8 \\ & n_4 & n_7 & \end{array} \right).$$

To formulate master equation for desorption and diffusion processes, we assume that they depend on the sum of the diffusion or desorption activation energies of noninteracting particles and the interatomic interaction energies by the Arrhenius law.

The time derivatives of the probabilities of two-site cluster configurations are given by the rates of desorption and diffusion processes involving one or both atoms of the considered cluster.

Let  $i$  and  $j$  are nearest neighbour sites. Then the total change of their configuration probability consists of contributions from desorption of both atoms, from desorption of one of the atoms with a nearest neighbour different from  $i$  or  $j$ , and from diffusion of the one of the atoms

$$\begin{aligned} - \frac{dP(n_i, n_j)}{dt} = & S_2(n_i, n_j) + S_1(n_i; n_j) + S_1(n_j; n_i) + \\ & + F_1(n_i; n_j) + F_1(n_j; n_i) \end{aligned} \quad (1)$$

The rate of desorption of  $i$  and  $j$  atoms, creating a free gas molecule is given as

$$S_2(n_i, n_j) = L_{des} (\delta_{n_i,1} \delta_{n_j,2} + \delta_{n_i,2} \delta_{n_j,1}) \quad (2)$$

$$\sum_{n_1, \dots, n_6} \exp \left[ - \frac{1}{kT} \left( \sum_{i=1}^3 K(n_i, n_i) + \sum_{j=4}^6 K(n_j, n_1) \right) \right] P \left( \begin{array}{cccc} & n_2 & n_4 & \\ n_1 & n_1 & n_j & n_6 \\ & n_3 & n_5 & \end{array} \right),$$

$$\text{where } L_{des} = \nu_{des} \exp \left[ - \frac{E_{des}}{kT} \right].$$

If the state of the site  $j$  is  $n_j$ , the desorption rate of the atom at the site  $i$  with an atom at a neighbouring site (further denoted as 1) may be written as

$$S_1(n_1; n_j) = L_{des} \sum_{n_1 \dots n_6} (\delta_{n_1, 1} \delta_{n_1, 2} + \delta_{n_1, 2} \delta_{n_1, 1}) \cdot \exp\left(-\frac{1}{kT} \left[ \sum_{i=2}^4 K(n_1, n_i) + \sum_{i=5}^6 K(n_1, n_i) + K(n_1, n_j) \right]\right) \cdot \left[ P \begin{pmatrix} n_3 & n_5 \\ n_2 & n_1 & n_1 & n_j \\ n_4 & n_6 \end{pmatrix} + 2P \begin{pmatrix} n_3 & n_j \\ n_2 & n_1 & n_1 & n_6 \\ n_4 & n_5 \end{pmatrix} \right]. \quad (3)$$

Diffusion, according to our assumption, consists of nearest-neighbour hops of  $i$  and  $j$  atoms to vacant sites and of an opposite process

$$F_1(n_1; n_j) = (L_{1,dif} \delta_{n_1, 1} + L_{2,dif} \delta_{n_1, 2}) \cdot \sum_{n_1 \dots n_5} \left[ \exp\left(-\frac{1}{kT} \left[ \sum_{i=1}^2 K(n_1, n_i) + K(n_1, n_j) \right]\right) \cdot \left( P \begin{pmatrix} n_1 & n_3 \\ 0 & n_1 & n_j & n_5 \\ n_2 & n_4 \end{pmatrix} + 2P \begin{pmatrix} 0 & n_3 \\ n_1 & n_1 & n_j & n_5 \\ n_2 & n_4 \end{pmatrix} \right) + \exp\left(-\frac{1}{kT} \left[ \sum_{i=1}^3 K(n_1, n_i) \right]\right) \cdot \left( P \begin{pmatrix} n_2 & n_4 \\ n_1 & n_1 & 0 & n_j \\ n_3 & n_5 \end{pmatrix} + 2P \begin{pmatrix} n_2 & n_j \\ n_1 & n_1 & 0 & n_5 \\ n_3 & n_5 \end{pmatrix} \right) \right]. \quad (4)$$

$$L_{1,2,dif} = \nu_{1,2,dif} \exp\left(-\frac{E_{1,2,dif}}{kT}\right)$$

$L_{des}, L_{1,2,dif}$  are the desorption and diffusion rates of atoms with vacant neighbouring sites,  $K(n_1, n_k)$  are the nearest-neighbour interaction energies,  $E_{des}$  is the activation energy of desorption of the molecule,  $E_{1,dif}, E_{2,dif}$  are the activation energies of the first and the second kind of atom.

The number of terms in (1-4) was reduced by symmetry considerations.

Similarly, we can write master equations for time derivatives of configuration probabilities of arbitrary large clusters.

To solve the system of differential equations (1), we must express the probabilities of large clusters appearing at their right-hand sides in terms of two-site cluster probabilities. This may be done by requiring that the entropy of information contained in the eight-site cluster probabilities  $P(n_1, \dots, n_8)$  has its maximum [15] if the condition that

two-site cluster probabilities are given by the solution of (1) at arbitrary moment of time is satisfied, i.e. we have to find the maximum of the expression

$$\sum_{\langle n \rangle_k} P(n_1, \dots, n_8) \ln P(n_1, \dots, n_8) + \sum_{\langle i, j \rangle} \mu(i, j) \left( \sum_{\substack{\langle n \rangle_k \\ k \neq i, j}} P(n_1, \dots, n_8) - P(n_i, n_j) \right) \quad (5)$$

with respect to  $P(n_1, \dots, n_8)$ .

$\mu(i, j)$  are the Lagrange multipliers and  $\langle i, j \rangle$  are all the nearest neighbours in the cluster shown in Fig.1.

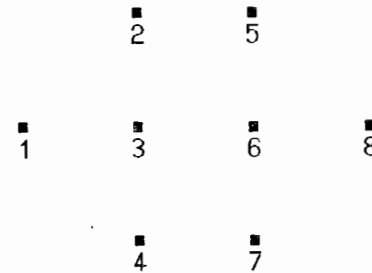


Fig.1. Basic cluster in the square lattice.

Differentiating (5) with respect to  $P(n_1, \dots, n_8)$  and putting the derivatives equal to zero, we find that the probabilities  $P$  may be expressed as a product of two-site cluster functions

$$P(n_1, \dots, n_8) = \prod_{\langle i, j \rangle} f_{i, j}(n_i, n_j).$$

From symmetry considerations, the condition

$$\sum_{\substack{\langle n \rangle_k \\ k \neq i, j}} P(n_1, \dots, n_8) = P(n_i, n_j),$$

and the requirement that the subproducts  $\prod_{\langle i, j \rangle} f_{i, j}(n_i, n_j)$  ( $i, j \in \{2, 3, 4, 5, 6, 7\}$  and  $i, j \in \{2, 3, 5, 6\}$ ) have the meaning of probabilities, as well, we get

$$P(n_1, \dots, n_8) = \frac{P(n_1, n_3)}{P(n_3)} R(n_2, n_5) R(n_2, n_3) R(n_5, n_6) \frac{R(n_3, n_6)}{P(n_3, n_6)} \cdot R(n_4, n_7) R(n_3, n_4) R(n_6, n_7) \frac{P(n_6, n_8)}{P(n_6)}, \quad (7)$$

where  $R(n_1, n_j)$  are to be determined from

$$P(n_2, n_5) = \sum_{n_3, n_6} R(n_2, n_5)R(n_5, n_6)R(n_6, n_3)R(n_3, n_2) \quad (8)$$

$$\text{and } P(n_1) = \sum_{n_j} P(n_1, n_j).$$

Substituting expressions (7-8) for the probabilities  $P$  in (1-4), we obtain a closed system of differential equations for the functions  $R(n_1, n_j)$  but their linearity is lost. The simple left-hand sides of eqs. (1) are

replaced by a linear combination of  $\frac{dR(n_k, n_1)}{dt}$  with coefficients that are non-linear functions of  $R$ 's.

Because the measured thermal desorption spectra are, as a rule, presented in the form of number of desorbed molecules as a function of temperature, we substitute  $t=t(T)$  and introduce a new variable in eqs. (1) - the temperature  $T$ . In most experiments the dependence of the temperature on time is linear  $T(t)=\alpha t+T_0$ . As a result of the substitution, the right-hand sides of the differential equations (1) are now explicit functions of the variable  $T$  and the preexponential factors  $\nu$  are multiplied by  $\frac{dt}{dT} = \alpha^{-1}$ . The heating rate  $\alpha$  never appears in the master equations separately;  $\alpha^{-1}$  is always multiplied by one of the preexponential factors  $\nu$ . Let us further denote these products as  $\mu_{des} = \alpha^{-1}\nu_{des}$ , etc.

The system of the first-order differential equations for  $R(0,0), R(0,1), R(0,2), R(1,1), R(1,2), R(2,2)$  has been solved numerically.

For very high diffusion rate of one of the components, the numerical treatment of the differential equation was too slow. To speed up the calculation, for the diffusion rate of the mobile component  $10^3$  higher than the desorption rate, this component was assumed to be in thermal equilibrium and its properties have been calculated separately for fixed configuration probabilities of the component with low mobility and zero desorption.

### 3. Results

The resulting thermal desorption spectra do not depend only on the parameters appearing in eqs. (1-4) but on the initial state of the adsorbate, as well. As in experiment the gas is adsorbed at low temperatures, the system of adsorbed molecules is not in thermal equilibrium due to low mobility of the species. The dissociation of

molecules may be not complete at low temperatures, as well [6], but further we shall not consider this possibility and we ignore the physisorbed as well as the nondissociated molecules.

The two-site configuration probabilities describing the short-range order of the adsorbate before the desorption starts have been obtained by solving a system of differential equations similar to (1), where, instead of the terms describing desorption, adsorption terms with dissociation to nearest-neighbour sites have been included. This process would not be able to fill all sites of the surface lattice. That is why a very small surface diffusion was also allowed. The following initial nearest-neighbour configuration probabilities have been obtained:  $P(1,1) = P(2,2) = 0.231$ ,  $P(1,2) = 0.258$ ,  $P(0,1) = P(0,2) = 0.0055$ ,  $P(0,0) = 0.0000$ , i.e. the initial coverage is 99%. The molecules are assumed to be adsorbed at random and the values of nearest-neighbour configuration probabilities are not influenced by lateral interactions, as the components of the created pair of atoms are practically immobile at low temperature.

The thermal desorption spectra of dissociated molecules, which are not in thermal equilibrium display one, two, or three peaks depending on the values of the interaction energies between atoms. For sufficiently small interactions the thermal desorption spectra have a simple form with one maximum and two exponential tails. The thermal desorption spectra of interacting adsorbate in thermal equilibrium have two peaks as a maximum. We shall not study these cases here as they were discussed elsewhere [8].

We have performed calculations for three types of parameter sets characterizing the behaviour of the adsorbate at low temperatures: i) the mobility of both kind of atoms is low, ii) the mobility of the first kind is low and the second kind is in thermal equilibrium, iii) the same as ii) but the atoms of the first kind are totally immobile at all temperatures.

When the atoms at the beginning of desorption are in the nonequilibrium state described earlier their interaction energy is higher than in an equilibrium state. Thus, the desorption starts at lower temperatures than in the equilibrium case and the first desorption peak is shifted to the left. If the mobility increases inside the first peak the species are rapidly redistributed in the adsorbed layer and the desorption rapidly drops due to the decrease of the interaction energy. If the number of desorbed molecules in the first peak is less than one half of the original coverage a remnant of the first equilibrium peak (now the second one) is present in the spectrum. The third peak originates from the desorption of noninteracting atoms with the nearest-neighbour probabilities  $P(1,1)$ ,  $P(1,2)$ ,  $P(2,2)$  close to zero.

Two examples of the thermal desorption spectra of dissociated molecules with large diffusion activation energies of their components and thus their low mobilities are shown in Figs.2 and 3. The preexponential factors  $\mu_{des}$  and  $\mu_{dif}$  are assumed to be equal. The interparticle interaction is larger between different species in Fig.2 and larger between identical atoms in

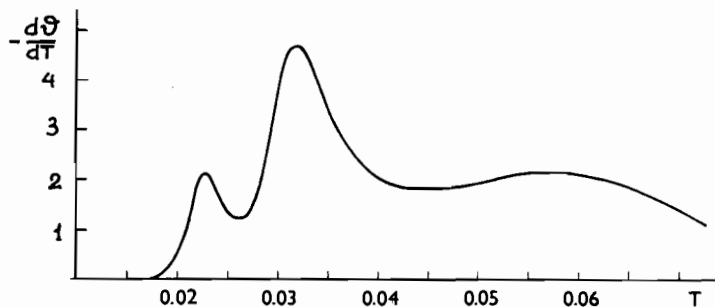


Fig.2. Thermal desorption spectrum of dissociated diatomic gas with low mobility of both atoms when  $E_{des}=1.1$ ,  $E_{1,dif}=E_{2,dif}=0.7$ ,  $\mu_{des}=\mu_{1,dif}=\mu_{2,dif}=10^{10}$ ,  $K(1,1)=K(2,2)=0.08$ ,  $K(1,2)=0.12$ . Temperature T is in energy units.

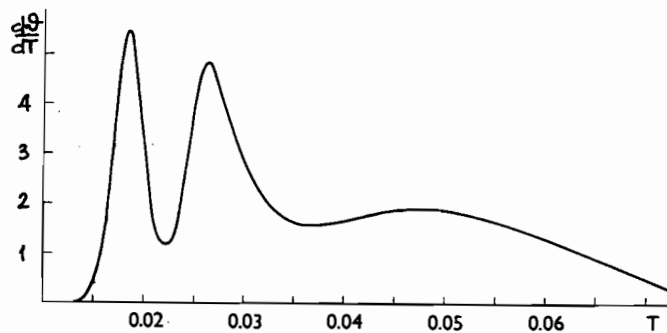


Fig.3. Thermal desorption spectrum of dissociated diatomic gas with low mobility of both atoms when  $E_{des}=1.0$ ,  $E_{1,dif}=E_{2,dif}=0.65$ ,  $\mu_{des}=\mu_{1,dif}=\mu_{2,dif}=10^{10}$ ,  $K(1,1)=K(2,2)=0.12$ ,  $K(1,2)=0.08$ .

Fig.3. The shape of the curves in both cases is the same. The ratio of the areas under first two peaks is a function of the temperature of the mobility threshold. The smaller is the diffusion activation energy the larger is the area under the second peak (at the expense of the first peak). For lower initial coverages, the low temperature peak is gradually disappearing.

In Figs.4 and 5 the mobility of one of the the atoms is as low as in two previous cases but the other atom has a very high mobility and the system of these atoms forms an equilibrated subsystem.

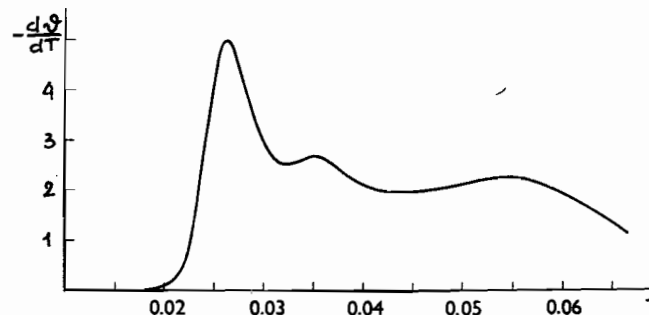


Fig.4. Thermal desorption spectrum of dissociated diatomic gas with low mobility of the atoms of the second kind when  $E_{des}=1.1$ ,  $E_{2,dif}=0.85$ ,  $\mu_{des}=\mu_{2,dif}=10^{10}$ ,  $K(1,1)=K(1,2)=0.08$ ,  $K(2,2)=0.14$ . Atoms of the first kind are at thermal equilibrium at all temperatures.

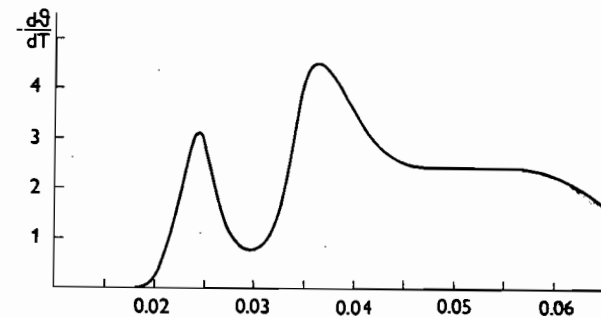


Fig.5. Thermal desorption spectrum of dissociated diatomic gas with low mobility of the atoms of the second kind when  $E_{des}=1.1$ ,  $E_{2,dif}=0.80$ ,  $\mu_{des}=\mu_{2,dif}=10^{10}$ ,  $K(1,1)=0.10$ ,  $K(1,2)=0.06$ ,  $K(2,2)=0.14$ . Atoms of the first kind are at thermal equilibrium at all temperatures.

In the minimum after the first peak, the thermal equilibrium is restored in all above discussed examples. If the desorption process is terminated at this moment and the missing molecules are readsorbed the new initial configuration is close to an equilibrium one and in the subsequent desorption the first peak in the spectrum is absent.

Fig.6 shows that the three peak spectrum is present even in the case when one of the species is totally immobile.

The temperature in all diagrams is given in energy units and after appropriate rescaling of the energy, they describe any system with given ratios of activation energies.

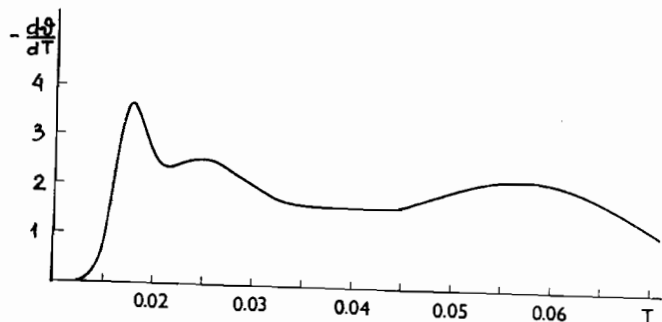


Fig.6. Thermal desorption spectrum of dissociated diatomic gas with immobile atoms of the second kind when  $E_{des}=1.1$ ,  $\mu_{des} = 10^{10}$ ,  $K(1,1) = K(2,2) = 0.14$ ,  $K(1,2) = 0.08$ . Atoms of the first kind are in thermal equilibrium at all temperatures.

Fig.7 shows the result of calculation for a system which displays qualitatively the same behaviour at desorption as the dissociatively adsorbed CO molecules on W(100) observed by Wang and Gomer [6]. As we use a simplified model for the system of dissociated CO molecules including only nearest-neighbour interactions between the species, we do not attempt to fit the observed spectrum. We want only to stress similar shapes of both theoretical and experimental spectra and identical behaviour of the systems after desorption and following readsorption of CO molecules. It has been shown in the above examples that the shapes of the spectra are not very sensitive to the actual values of interaction constants and constants determining the diffusion properties. Hence, for the sake of simplicity, we take the same hopping rates for both atoms and a greater repulsion between CO pairs of atoms than between CC and OO pairs.

The experimental desorption spectrum of CO on W(100) [6] is displayed in the inset of Fig.7. Since the area below  $\beta_1$  and  $\beta_2$  peaks is slightly smaller than that below the  $\beta_3$  peak, we have simulated the initial state of the system by random adsorbing pairs of CO atoms to nearest-neighbouring sites, without any further diffusion. This procedure leaves some sites vacant with the probabilities  $P(0,1)$  and  $P(0,2)$  equal to 0.0605 and  $P(0,0)$  equal to zero for the saturated monolayer. This state corresponds to the experimentally prepared saturated layer at 100 K. The remaining probabilities are the following:  $P(1,1) = P(2,2) = 0.1762$ ,  $P(1,2) = 0.2028$ . The coverage is 88%. The activation energy of desorption  $E_{des} = 1.1$  sets the energy scale. Then, the interaction energies are  $K(1,1) = K(2,2) = 0.062$ ,  $K(1,2) = 0.09$ . The preexponential factor  $\mu_{des}$  is equal to

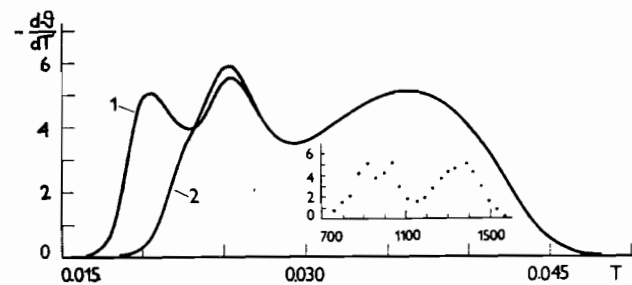


Fig.7. Thermal desorption spectra of dissociated diatomic gas with low mobility of both atoms when  $E_{des}=1.1$ ,  $E_{1,dif} = E_{2,dif} = 0.635$ ,  $\mu_{des} = 5 \times 10^{15}$ ,  $\mu_{1,dif} = \mu_{2,dif} = 10^{11}$ ,  $K(1,1) = K(2,2) = 0.062$ ,  $K(1,2) = 0.09$ . Temperature  $T$  is in energy units. Line 1: Spectrum obtained after low temperature adsorption to clean surface. Initial coverage is 88%. The peaks from left to right are denoted as  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ . Line 2: Spectrum obtained after partial desorption and subsequent readsorption at low temperature. Initial coverage is 79%.

Inset: Step desorption spectrum of a layer prepared by dosing a clean W(100) surface to saturation at surface temperature 100 K [6]. Temperature is in degrees of Kelvin.

If  $T = 0.02$  from the plot is identified with  $T = 800$  K from the inset,  $E_{des} \approx 90$  kcal/mol.

$5 \times 10^{15}$ . Practically the same spectra are obtained for a large number of pairs of constants  $E_{dif}$  and  $\mu_{dif}$ . To obtain the three-peak spectrum shown in Fig. 7 for  $\mu_{dif} = 10^{11}$ , we get  $E_{dif} = 0.635$ .

Details of the spectra are sensitive to variations of the input constants.  $\mu_{des}$  controls the width of the spectrum and the relative height of the high-temperature  $\beta_3$  peak, the interaction constants  $K$  the depth of the minimum and the distance between  $\beta_2$  and  $\beta_3$  peaks, the difference  $K(1,2) - K(1,1)$  the depth of the minimum and the distance between  $\beta_1$  and  $\beta_2$  peaks, and the diffusion rate the ratio of  $\beta_1$  and  $\beta_2$  peaks. As the preexponential factors  $\mu_{des}$  and  $\mu_{dif}$  are inversely proportional to the heating rate  $\alpha$ , the decrease of  $\alpha$  makes  $\mu$ 's greater and we get the spectrum narrower, with higher  $\beta_3$  peak and with lower  $\beta_1$  peak because of the increase of the diffusion terms in the master equation.

A three-peak spectrum is obtained only for a relatively narrow range of hopping rates. For  $E_{dif} > 0.66$  and/or  $\mu_{dif} > 10^{12}$  we get only the  $\beta_1$  and  $\beta_3$  peak and a practically negligible  $\beta_2$  peak and for  $E_{dif} < 0.61$  and/or  $\mu_{dif} < 10^{10}$  no  $\beta_1$  peak.

After finishing the desorption process at the temperature  $T = 0.024$  (what corresponds to the first minimum), the thermal equilibrium is practically restored. After subsequent readsorption at low temperature, the saturation coverage is only 79% (i.e. 90% of the original coverage). The starting values of the correlators are:  $P(1,1) = P(2,2) = 0.2008$ ,  $P(1,2) = 0.0793$ ,  $P(0,1) = P(0,2) = 0.1100$ ,  $P(0,0) = 0.0000$ . Only a small remnant of the  $\beta_1$  peak is found in the spectrum and the area and height of the  $\beta_2$  peak increases (line no. 2 in Fig. 7). Both the decrease of the initial coverage and the irreversible behaviour of the system are confirmed by the experiment (Fig. 6 in [6]).

The unlabeled low temperature shoulder in the inset of Fig. 7 cannot be explained from our model. (It is also not commented by the authors of [6].)

A slight modification of the expression for the desorption probability is necessary to treat thermal desorption of molecules consisting of two identical atoms. However, we do not expect spectra with three peaks in this case as there does not exist any nonequilibrium monoatomic layer at full coverage. It is possible for systems with a not fully-occupied initial state. On the other hand, the  $\beta_1$  peak is suppressed at lower initial coverages.

Anders and Estrup [16] have found only two  $\beta$  peaks ( $\beta_2$  and  $\beta_3$ ) in the flash desorption spectrum of CO/W(100), instead of three peaks ( $\beta_1, \beta_2, \beta_3$ ) of Wang and Gomer, with  $\beta_3$  peak very low. From the point of view of our

calculations, this may be explained by the larger desorption rate (i.e. smaller  $\mu$ 's) in the flash desorption experiment which turns the  $\beta_3$  peak to a shoulder (see figs. 2-6). On the other hand, assuming the same initial state of the adsorbed layer as in our calculations, we would expect the first peak to occur at lower temperature (to be a  $\beta_1$ -like).

For the conclusion, we state that we have succeeded to describe qualitatively the properties of thermal desorption spectra of CO/W(100) as found in [6]. The actual values of the interaction parameters are very probably different from the ones we used in the calculation, but we believe without effect to the shape of the resulting spectrum.

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