PHYSICAL REVIEW B VOLUME 47, NUMBER 20 15 MAY 1993-II

Low-temperature adsorption kinetics of CO on Pt(111) derived from nonequilibrium time-resolved electron-energy-loss spectroscopy measurements

A. Cudok, H. Froitzheim, and M. Schulze
Institut für Physikalische und Theoretische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 3, D-8520 Erlangen, Germany

(Received 25 January 1993)

Using time-resolved high-resolution electron-energy-loss spectroscopy, nonequilibrium adsorption of CO on Pt(111) has been measured and quantitative comparison made with equilibrium absorption over the whole range of coverage between 300 and 100 K. It is unambiguously shown that there is no site conversion of CO between on-top and bridge sites below 150 K. The ambiguity of equilibrium parameters derived from equilibrium data without knowledge of nonequilibrium data is demonstrated. An adsorbate-induced surface-reconstruction model has been proposed to explain the adsorption kinetics of CO on Pt(111) between 100 and 400 K.

The knowledge of potential-energy surfaces is central to the understanding of the kinetics of gas-surface interactions, because it determines the main processes relevant in surface chemical reactions. This has motivated many studies on this problem. Consideration of only those studies which are directly related to the topic of the present paper indicates that their results are at strong variance. By assuming equilibrium and a fixed number of adsorption sites, given by the intrinsic surface structure, Mieher, Whitman, and Ho[1] as well as Schweizer *et al.*[2] determined the difference of the binding energies of CO on bridge and on-top sites as functions of coverage by analyzing temperature-programmed (TP)–electron-energy-loss spectroscopy and infrared-reflection absorption spectroscopy data, taken between 300 and 100 K, respectively. Mieher, Whitman, and Ho[1] report values between 3.8 kJ/mol for zero coverage and −0.84 kJ/mol for $\Theta_{\mathrm{CO}}=0.4$, in contrast to values between 6.3 kJ/mol for $\Theta_{\mathrm{CO}}=0$ and −6.3 kJ/mol at saturation as reported by Schweizer *et al.*[2] Their value at saturation depends on temperature. A similar discrepancy exists between reported values of the barrier between bridge and on-top sites of Pt(111)/CO. Analyzing time-resolved IR intensities, Reutt-Robey *et al.*[3] derived a top-top hopping-time constant of about 1/s by measuring the diffusion speed of CO from terrace sites to nearest-step edges. This value is in strong contrast to that reported by Poelsema, Verheij, and Comsa.[4] They used the same effect to analyze He-scattering data from stepped Pt(111) surfaces, predosed with CO. Below 150 K they observed a diffusion cutoff and derived a mean hopping-time constant of about 10^{-5}/s corresponding to 29 kJ/mol with an estimated prefactor of 10^{11}/s. An even higher value of 58.8 kJ/mol was obtained from pioneering field-emission studies by Lewis and Gomer.[5]

These large discrepancies motivated us to investigate this system at temperatures below 300 K also with our recently developed method[6,7] of using time-dependent high-resolution EELS (HREELS) with a synchronized supersonic molecular-beam source as doser. This doser produces a uniform adsorbate flux at the sample with intensities up to 5×10^{-1} L/s (1 L$=10^{-6}$ Torr s). A steady flux of 5×10^{-1} L/s produces a background pressure of 5×10^{-10} mbar. Test measurements were carried out with background dosing in order to exclude extra effects due to the kinetic energy of the molecules ($\simeq$65 meV). The relative loss intensities of the two stretching modes were used as a measure of bridge- and on-top population. The proportionality between these intensities and coverage was tested by comparison with integrated thermal desorption (TD) data. For their absolute calibration the $c(4\times2)$ low-energy-electron-diffraction pattern at $\Theta_{\mathrm{top}}=\Theta_{\mathrm{bridge}}=0.25$ (Ref. 8) was used as already described in more detail.[1,7] Using this kind of measurement between 415 and 350 K,[7] we derived a constant binding energy for on-top CO of 130±5 kJ/mol with a prefactor of 5×10^{14}/s±50% and an almost constant value for bridge CO of 100±5 kJ/mol with $\nu_b=10^{13}$/s±50%. For the barrier a value of 50±10 kJ/mol with a prefactor of 5×10^{6}/s±50% was found. It is believed to be of substantial general interest to investigate whether kinetic parameters derived at these high temperatures can be extrapolated to low temperatures or vice versa (from low to higher temperatures) where real chemical reactions occur.

Below, our data will be interpreted in terms of a more general kinetic model shown schematically in Fig. 1 as a model potential-energy surface with two different adsorption sites and all possible CO fluxes. In the case of Pt(111)/CO the two sites are on-top and twofold bridge positions. It is easy to see that this scheme is analytically described by two rate equations:

$$\dot{\Theta}_t=j_{\mathrm{CO}}S_t-D_t\Theta_t-T_{tb}\Theta_t(\Theta_{bm}-\Theta_b)+T_{bt}\Theta_b(\Theta_{tm}-\Theta_t)\ , \tag{1}$$

$$\dot{\Theta}_b=j_{\mathrm{CO}}S_b-D_b\Theta_b+T_{tb}\Theta_t(\Theta_{bm}-\Theta_b)-T_{bt}\Theta_b(\Theta_{tm}-\Theta_t)\ . \tag{2}$$

The meaning of the different terms is explained by the schematics in Fig. 1. All parameters, especially the two

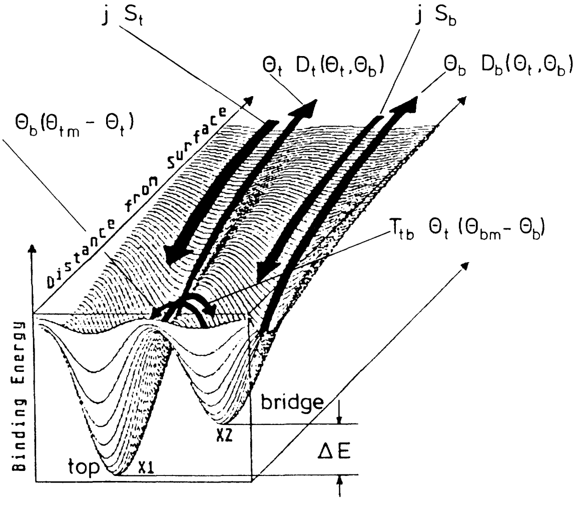

FIG. 1. Schematic diagram of the potential-energy surface of a two-state system. The possible CO fluxes together with their formal descriptions are also indicated.

sticking coefficients, are generally functions of Θ_b, the bridge coverage, Θ_t, the on-top coverage, and temperature. This accounts for all interactions and the order of desorption and adsorption. The two-site conversion terms are explained as follows: A CO molecule which tries to move from on-top to bridge sites (the rate of these trials is given by $T_{tb}\Theta_t$) has only success if it finds an empty attractive bridge site within its hopping distance. The rate $T_{tb}\Theta_t$ has to, therefore, be multiplied by this probability which is proportional to the number of empty sites given by $(\Theta_{bm}-\Theta_b)$ and vice versa for a move from bridge to on-top sites. It should further be stressed that the maximum densities of attractive bridge sites, Θ_{bm} and attractive on-top sites, Θ_{tm} have, in general, not to be constants but they may also be functions of the actual coverages Θ_t and Θ_b and T.

At equilibrium the conditions of detailed balance have to be fulfilled yielding for the site conversion

$$\Theta_{b\mathrm{eq}}(\Theta_{tm}-\Theta_{t\mathrm{eq}})/\Theta_{t\mathrm{eq}}(\Theta_{bm}-\Theta_{b\mathrm{eq}}) = T_{tb}/T_{bt}=\nu_{tb}/\nu_{bt}\exp(-\Delta E/kT) \ . \quad (3)$$

This equation is at variance with that used by Mieher, Whitman, and Ho.[1] These authors neglected the term $(\Theta_{tm}-\Theta_t)/(\Theta_{bm}-\Theta_b)$ despite the fact that it may vary by several orders of magnitude. If $\Theta_t>0$ and $\Theta_b>0$, a rough estimation shows that nonequilibrium deviations ϵ_t and ϵ_b from $\Theta_{t\mathrm{eq}}$ and $\Theta_{b\mathrm{eq}}$ are limited according to $\epsilon_b=-\epsilon_t\le j_{\mathrm{CO}}/\min(T_{bt},T_{tb})$. Thus, if T_{tb} and T_{bt} are large compared to the CO flux the CO distribution will stay close to equilibrium.

Figure 2(a) shows a "slow" ($p=1.7\pm0.2\times10^{-9}$ mbar) adsorption isobar and Fig. 2(b) shows a "fast" ($p=1\pm0.2\times10^{-7}$ mbar) adsorption isobar at $T=300$ K. The curves are derived from HREELS loss intensities as mentioned before and represent the evolution of bridge and on-top population versus time.

At first glance one sees that in the slow data, the bridge coverage does not achieve saturation in contrast to on-top coverage. This directly indicates that at room temperature the desorption from bridge sites is still strong enough to keep their coverage at about $\Theta_b=0.2$ in balance with the adsorption rate into these sites at $p_{\mathrm{CO}}=1.7\times10^{-9}$ mbar. That means there must be a strong positive difference of the binding energies of on-top and bridge sites ΔE also at total coverages around $\Theta_{\mathrm{tot}}=0.5$ in strong contrast to the data of Mieher and Schweizer.[1,2] From the fast measurement it can be seen that a pressure of 1×10^{-7} mbar is sufficient to fully compensate for this desorption. As this is a critical point it was checked independently of calibration by monitoring directly the decrease of the bridge intensity after switching from $p_{\mathrm{CO}}=1\times10^{-7}$ mbar to 1.7×10^{-9} mbar at

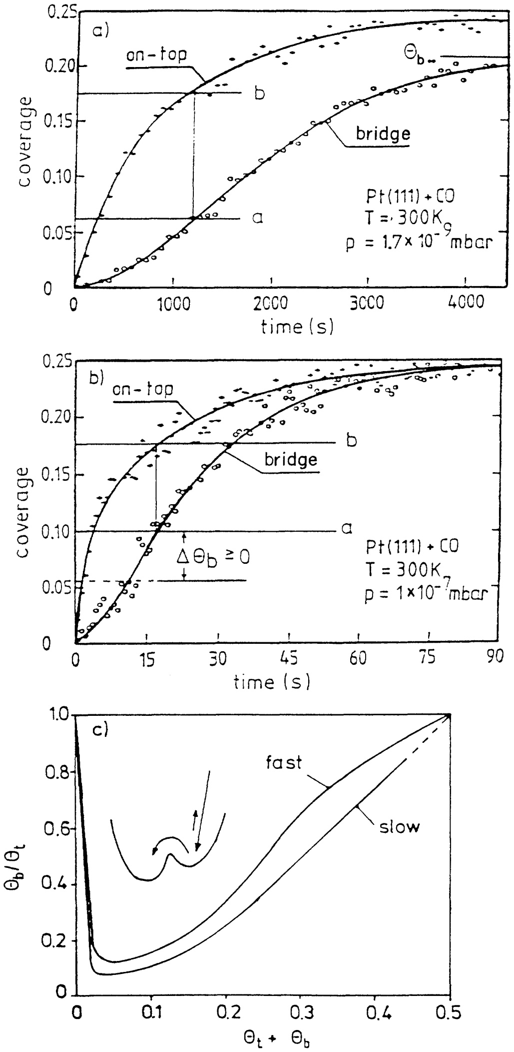

FIG. 2. Development of CO coverages of on-top and bridge sites at room temperature. (a) Slow adsorption with $p_{\mathrm{CO}}=1.7\times10^{-9}$ mbar. (b) Fast adsorption with $p_{\mathrm{CO}}=1\times10^{-7}$ mbar. (c) Comparison of the ratios of Θ_b and Θ_t between the slow and fast adsorption vs total coverage.

$\Theta_t = \Theta_b = 0.25$. Under this condition the initial value of the logarithmic derivative of the bridge loss intensities $-\dot{I}_b/I_b$ is a perfect measure of the desorption rate constant D_b at $\Theta_{\mathrm{tot}} = 0.5$ and $T = 300$ K [see Eqs. (1) and (2)]. After about 10^3 s the bridge level had decreased to 0.85 of its initial level which corresponds to $D_b = 10^{-4}$/s in full agreement with Fig. 2 and our high-temperature value. In accordance with Fig. 2 a change of Θ_t could not be observed under these conditions.

Besides this information, directly obtainable from visual comparison of the two isothermal adsorption isobars at about saturation, which clarifies already two controversial literature results, the most exciting difference between slow and fast adsorption at room temperature is found by comparing the bridge coverages (lines *a*) at equal on-top coverages (lines *b*). This shows that the ratio Θ_b/Θ_t in the fast measurement is always higher than in the slow case, clearly indicating a nonequilibrium distribution of the adsorbate over the whole range of coverage experimentally shown here. A different time-independent representation of this nonequilibrium distribution pronouncing more clearly its amount with respect to the total coverage is given in Fig. 2(c).

In terms of the general kinetic model represented in Fig. 1 and Eqs. (1) and (2), this nonequilibrium distribution with the bridge coverage always higher than its equilibrium value has to be interpreted as a kinetic buildup which necessarily implies a direct and separate adsorption flux into bridge sites too strong to be fully balanced by the net-conversion flux from bridge to on-top sites. This is clarified by the insertion in Fig. 2(c) where only those fluxes are indicated which are absolutely necessary to explain the data. There is most likely a direct adsorption flux into on-top sites, too, but this cannot strictly be decided from only this set of room-temperature data. The on-top sites could also be filled via site conversion from bridge to on-top coverage only.

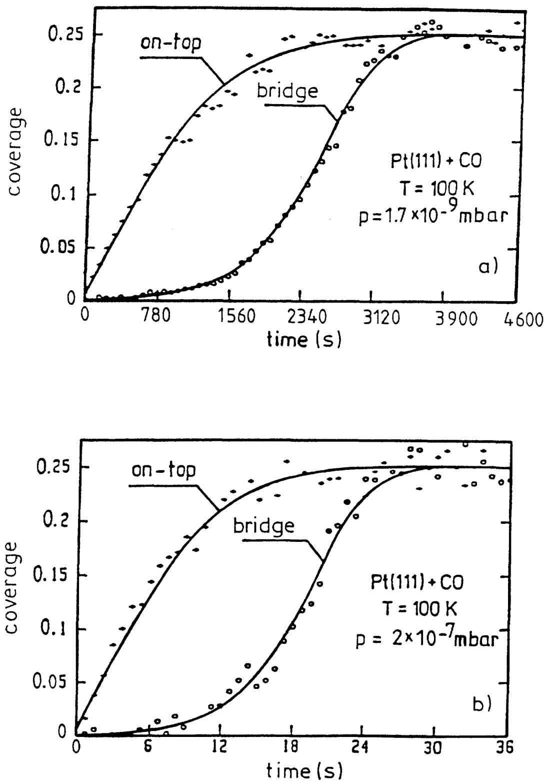

FIG. 3. Contours of the CO coverages of on-top and bridge sites at $T = 100$ K vs time. The upper part shows the slow adsorption with $p_{\mathrm{CO}} = 1.5\times10^{-9}$ mbar and the lower part, the fast adsorption with $p_{\mathrm{CO}} = 2\times10^{-7}$ mbar. (Note the different time scales in Figs. 2 and 3.)

In order to get some more information on the system a series of slow and fast adsorption measurements at different temperatures was carried out, of which here only the data taken at 100 K are presented because they, together with the room-temperature data, pronounce most clearly the important characteristics of the system.

Since the CO pressure is obviously high enough to produce a nonequilibrium distribution of the adsorbate with an increased ratio $\Theta_{b\mathrm{fast}}/\Theta_{t\mathrm{fast}}$, already at $T = 300$ K one could expect at 100 K an even larger difference between the fast and the slow adsorption with ratios of $\Theta_{b\mathrm{fast}}/\Theta_{t\mathrm{fast}}$ probably close to 1. This would follow from simple extrapolation of the room-temperature data assuming a much smaller site-conversion speed due to the lower temperature. The experimental result can be seen in Fig. 3. Instead of the expected stronger difference the slow and the fast data scale perfectly by a factor $K = p_{\mathrm{fast}}/p_{\mathrm{slow}} \simeq 130$ within the limit of accuracy.

As a consequence of this scaling the coverages and their derivatives fulfill the following relations:

$$\Theta_{t\mathrm{fast}}(t) \simeq \Theta_{t\mathrm{slow}}(Kt) \ ,$$

$$\Theta_{b\mathrm{fast}}(t) \simeq \Theta_{b\mathrm{slow}}(Kt) \ ,$$

$$\dot{\Theta}_{t\mathrm{fast}}(t) \simeq K\dot{\Theta}_{t\mathrm{slow}}(Kt) \ ,$$

$$\dot{\Theta}_{b\mathrm{fast}}(t) \simeq K\dot{\Theta}_{b\mathrm{slow}}(Kt) \ ,$$

and

$$j_{\mathrm{fast}} \simeq K j_{\mathrm{slow}} \ .$$

These relations introduced into Eqs. (1) and (2) yield with $D_t \simeq D_b \simeq 0$

$$\begin{aligned}\dot{\Theta}_{t\mathrm{fast}} - K\dot{\Theta}_{t\mathrm{slow}} &\simeq -\dot{\Theta}_{b\mathrm{fast}} + K\dot{\Theta}_{b\mathrm{slow}} \\ &\simeq (1-K)[T_{tb}\Theta_t(\Theta_{bm}-\Theta_b) - T_{bt}\Theta_t(\Theta_{tm}-\Theta_b)] \simeq 0 \ .\end{aligned}$$

This unambiguously demonstrates that site conversion can completely be neglected at 100 K and that bridge and on-top sites are only populated by their own separate adsorption fluxes.

It should be pointed out here that the physical meaning of the above condition is completely different from the formally identical one describing equilibrium data [Eq. (3)]. The latter only demands compensation of the two opposite site-conversion rates, whereas the above condition demands vanishing of both rates or

$$\Theta_t T_{tb}(\Theta_{bm}-\Theta_b)\simeq 0\ ,$$
$$\Theta_b T_{bt}(\Theta_{tm}-\Theta_t)\simeq 0\ .$$

This follows from the fact that at room temperature the site-conversion speeds T_{tb} ($T=300$ K) and T_{bt} ($T=300$ K) were already too small to keep the coverages at $p_{\rm CO}\simeq 10^{-7}$ mbar at equilibrium level. As a consequence the evolution of the two coverages in the slow as well as in the fast data solely reflects the coverage dependences of the adsorption probabilities $S_t(\Theta_t,\Theta_b,\ T=100\ \text{K})$ and $S_b(\Theta_t,\Theta_b,\ T=100\ \text{K})$. We observed this domination of S_t, and S_b up to 150 K. For further discussion of the low-temperature data the on-top adsorption will be considered first. It can be noted that it is quite similar for all temperatures between 100 and 415 K (note the different time scales in Figs. 2 and 3) and that at 100 K the on-top coverage is already close to saturation before a significant amount of CO occupies bridges; it may therefore be a sufficient approximation to only take S_t as a function of Θ_t, and neglect all other dependences. Thus, without site conversion at $T=100$ K, $S_t(\Theta_t)\simeq\dot{\Theta}_t/j$, with $\dot{\Theta}_t$ being the time derivative of the Θ_t isobar in Fig. 3. Carrying out the differentiation numerically a least-squares fit to the result shows that it is well described by $S_t(\Theta_{\rm top},\ T=100\ \text{K})\simeq 1-(\Theta_t/0.25)^2$.

Turning over to a discussion of the bridge-sticking probability, we first relate this coefficient to the site conversion by factorizing

$$S_b(\Theta_b,\Theta_t,T)=S_{0b}(\Theta_b,\Theta_t,T)[\Theta_{bm}(\Theta_b,\Theta_t,T)-\Theta_b]$$

with S_{0b} being the accommodation factor and the term in square brackets being the number of empty, attractive bridge sites. Taking Θ_{bm} not as a constant but as a function of Θ_b, Θ_t, and T as indicated by the argument, then the low-temperature adsorption can be formally related to the behavior of Θ_{bm} as follows: The small initial slope of Θ_b below $\Theta_t\simeq 0.2$ can be explained by a small value of Θ_{bm} simultaneously limiting the sticking probability and the site conversion. $\Theta_t T_{tb}(\Theta_{bm}-\Theta_b)$ and $\Theta_b T_{bt}(\Theta_{bm}-\Theta_t)$ are small because $(\Theta_{bm}-\Theta_b)\leq\Theta_b\leq\Theta_{bm}$. Above $\Theta_t\simeq 0.2$, S_b increases rapidly with a maximum at the point of inflection. However, this increase has only a negligible influence on the site conversion from bridge to on-top coverage because $\Theta_{tm}-\Theta_t$ is already small. Here it is assumed that similar to 300 K at 100 K the net-site-conversion rate also goes from bridge to on-top coverage. This assumption is supported by the fact that the slope at the points of inflection are almost the same at 300 and 100 K indicating accommodation factors of the same magnitude at both temperatures. Assuming in addition $T_{tb}(100\ \text{K})<T_{bt}(100\ \text{K})\ll 1\ \text{s}^{-1}$ then the above arguments in regard to Θ_{bm} stay correct because one still needs an explanation for the small initial adsorption rate into the bridge sites without site conversion.

It should be pointed out that due to the vanishing of the site conversion there is a complete loss of information on the values of T_{bt} and T_{tb}. A similar ambiguity exists at 300 K because at this temperature the bridge adsorption may reflect a nonquantifiable composition of the bridge-adsorption probability and site conversion. Because there is at present no experimental method which could avoid these uncertainties, there is little point in the quantitative determination of kinetic parameters. At best one would obtain so-called effective numbers with values that strongly depend on the assumed models and the way of determination. This might be the reason why data in the literature vary that much. We therefore confined ourselves here to a qualitative interpretation of the observed effects. Following the above discussion of the relation between on-top and bridge sticking, site conversion, and the maximum number of attractive bridge sites $\Theta_{bm}(\Theta_t,\Theta_b,T)$ the behavior of the bridge adsorption and its temperature-dependent delay may be explained by proposing an adsorption model as follows: Within this model it is assumed that the intrinsic Pt(111) surface offers only on-top sites as stable adsorption sites for CO and that the occupation of an on-top site induced a reversible, structural relaxation in the vicinity of this site, such that also bridge sites become stable adsorption sites. Thus each occupied on-top site can be regarded as a center of a reconstructed patch. If this local reconstructive is activated, the sizes of the patches grow with temperature so that Θ_{bm} becomes a function of Θ_t and T. Thus, there are more attractive bridge sites at given on-top coverage at higher than at lower temperatures which explains the decreasing delay of the bridge occupation in regard to the on-top coverage with increasing temperatures. At temperatures around 400 K there is no delay at all.[7]

Inspection of the data of Ref. 3 indicates that the value of 1 s^{-1} for the top-top hopping-time constant is the lowest limit. Larger values (10^{-3}–10^{-4} s^{-1}) seem to be more likely and would agree well with data reported by Poelsema, Verheij, and Comsa[4] and our high-temperature data.[7] In this case the development of a poor but still visible $c(4\times 2)$ pattern at 100 K with negligible site conversion suggests that the creation of stable bridge sites about an occupied on-top site may occur only at distances that are suitable to form small domains with $c(4\times 2)$ order, statistically oriented and distributed over the surface. The ordering process to a well-developed $c(4\times 2)$ pattern observable after annealing to higher temperature[8] may then occur by further minimizing the surface energy including lateral interactions.

This proposed model is supported by numerous LEED data.[10] Another support derives from the observation that no bridge adsorption of CO occurs at stepped Pt(111) surfaces with terraces smaller than five atoms.[11] This can be understood in terms of the above model if one assumes that close to step edges the surface relaxation is blocked. It is clear that the model has been reasoned from indirect arguments and that a direct verification possibly by diffuse LEED measurements is desired. These and the present experiment could yield further fruitful information on the amount of relaxation which is necessary to alter the surface potential energy such that the sticking probability changes by the amount necessary to explain the present data. This is considered to be of general interest also for other adsorption systems.

It has been shown that the sensitivity and the time resolution of our method is sufficient to measure equilibrium and nonequilibrium states of an adsorption system over the whole range of coverage and over a large dynamic range of kinetic parameters. We exemplified with the present case of Pt(111)/CO that only a qualitative interpretation of low-temperature adsorption data is reasonable. Any attempt to derive quantitative values of specific kinetic parameters from only slow measurements under the assumption of equilibrium data and a fixed number of adsorption sites given by the intrinsic surface structure has to be speculative. This includes also the extrapolation of high-temperature data to low temperatures. This may explain the large scattering of data derived previously and demonstrates the general necessity of equilibrium and nonequilibrium measurements in comparison in order to obtain additional information which is necessary to make correct assumptions in regard to reliable models describing gas-surface interactions.

The authors are indebted to Professor Dr. G. Wedler for helpful discussions. The financial support of the Deutsche Forschungsgemeinschaft, Bonn, is gratefully acknowledged.

---

[1] W. D. Mieher, L. J. Whitman, and W. Ho, J. Chem. Phys. **91**, 3228 (1989).

[2] E. Schweizer, B. N. J. Persson, M. Tüshaus, D. Hoge, and A. M. Bradshaw, Surf. Sci. **213**, 49 (1989).

[3] J. E. Reutt-Robey, D. J. Doren, Y. J. Chabal, and S. B. Christman, Phys. Rev. Lett. **61**, 2778 (1988).

[4] B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **49**, 1731 (1982).

[5] R. Lewis and R. Gomer, Nuovo Cimento **5**, 506 (1967).

[6] H. Froitzheim, K. Köhler, and H. Lammering, Phys. Rev. B **34**, 2125 (1986).

[7] H. Froitzheim and M. Schulze, Surf. Sci. **211**, 837 (1989).

[8] H. Steininger, S. Lehwald, and H. Ibach, Surf. Sci. **123**, 264 (1982).

[9] It is easy to see that a value of $\Delta E \simeq 0$ at $\Theta_{\mathrm{tot}} = 0.5$ as derived by Mieher, Whitman, and Ho (Ref. 1) is caused by the fact that these authors used a simplified form of Eq. (3).

[10] W. Moritz, R. Imbihl, R. J. Behm, G. Ertl, and T. Matsuhima, J. Chem. Phys. **83**, 1959 (1985).

[11] R. G. Greenler, K. D. Burch, K. Kretzschmar, R. Klauser, and A. M. Bradshaw, Surf. Sci. **152**, 338 (1985).