

Spatial Distributions of Desorption Flow as an Indicator for a Precursor State in Several Systems

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Received May 27, 1998

Abstract—Spatial distributions of the desorption flow (SDDF) of CH₄, N₂ and azomethane (CH₃N=NCH₃) on molybdenum, O₂ and N₂ on iridium, and N₂ on iron were measured by TPD/TPR with angular resolution and described by the Comsa equation. The activation energy of chemisorption and the effect of the precursor state on the total desorption rate were estimated from the parameters of the Comsa equation. The pathway via a precursor state is the main one (60–90%) for oxygen on iridium and for nitrogen and azomethane on molybdenum. For other systems, this pathway cannot be completely excluded either. According to our upper estimates, its contribution can be essential (~40%).

INTRODUCTION

The classic Langmuir model was an important step toward the understanding of adsorption phenomena, but it is often inapplicable to the quantitative description of real systems. For example, according to Langmuir, the adsorption rate is proportional to the portion of the free surface of an adsorbent, although in many cases, the sticking probability does not in fact depend on the surface coverage by an adsorbate up to high coverages. Based on this fact, P.J. Kisliuk conjectured that, in addition to the main, strongly bound adsorbate state, there is a precursor state and proposed the corresponding mathematical model [1].

This model is applicable to many systems for the dissociative chemisorption of gases [2]. The interaction potential of the molecule AB and the surface site Z is a combination of two Lennard-Jones curves [3] (Fig. 1).

As can be seen from Fig. 1, the resulting curve has two minima corresponding to molecular (probably physical) adsorption and dissociative chemisorption. Usually, the first minimum is assigned to the precursor state. A barrier separates these two minima, and if the point X is higher than the ground state of a gaseous molecule, then the chemisorption is activated.

Some indirect evidence for desorption via a precursor state can be obtained by measuring the spatial distribution of a desorption flow (SDDF) of chemisorbed gases. If molecules are desorbed directly from a chemisorbed state, they acquire additional translational energy along the normal to the surface when overcoming the activation barrier (point X in Fig. 1). This results in a sharply directed SDDF. Van Willigen observed for

the first time these SDDFs and described them by the equation [4]

$$I/I_0 = [(\varepsilon + \cos^2 \varphi) \exp(-\varepsilon \tan^2 \varphi)] / [(\varepsilon + 1) \cos \varphi], \quad (1)$$

derived from the principle of microscopic reversibility. In this equation, I_0 and I are the intensities of the desorption flow directed along the normal and at a certain angle φ to the surface, respectively; $\varepsilon = E_{\text{ads}}/RT$, E_{ads} is the activation energy of adsorption.

Equation (1) at $\varepsilon = 0$ transforms into the well-known Knudsen equation

$$I/I_0 = \cos \varphi, \quad (2)$$

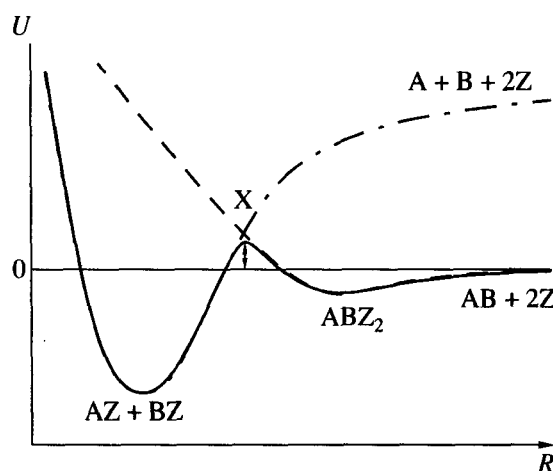


Fig. 1. Potential energy (U) of a diatomic molecule AB as a function of distance (R) between the molecule and surface (solid line) obtained from two Lennard-Jones curves (dashed line). A and B are free atoms, AZ and BZ are adsorbed atoms, Z is active site on the surface, ABZ₂ is a molecular form of adsorption on a double site, and X is a barrier to dissociative chemisorption.

[†] Deceased.

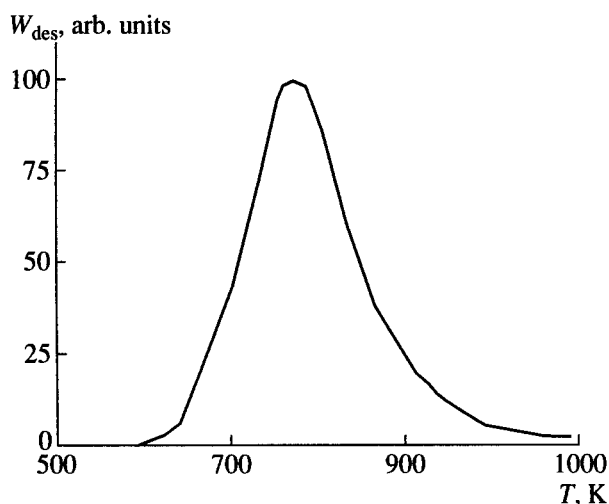


Fig. 2. TPR spectrum of nitrogen obtained for the decomposition of the adsorbed monolayer of NO on iron. The heating rate is 60 K/s.

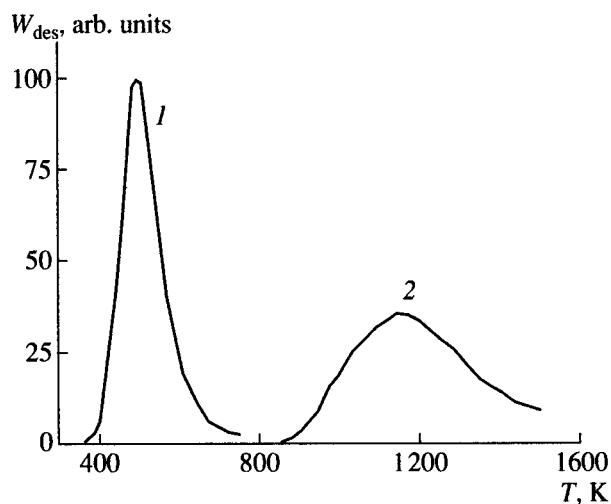


Fig. 3. TPR spectrum of (1) nitrogen and (2) oxygen obtained for the decomposition of the adsorbed monolayer of NO on iridium. The heating rate is 50 K/s.

which describes nonactivated adsorption.

Comsa and David [5] found that, in many cases, the following equation is more accurate for SDDF

$$I/I_0 = (1 - \alpha) \times \{[(\epsilon + \cos^2 \varphi) \exp(-\epsilon \tan^2 \varphi)] / [(\epsilon + 1) \cos \varphi]\} + \alpha \cos \varphi. \quad (3)$$

This equation is obtained by summing equations (1) and (2) with coefficients $(1 - \alpha)$ and α , respectively. These coefficients characterize the contributions of the van Willigen and Knudsen distributions to the overall SDDF. By contrast to equation (1), Comsa and David's equation (3) takes into account molecules desorbed via a precursor state, which leave the surface with thermal rates and, correspondingly, with the Knudsen SDDF.

In this work, we studied several systems characterized by activated chemisorption and estimated a portion of molecules desorbed via a precursor state according to the Comsa model.

EXPERIMENTAL

Experiments were carried out in an ultrahigh vacuum setup with a maximal residual pressure of gases of 5×10^{-10} torr. The setup was equipped by a mass spectrometer. The detailed description of the technique of temperature programmed desorption/reaction (TPD/TPR) with spatial resolution can be found in our previous papers [6, 7].

SDDFs were measured in the following systems: N_2 /Ir, N_2 /Fe, N_2 /Mo, O_2 /Ir, CH_4 /Mo, and $CH_3N=NCH_3$ /Mo. The desorption of N_2 /Ir, N_2 /Fe, and O_2 /Ir was studied in temperature-programmed NO dissociation. Recombinative desorption in the CH_4 /Mo system was studied in an adlayer of methyl radicals. Methane desorbed from

this layer as a result of dissociation and recombination reactions [7].

Samples with dimension of 10×4 mm were made of 0.05-mm thick metal foil. They were fixed in a manipulator, which enabled the rotation of the samples to any angle with respect to the direction of the entrance slot of the mass spectrometer. Samples were heated with an electric current, and their temperature was measured with a thermocouple.

Gases under study (O_2 , N_2 , NO, and azomethane) and CH_3 radicals were adsorbed at room temperature on the face side of the samples from the effusion molecular beam formed with a capillary. Methyl radicals were generated by azomethane pyrolysis in a quartz capillary heated to 1100 K. Then, during programmed heating, TPD/TPR spectra were measured at various rotation angles of the sample. These measurements enabled the determination of the intensity of the flow of desorbed species as a function of the angle of their escape from the surface.

RESULTS AND DISCUSSION

Figures 2–4 show the TPD spectra of N_2 /Mo and $CH_3N=NCH_3$ /Mo. These spectra were measured after preliminary adsorption of the respective gases up to saturation coverages. Figures 2–4 also present the TPR spectra of N_2 /Ir, N_2 /Fe, O_2 /Ir, and CH_4 /Mo (products of NO dissociation and the reactions of adsorbed methyl radicals, respectively) and the heating rates of the samples. Only one peak for each gas was observed.

The activation energy of desorption (E_{des}) for all gases except methane was estimated using the Redhead equation [8]

$$E_{des} = 25 RT_{max}, \quad (4)$$

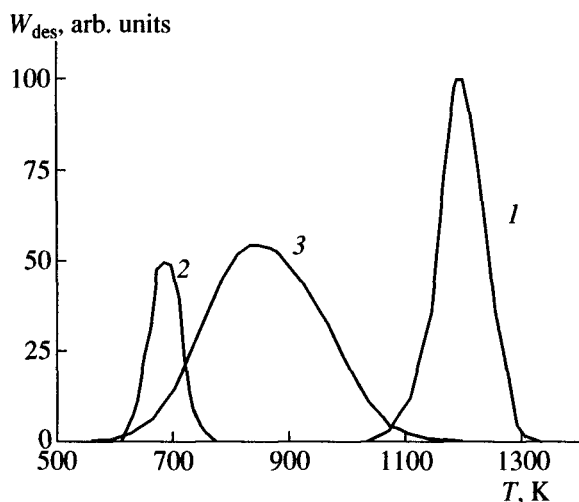


Fig. 4. TPR spectrum of (1) nitrogen and (2) azomethane obtained after their monolayer adsorption and TPR spectrum of (3) methane obtained as a result of dissociation and recombination reactions in the layer of adsorbed methyl radicals on molybdenum. The heating rate is (1, 3) 37 K/s and (2) 300 K/s.

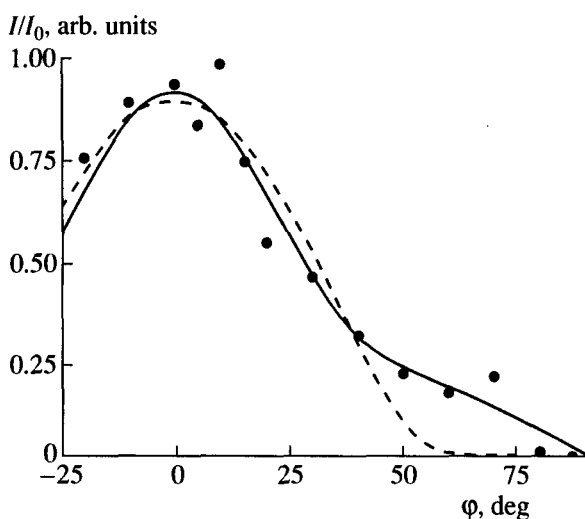


Fig. 6. SDDF of N_2/Mo (dots) and its fitting to equations (1) (dashed line) at $\epsilon = 1.8$ and (3) (solid line) at $\epsilon = 4.1$ and $\alpha = 0.37$.

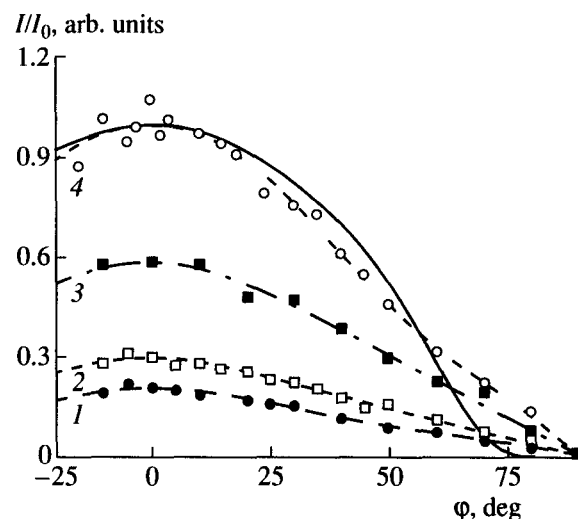


Fig. 5. SDDF of O_2/Ir at different initial surface coverages (θ): (1) 0.2, (2) 0.3, (3) 0.6, and (4) 1 (dots) and their fitting to equation (3) (dashed line) at $\epsilon = 3.2$, $\alpha = 0.68$ (1); $\epsilon = 3.5$, $\alpha = 0.74$ (2); $\epsilon = 2.7$, $\alpha = 0.78$ (3); $\epsilon = 1.7$, $\alpha = 0.65$ (4). Solid line illustrates fitting the data to equation (1) for $\theta = 1$ at $\epsilon = 0.4$.

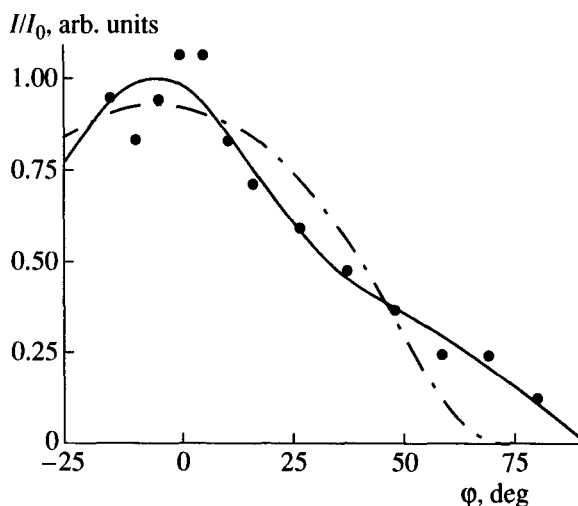


Fig. 7. SDDF of $CH_3N=NCH_3/Mo$ (dots) and its fitting to equations (1) (dashed line) at $\epsilon = 0.7$ and (3) (solid line) at $\epsilon = 5.0$ and $\alpha = 0.58$.

where T_{max} is the temperature of the TPD/TPR peak maximum.

Earlier, we determined the rate of recombinative desorption of methane from molybdenum [7]



Figures 5–10 show the results of SDDF determination for gaseous molecules. These figures present the heights of TPD/TPR peaks as functions of the angle (ϕ) between the normal to the sample surface and the direction of desorption flow. These data were approximated by equations (1) and (3).

Figures 5–10 show that all systems can be divided into two groups. O_2/Ir , N_2/Mo , and $CH_3N=NCH_3/Mo$ belong to the first group. SDDF of these systems are described by the Comsa equation (3) within the experimental error, and the attempts to approximate these functions by the van Willigen equation (1) proved unsatisfactory. This is particularly appreciable at angles ϕ close to 90° . Thus, qualitative analysis reveals that the rate of precursor-mediated desorption is substantial in the systems belonging to the first group. The data obtained at different surface coverages ($\theta = 0.2, 0.3, 0.6$, and 1) are presented for O_2/Ir . In this case, the dependence of α and ϵ on θ is weak.

Parameters of the TPD/TPR spectra with spatial resolution, parameters of equation (3) (ϵ and α), activation energies for adsorption and desorption, portion of molecules desorbed via the precursor state (β) for systems under study

Gas	Metal	T_{\max} , K	α	β	ϵ	E_{ads} , kJ/mol	E_{des} , kJ/mol
N ₂	Fe	770	0.15 ± 0.15	≤ 0.5	1.2 ± 0.3	≥ 7	160 ± 15
N ₂	Ir	500	0.12 ± 0.12	≤ 0.45	1.3 ± 0.2	≥ 6	100 ± 10
N ₂	Mo	1200	0.37 ± 0.1	0.6 ± 0.2	4 ± 2	≥ 19	240 ± 20
O ₂	Ir	1100	0.71 ± 0.05	0.89 ± 0.06	3.5 ± 1.5	≥ 18	220 ± 20
CH ₄	Mo	870	0.05 ± 0.05	≤ 0.3	3.0 ± 0.3	≥ 20	120 ± 10
CH ₃ N=NCH ₃	Mo	680	0.5 ± 0.1	0.80 ± 0.15	5 ± 1	≥ 22	135 ± 20

SDDFs for the second group (N₂/Ir, N₂/Fe, and CH₄/Mo) can be described with approximately the same accuracy by both equations (1) and (3). This does not exclude a certain role of the precursor state in these systems as well. Below we will quantitatively estimate the contribution of the precursor state to the desorption rate for all systems studied in this work.

The table presents the results of the calculation of E_{ads} , E_{des} , and the parameters of equation (3) (ϵ and α).

Note that the values of ϵ obtained for polycrystalline samples are often strongly underestimated [9]. This is first due to the imperfection of the surface of such samples resulting in a certain distribution of local normals near the averaged direction of the normal to the surface. This leads to broadened SDDFs as compared to the ideal flat surface.

Earlier we proposed a model that permitted us to take into account the influence of surface imperfection on SDDF broadening [10]. This model was experimentally confirmed for CO desorption from the tungsten surface [11]. The relief of this surface was characterized by tunneling microscopy.

In this work, we did not measure imperfection coefficients of the surface of the samples. Therefore, we were only able to find rough lower estimates for E_{ads} using the values of ϵ (see the table).

Earlier we showed [10] that surface imperfection leads to the broadening of sharply directed SDDF and does not affect the distributions described by the Knudsen law. Figures 5–10 show that SDDF can satisfactorily be described by equation (3) for all systems studied in this work. This distinguishes molecules with sharply directed SDDF and molecules desorbed according to the Knudsen law. We assume that the broadening of the sharply directed part of distribution due to the surface roughness does not affect the flow of the corresponding desorbed molecules. This flow is determined as an integral over all the directions of molecules desorbing from the surface.

The value of α from equation (3) determines the contribution of molecules desorbed via the precursor state only for the species directly along the normal to the sample surface. Their part (β) in the integral flow from the surface (F) is interesting for us. The value of F can be expressed as an integral in spherical polar coordinates, where the polar axis coincides with the normal to the surface:

$$F = \int_0^{2\pi} d\psi \int_0^{\pi/2} I \sin \varphi d\varphi, \quad (5)$$

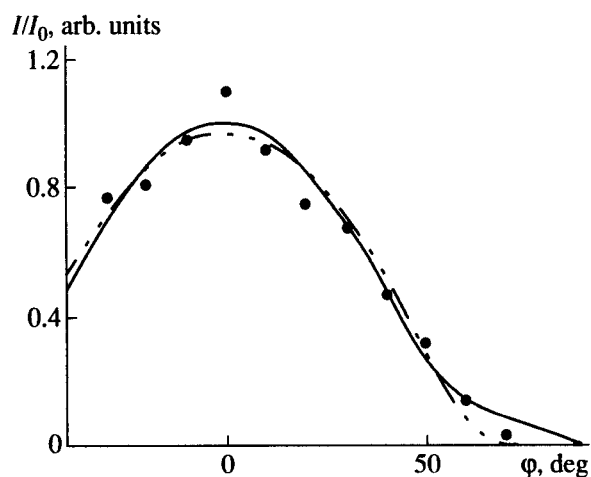


Fig. 8. SDDF of N₂/Fe (dots) and its approximation by equations (1) (dashed line) at $\epsilon = 0.9$ and (3) (solid line) at $\epsilon = 1.5$ and $\alpha = 0.26$.

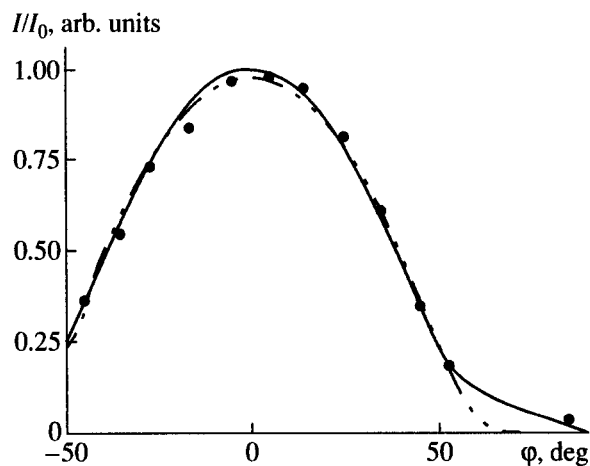


Fig. 9. SDDF of N₂/Ir (dots) and its fitting to equations (1) (dashed line) at $\epsilon = 1.09$ and (3) (solid line) at $\epsilon = 1.49$ and $\alpha = 0.2$.

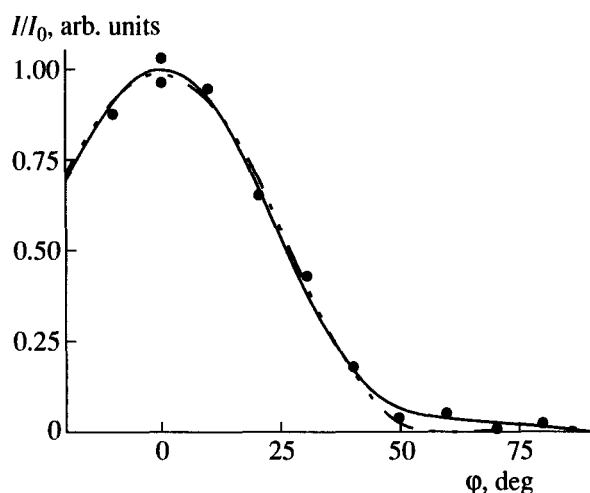


Fig. 10. SDDF of CH_4/Mo (dots) and its approximation by equations (1) (dashed line) at $\epsilon = 2.8$ and (3) (solid line) at $\epsilon = 3.3$ and $\alpha = 0.08$.

where φ and ψ are the polar and the azimuth angles, respectively, and I is the flow intensity under angles φ and ψ .

We assume that sample surfaces are isotropic; that is, I only depends on the polar angle and can be described by equation (3). The substitution of the expression for I from (3) to (5) gives

$$F = I_0 \int_0^{2\pi} d\psi \int_0^{\pi/2} \{ (1 - \alpha) \times [(\epsilon + \cos^2 \varphi) \exp(-\epsilon \tan^2 \varphi)] / [(\epsilon + 1) \cos \varphi] + \alpha \cos \varphi \} \sin \varphi d\varphi. \quad (6)$$

Earlier we showed [9] that the expression in square brackets in equation (6) can be approximated with good accuracy by a simpler one

$$[(\epsilon + \cos^2 \varphi) \exp(-\epsilon \tan^2 \varphi)] / [(\epsilon + 1) \cos \varphi] \approx \cos^n \varphi, \quad (n \approx 2\epsilon + 1). \quad (7)$$

In this approximation, integral (6) is taken in the explicit form

$$F = 2\pi I_0 (1 + \epsilon \alpha) / (\epsilon + 1), \quad (8)$$

and the value of β is determined by the simple formula

$$\beta = \left(\alpha I_0 \int_0^{2\pi} d\psi \int_0^{\pi/2} \cos \varphi \sin \varphi d\varphi \right) / F = \alpha (1 + \epsilon) / (1 + \epsilon \alpha). \quad (9)$$

The values of β calculated using formula (9) are presented in the table. It is easy to see from this table that, for oxygen on iridium and for nitrogen and azomethane on molybdenum, the main pathway of desorption is via the precursor state (60–90%). For other systems, the contribution of this pathway also cannot be excluded completely. According to upper estimates, it can be substantial (~40%).

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research, project no. 95-03-08114.

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