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# The influence of adsorbate interactions on kinetics and equilibrium for CO on Ru(001). I. Adsorption kinetics

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After careful calibration, the work function change induced by CO adsorption on Ru(001) has been used to measure the sticking coefficient $s$ as functions of sample temperature (between 100 and 400 K) and coverage, with the gas temperature always at about 295 K. The main results are: At $\theta = 0$, the sticking coefficient is independent of sample temperature between 100 and 400 K, at $s_0 = 0.7$ for $0 < \theta < 0.2$. $s$ drops proportional to $(1-\theta)$ for $T_s > 200$ K, and more gradually below 200 K; at 100 K, $s$ drops slowly up to $\theta = 0.5$. Above $\theta = 0.23$ a sharp decrease of $s$ sets in for $T_s > 120$ K; a second plateau becomes obvious around $\theta \sim 0.35$ for $T_s < 360$ K. Close to saturation, $s$ drops to below $10^{-2}$. These results are discussed in terms of a precursor model with strong effects of the chemisorbed layer on the properties of the precursor. A critical evaluation of the formal precursor states involved suggests that classical precursor states exist only at appreciable coverage and are defined by the lateral and vertical interactions, while at low coverage the collisional dynamics are determined for sticking of molecules.

## I. INTRODUCTION

In chemisorption systems, the interaction between substrate surface and adsorbate particle is the leading one; interaction energies between adparticles are typically one order of magnitude smaller. Nevertheless, they can lead to dramatic changes of the properties of the adlayer as a function of coverages, as the lateral interactions have statistical as well as energetic consequences. Large variations of equilibrium properties which can for instance show up in phase transitions, as well as in kinetic parameters, are the consequence. The influence of lateral interactions on adlayer equilibrium properties can be described by statistical thermodynamics.[1] As equilibrium results from equalization of adsorption and desorption rates, a direct connection exists between these and lateral interactions as well.[2,3] Furthermore, many adsorption processes appear to proceed via intermediate "precursor"[4,5] states whose properties should depend on the coverage of *chemisorbed* species (Ref. 5; "intrinsic" and "extrinsic" precursors as extremes [6]). This influence of chemisorbed on intermediate species can be considered as another adsorbate interaction, albeit "vertical" instead of lateral. As has been discussed by several authors (see Refs. 2, 3, 6, and work cited there), the existence of precursors must show up in desorption as well, so that adsorbate interactions of both types should become very important in equilibrium as well as in adsorption and desorption rates.

While these effects are quite well understood in principle, there are not too many detailed coverage-dependent measurements of kinetic and equilibrium properties for well-defined adsorbate systems which are accurate enough so that results can be checked by circular comparison (adsorption–desorption vs equilibrium, or any other combination), and models of the interactions can be credibly tested. The present work has the aim to examine a well-characterized chemisorption system in this respect.

The adsorption system CO on the basal Ru(001) face has been investigated by a large number of methods and is well characterized, therefore (see, for instance, Ref. 7 and the references given therein). CO is known to adsorb vertically with the C end attached to the surface. At each coverage essentially only one species exists in the layer, whose properties shift by interaction. The preferred site is the on-top site which is the only one realized up to the coverage $\theta = 1/3$ (relative to Ru surface atoms). Strong nearest neighbor repulsive interactions make this coverage unique and the corresponding $\sqrt{3}\times\sqrt{3}-R\ 30°$ structure (called $\sqrt{3}$ structure subsequently) the best defined structure. Island growth of this structure at low coverages and order–disorder phase transitions[8-10] whose properties change with coverage and temperature indicate the existence of attractive interactions as well. A preliminary interpretation of desorption measurements[11] tied in with these results very well.

Detailed accurate measurements of the temperature and coverage dependences of the sticking coefficients of CO on Ru (001) will be reported in this paper and discussed in context of the models mentioned above. In paper II,[12] a detailed account of the desorption and equilibrium measurements will be given for which only a short account exists to date,[11] and the data of the sticking measurements will be used to arrive at a more accurate evaluation and interpretation of these data. It will become obvious that there are not only indirect but direct connections to the phase transitions.

## II. EXPERIMENTAL APPARATUS AND PROCEDURES

### A. Apparatus

For these experiments two standard stainless steel UVH chambers were used. One of them, used for all measurements except the calibration of the initial sticking coefficients, was equipped with an ion getter pump, a titanium sublimation pump and a LN-trapped diffusion pump with poppet valve. The combination of these pumps made it possible to routinely obtain a

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base pressure of $1\times 10^{-11}$ mb. Besides LEED optics, a mass spectrometer (Balzers QMG 311) with a glass shield,[13] and a fast vibrating capacitor[14] were mounted in the chamber. The construction and use of these devices are described in detail in the references given. Here we stress the fast ($\tau < 20$ ms) and accurate (to 0.1 mV at 1 Hz bandwidth) action of the vibrating capacitor and the resettability (within 1 mV) of its reading when the sample was moved away and back into measurement position. Also, as the signal is picked up at the vibrating counterelectrode, measurements are possible while heating the sample. The glass shield around the quadrupole serves to restrict the part of the crystal monitored in thermal desorption to the central well-ordered region, and to suppress the background.[13] The other system, used mainly for LEED measurements,[10] and only for the $s_0$ calibration in this context, was roughly similar.

The Ru samples were oriented with a Laue camera to better than 0.5°, cut by spark erosion, and polished exclusively with diamond pastes down to a grain size of 0.25 $\mu$m. Two short tantalum wires spotwelded to the backside of the crystal were mounted to the sample holder. Through these wires the crystal could be heated to 1570 K by dc current and cooled down to 80 K with liquid nitrogen. Using a microprocessor-controlled regulator, the temperature could be varied linearly with time up or down with <0.1 to 50 K/s, or held constant to 0.1 K.

The sticking coefficient $s$ can be determined by measuring the change of coverage $\theta$ with time at a given incident gas flux. An excellent and accurate way to monitor $\theta$, which can be carried out continuously and at any sample temperature is to record the adsorption-induced work function change $\Delta\phi$, provided the exact relationship between $\theta$ and $\Delta\phi$ is known. Of course, only net sticking coefficients can be determined. This caused no problem here, as adsorption was irreversible under the used conditions, except at high coverages and temperatures. For calibration, the work function change caused by a certain coverage, as measured with the vibrating capacitor, was correlated with the relative amount of gas on the surface, obtained from integration of thermal desorption measured with the enclosed mass spectrometer. Relative coverages were converted to an absolute scale by equating the coverage which yielded the optimum $\sqrt{3}$ structure with $\theta = 0.33$.[10] For some details see Appendix A. Figure 1 shows the obtained calibration curve which is seen to be linear up to $\theta = 0.33$ but shows indications of depolarization thereafter; the earlier assumption of linearity throughout the coverage range[11] has to be corrected. The curve drawn in Fig. 1 which fits the data well, corresponds to the equation

$$\theta = 7.58\times 10^{-4}\Delta\phi + 8.01\times 10^{-7}(\Delta\phi - 440)^2 \qquad (1)$$

(with $\Delta\phi$ in mV) above 440 mV; below this value only the first term is valid. An important condition for the present use of $\Delta\phi$ as coverage indicator is that there are no temperature influences on $\Delta\phi(\theta)$. Various checks on this were carried out[9,12] and except for a small continuous shift of $\phi_0$ with $T$[12] no influence was found.

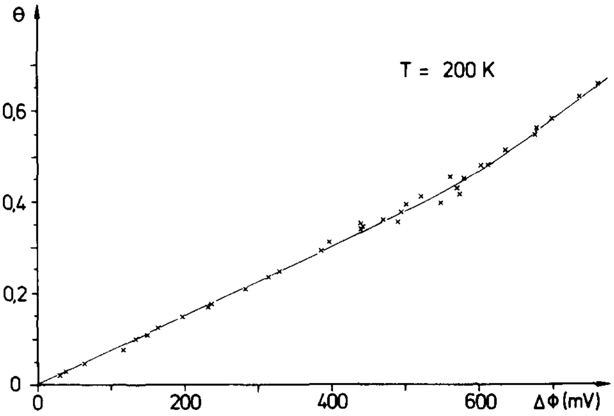


FIG. 1. Calibration of the work function change $\Delta\phi$ induced by CO adsorption of Ru(001) vs coverage at 200 K [relative coverage taken from integration of TPD traces; absolute calibration at $\theta = 0.33$ by comparison with LEED (Ref. 10)].

If not only coverages, but also the doses for their attainment are to be obtained in a continuous way, any shielding effects by the counterelectrode have to be eliminated. This can be done using the treatment outlined in Appendix A. As shown there, the shielding effect is not only disturbing but can also be used for an independent absolute determination of the sticking coefficient at zero coverage which has been used to check the sticking coefficient scales of the results obtained from pressure-time determinations.

## III. RESULTS OF THE STICKING COEFFICIENTS AS FUNCTIONS OF COVERAGE AT VARIOUS SAMPLE TEMPERATURES

Gas was adsorbed at crystal temperatures between 100 and 400 K and ambient gas pressures between $2\times 10^{-8}$ and $1\times 10^{-7}$ mb. The vibrating capacitor electrode was in front of the crystal as close as possible. $\Delta\phi$ data were recorded as a function of time. These data were converted to coverage according to Eq. (1) and digitally differentiated to yield sticking coefficients. The absolute scale of the latter was fixed by the direct determination (see Appendix A) of $s_0$ (200 K) = 0.7.

Figures 2(a) and 2(b) show the sticking coefficient as a function of coverage at the indicated constant sample temperatures. The data are replotted in Fig. 3 to give $s$ ($T_s$) for certain coverages. There are several interesting features:

(a) Within experimental accuracy (± 3%) the sticking coefficient at zero coverage $s_0$ is *constant* over the entire accessible range of surface temperature from 100 to 400 K.

(b) Between $\theta = 0$ and 0.2, the sticking coefficient decreases linearly with increasing coverage. The slope is changing mainly between $T_s = 100$ and 200 K, possibly with a slightly decreasing tendency at higher temperatures. The average slope between 200 and 400 K is proportional to $(1-\theta)$ [see the extrapolation in Fig. 2(a)].

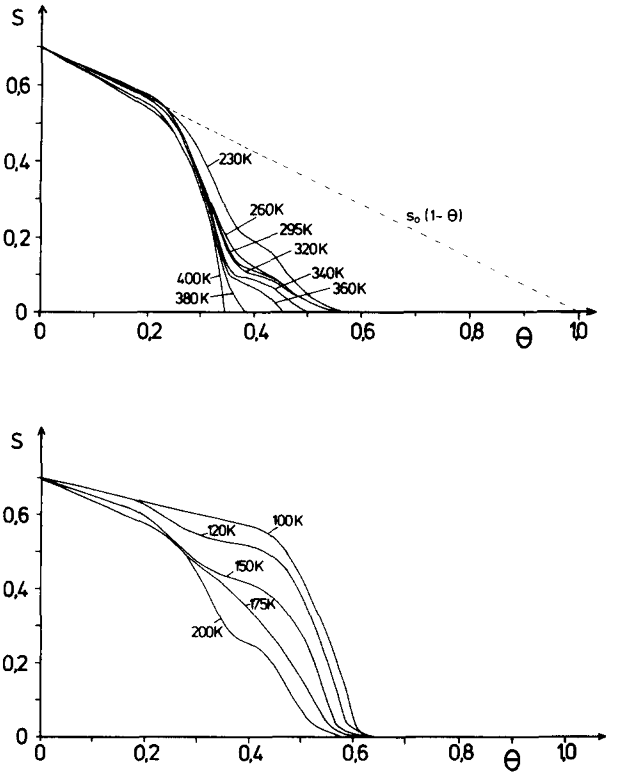


FIG. 2. (a) and (b): The sticking coefficient of CO on Ru(001) as a function of coverage at the adsorption temperatures indicated. The gas temperature is always about 295 K. In Fig. 2(a) the initial $(1-\theta)$ dependence is indicated by extrapolation.

(c) For temperatures $T_s > 200$ K the sticking coefficient decreases strongly above $\theta = 0.23$ and reaches a second plateau between $\theta = 0.36$ and 0.43. At higher coverages it drops again and falls below $10^{-2}$ for coverages above 0.55. The cutoff at lower coverages for $T_s > 340$ K is due to nonnegligible desorption at these temperatures near saturation coverage.

(d) For $T_s$ below 200 K the onset of the strong decrease is shifting to lower coverages with falling temperatures and weakened. The second plateau is extended and shifts to higher $s$ values for decreasing $T_s$, so that at 100 K the difference between first and second plateau is smeared out.

(e) Even at 100 K the sticking coefficient for $\theta > 0.61$ is below $10^{-2}$. The sticking coefficient up to the saturation coverage of 0.68 is extremely small and not accessible by this method of measurement.

## IV. INTERPRETATION OF THE RESULTS

### A. Formal model

Adsorption kinetics of chemisorbed layers are usually discussed in terms of direct and precursor-mediated sticking. The concept of precursor states[4,5,16] was introduced to account for the experimentally observed coverage dependences of sticking coefficients which frequently fall much slower with coverage than expected for direct adsorption which should be governed by the fraction of accessible vacant chemisorption sites.[15] For our case, we want to take into account both these possibilities and in particular the influences of coverage and state of the chemisorbed layer; we therefore shall draw heavily on other information about this system. As a working hypothesis, we shall start with a model similar to those of Cassuto and King,[6] introducing intrinsic and extrinsic types of precursors in a formal way. The physical reality of these entities will be examined critically in Sec. V; here we naively regard them as an indication of different adsorption paths.

The found $(1-\theta)$ dependence for $\theta < 0.2$ indicates that adsorption is not governed by direct adsorption in the normal sense. The known[8–12] strong repulsion among adsorbate molecules for lateral distances smaller than $a\sqrt{3}$ (where $a$ is the surface lattice constant) effectively excludes occupation of nearest neighboring sites. If direct adsorption were governing, this should lead to a dependence of $s \sim (1 - 7\theta)$ for $\theta \to 0$ and of $\sim (1 - 3\theta)$ near $\theta = 0.33$ which is very different from the observed one $[\sim (1-\theta)]$. At higher coverages, precursors will be even more important. We therefore omit the explicit term for direct adsorption which is contained in the equations of Ref. 6. It should be noted, however, that the remaining general equations for precursor adsorption can still contain direct adsorption as a limiting case so that the omitted term is not really necessary, generally. In fact it will turn out that at low coverage sticking *can* be viewed as proceeding via direct adsorption (see Sec. V).

In order to devise an appropriate precursor model, we draw upon LEED data which give indications of the minimal set of parameters necessary to describe the adsorption process properly for the present case. We must at least assume the possible existence of an extrinsic precursor located above the chemisorbed molecules and an intrinsic precursor above the empty sites. It is advantageous, however, to further split the intrinsic precursor into at least two different states, because of the different chemisorption probabilities of intrinsic precursors located on sites next to chemisorbed molecules and of those above sites where chemisorption is allowed as no chemisorbed molecules are in the direct neighborhood. These precursors will be

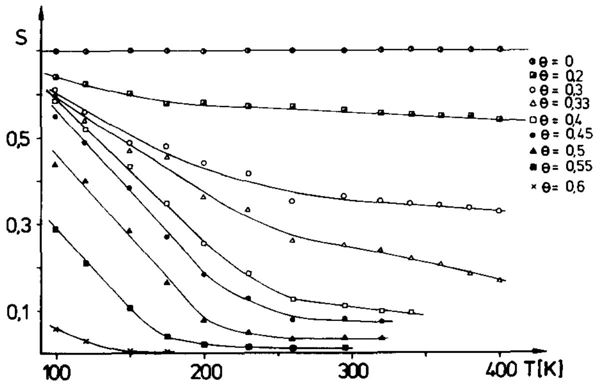


FIG. 3. Replot of the data of Fig. 2 to show the dependence of $s$ on $T_{ad}$ for fixed coverages.

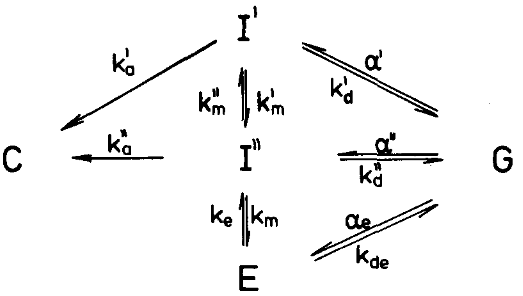


FIG. 4. Scheme of states and rate constants involved in molecular adsorption, if two intrinsic ($I'$ and $I''$) and one extrinsic (E) precursor states are assumed as possible intermediates on the surface between gas (G) and chemisorbed phase (C). If the simplified model (only one $I$ state) applies, all dashes are omitted.

denoted $I''$ and $I'$, respectively. This subdivision is suggested by the properties of the chemisorbed layer with its strong repulsion on NN sites, so that chemisorption from $I''$ species can only take place by shifting away the surrounding layer. These intrinsic precursor states can be energetically similar and can have the same trapping probabilities $\alpha$ from the gas phase, but still differ substantially in their rate constants for chemisorption. These assumptions are strongly supported by the $(1-\theta)$ dependence of $s$ up to $\theta = 0.2$ which shows that the excluded space in the precursor is simply proportional to the chemisorption coverage only, without additional blocking of neighbors. On the other hand, it will be seen that the precursor $I''$ spans a considerable range of changing properties, depending on coverage and detailed distribution (see Fig. 5 for a pictorial clarification). This model is an oversimplification in many respects, therefore.

The resulting adsorption scheme under the experimental adsorption conditions where desorption from the chemisorbed state can be neglected, is shown in Fig. 4. G, C, and E denote the gas phase, the chemisorbed phase, and the extrinsic precursor, respectively, the $k$'s are the rate constants between different states. A similar scheme can be drawn for desorption conditions and equilibrium with the gas phase, but will not be shown here.

To be sure any such model contains a considerable number of unknown parameters which make it difficult if not impossible to claim a unique solution; further subdivision of $I''$ would aggravate this situation. We therefore prefer to search for simple solutions which show clearly the physical influences involved, rather than to try and calculate a quantitative fit to the data. In order to do this, it is appropriate to simplify the model further wherever possible, and to expand it only in ranges where this is absolutely necessary. For instance, for small coverages the splitting into two intrinsic precursors can be omitted, as the concentration of $I''$ is low and the migration from $I''$ to $I'$ is rapid because $I''$ is surrounded by $I'$ and essentially no activation energy should be necessary to move from $I''$ to $I'$. Under these circumstances there is no difference in the chemisorption probabilities from the two precursor states as every molecule trapped in $I''$ can also be chemisorbed by quickly migrating to $I'$. This simplified model is identical to that proposed by Cassuto and King[6] for molecular adsorption. In our case it seems to be applicable up to $\theta = 0.2$. For higher coverages, we have to use our full model, taking into account the changing properties of $I''$.

### B. Low coverages

As just shown, we can directly use the model of Ref. 6 here. For details the reader is referred to this paper. Because adsorption takes place, under measuring conditions, far from equilibrium we cannot use the simplified equations for equilibrium conditions, but make use only of a stationary concentration in the precursor states. For molecular adsorption the sticking coefficient is then given[6] by

$$s = \frac{k_a (1-\theta)\{\alpha + \alpha_e \theta k_e / [k_{de} + k_e (1-\theta)]\}}{k_a + k_d + k_m k_{de} \theta / [k_{de} + k_e (1-\theta)])} , \tag{2}$$

where $k_a$ is the rate constant for the transfer from the (now single) intrinsic precursor state to the chemisorbed state. The rate constants $k_d$ and $k_{de}$ are the desorption constants from intrinsic and extrinsic precursors to the gas phase; $k_m$ and $k_e$ control the migration between these precursor states. $\alpha$ and $\alpha_e$ denote the trapping probabilities for adsorption into the intrinsic and extrinsic precursor states. If desorption takes place using the same channels, the desorption rate $r_d$ is strongly correlated with the rate of adsorption because of microscopic reversibility.[6]

#### 1. *Initial sticking coefficient*

Within this model the initial sticking coefficient $s_0$ is given by

$$s_0 = \frac{k_a \alpha}{k_a + k_d} . \tag{3}$$

The measured initial sticking coefficient was found to be independent of sample temperature. As $k_d$ and $k_a$ are in general strongly temperature dependent, a temperature independent $s_0$ can only be obtained by assuming that $k_a \gg k_d$ and $\alpha$ is temperature independent. Then the result is simply

$$s_0 = \alpha . \tag{4}$$

Possibly an accidental compensation of the temperature dependences of $k_a, k_d$, and $\alpha$ could also lead to $s_0$ being temperature independent. However, the first assumption is supported by the results for the desorption energies near $\theta = 0$[11,12]: Within experimental error there is no difference between the desorption energies derived from equilibrium and nonequilibrium measurements; $E_B = E_{\text{eff}}$.[3] For $\theta = 0$, the desorption rate is given by[6]:

$$r_d = N_s \theta \frac{k_D k_d}{k_a + k_d} \tag{5}$$

With an Arrhenius form of the rate constant, $E_{\text{eff}}$ is equal to $E_B$ only if $k_a \gg k_d$; than $E_{\mathrm{eff}} = E_D + E_d - E_a$.[3] As $k_d$ is growing faster with $T_s$ than $k_a$ and as adsorption takes place at much lower temperatures than desorption this assumption is valid in adsorption *a forteriori*. So at low coverages each molecule adsorbed into the intrinsic precursor is chemisorbed. Furthermore, the constancy of $s$ with $T_s$ shows that adsorption via the intrinsic precursor is not activated. The physical meaning of these results for the "intrinsic precursor" will be discussed in Sec. V.

#### *2. $0<\theta<0.2$*

At these coverages the assumptions made above concerning the precursor state $I''$ seem still to be valid ($I' = I''$), and the same model with only one intrinsic precursor can be used. However, more and more chemisorption sites become occupied now and a possible influence of the extrinsic precursor has to be taken into account. This state, located "on top" of chemisorbed molecules, is probably bound by van der Waals forces only; we expect it to be more weakly bound than the intrinsic precursor. On the other hand, every intrinsic precursor can still easily chemisorb. We therefore assume that $k_m \ll k_a$ because of the necessary activation energy to migrate from intrinsic to extrinsic precursor. In order to explain the observed $(1-\theta)$ dependence of $s$ at temperatures above 200 K it is sufficient to neglect the influence of the extrinsic precursor (i.e., to assume that the net condensation probability into the extrinsic precursor is much smaller than that for the intrinsic one). Setting therefore $\alpha_e = 0$ and $k_d, k_m \ll k_a$, one gets

$$s = \alpha(1-\theta) \ . \tag{6}$$

The same result is obtained with $\alpha_e \neq 0$, but $k_{de} \gg k_e$ (and $k_a \gg k_m, k_d$) as one can then omit the term with $\alpha_e$ in Eq. (4). In any case both assumptions break down at some temperature below 200 K, because now either $\alpha_e \neq 0$ or $k_e$ can compete with $k_{de}$. If again $k_m$ and $k_d \ll k_a$, the coverage dependence of $s$ stays linear only if the other extreme, $k_{de} \ll k_e$ is reached. Then

$$s = \alpha(1-\theta) + \alpha_e\theta = \alpha\left(1 - \frac{\alpha - \alpha_e}{\alpha}\,\theta\right) \ . \tag{7}$$

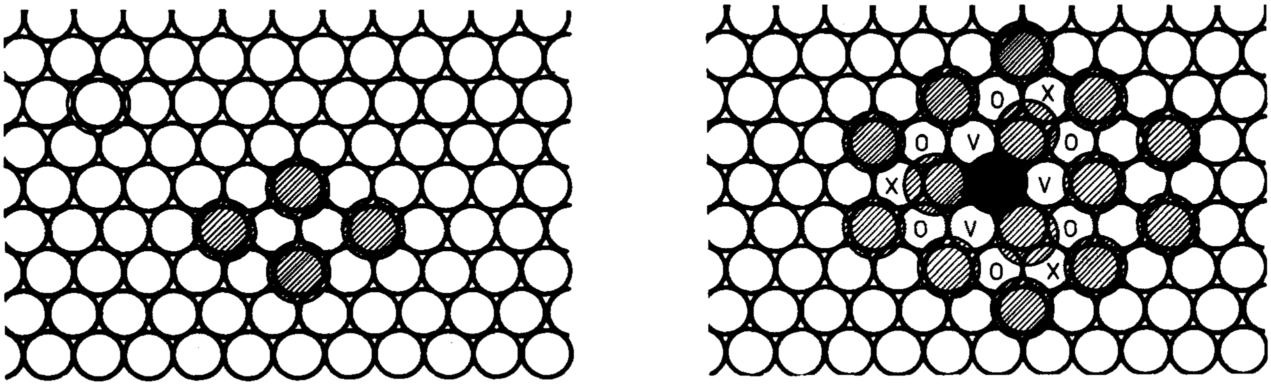
This could be the case for the lowest temperatures achieved. With this assumption, and assuming $\alpha_e$ as temperature independent, we can calculate $\alpha_e$ from the slope of $s(\theta)$ at 100 K for $\theta < 0.3$; we obtain a value of 0.4. In an intermediate range of temperatures, $k_{de}$ is of the same order of magnitude as $k_e$ and the dependence of $s$ on coverage is no longer strictly linear. The deviations from the linear behavior are small, however, and cannot be clearly identified in the measurements. Therefore the second possibility of a temperature dependent $\alpha_e$ and $k_e \gg k_{de}$ over the whole temperature range cannot be excluded.

### C. Intermediate to high coverages

#### *1. $0.2<\theta<0.5$*

To understand the behavior of the sticking coefficient for this coverage range it is advantageous again to use some results of LEED,[7–10] desorption kinetics,[11,12] and vibrational spectroscopy.[17,18] The drastic decrease of $s$ at higher temperatures for $0.23 < \theta < 0.36$ can be directly correlated with the filling of the chemisorption sites of the $\sqrt{3}$-LEED structure and the strong reduction of the measured desorption energies when sites between $\sqrt{3}$-ordered molecules become occupied at $\theta > 0.33$ From LEED-IV,[7] vibrational data,[17,18] and ESD results,[19] it follows that for $\theta \leqslant 0.33$ the geometric on-top sites between CO molecules chemisorbed in lateral $\sqrt{3}$ distances can be occupied, but only if the NN molecules are shifted further apart. This can be concluded from the rapid destruction of the $\sqrt{3}$-LEED structure for coverages above 0.33. As can be shown with the LEED data,[7,10] one additional chemisorbed molecule influences four others on the average. For lateral $\sqrt{3}$ distances there exists an interactional potential minimum. In order to press the molecules together to achieve $\theta > 0.33$ an activation energy is necessary which amounts to at least the difference between initial ($\sqrt{3}$ structure) and final configuration (additional molecule adsorbed at top site, neighbors shifted to energetically less favorable locations); but the activation energy for this additional adsorption step may be considerably higher than this limit.

This does not mean, however, that configurations of molecules which become stable at $\theta > 0.33$ are excluded as intermediates on the chemisorption paths at lower coverages. On the contrary we believe that at coverages where a considerable amount of $\sqrt{3}$ sites is already occupied and the number of $I''$ sites is comparable or even higher than that of $I'$ sites (say above $\theta = 0.2$), chemisorption from $I''$ without the detour via $I'$ becomes important as the migration to $I'$ is more and more hindered with increasing coverage and island size.[8,10] In this range the probability increases that a molecule in $I''$ is enclosed by three or even more chemisorbed CO molecules in $\sqrt{3}$ sites [see Fig. 5(b)]. In order to chemisorb at its present $x, y$ position it has to behave like a particle at $\theta > 0.33$, i.e., it has to deliver the necessary activation energy and can chemisorb only with the reduced chemisorption rate constant $k_a''$. On the other hand migration to an $I'$ site from such an *enclosed* $I''$ site needs an activation energy because the precursor molecule has to pass between/over two chemisorbed CO's to get to a precursor site ($I'$ or $I''$) not enclosed. This process therefore needs high activation energy. Otherwise, if this diffusion barrier were small compared to $E_d$, so that the particle could easily migrate over long distances without desorbing, a decrease of $s$ stronger than $(1-\theta)$ should be observed only very close to $\theta = 1/3$, which is not the case. For such an enclosed $I''$ molecule it would be perhaps more advantageous to wait until the surrounding chemisorbed molecules change their sites by a concentration fluctuation so that adsorption $I''$ becomes possible.[20] The necessary coordinated motion of molecules, however, makes this process rather improbable. For these reasons the adsorption rate constant from enclosed $I''$, $k_a''$, is much smaller than $k_a'$ and therefore the desorption from the $I''$ state becomes important for the chemisorption probability, as can be seen from the fact that $s$ becomes



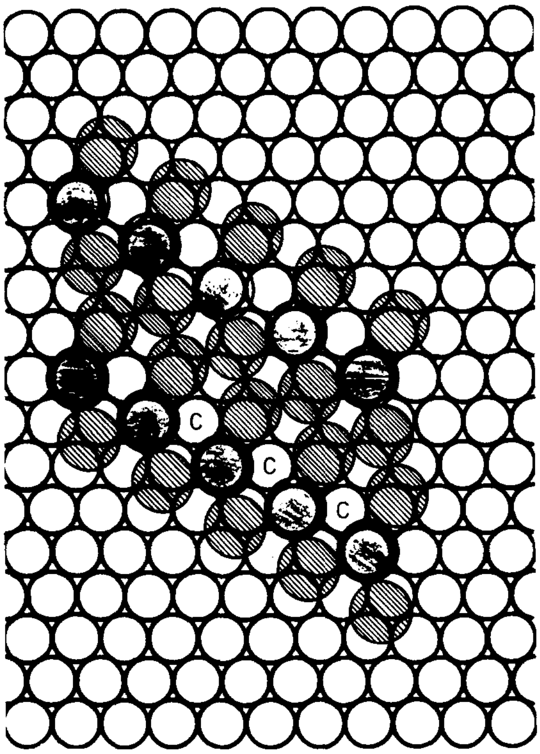


FIG. 5. Pictorial representation of various geometrical situations in the layer. (a) Exclusion of NN sites by adsorption at low coverages (left) and basic unit of √3 structure formed by NN repulsion and NNN attraction. (b) Adsorption step leading to increase of coverage at $\theta = 0.33$. One additional CO molecule (shaded) influences at least three molecules already present and pushes them aside. *v*: excluded NN sites; *x*: sites made unlikely for next adsorption step by relaxation of molecules in preceding step. *o*: likely sites for next step. (c) One domain of a $2\sqrt{3} \times \sqrt{3}\, R\, 30°$ chain structure [with $\theta = 0.50$ (Ref. 21)] which is a possible explanation of the $2\sqrt{3}$ structure observed at low temperatures. Further adsorption is easiest on sites *c*. The models can also be used to depict the various precursor sites discussed in the text: $I'$ and unenclosed $I''$ in (a); various types of enclosed $I''$ for various coverages in (b) and (c); E above all occupied sites.

more and more temperature dependent at increasing coverages (see Fig. 3). There is an interesting correlation between the $\theta$ range where $s$ drops sharply, and that of the observed[10] continuous phase transition. This is understandable as both adsorption paths from enclosed $I'$ (squeezing into the layer, or migration to the island edge) will be the slower the higher the order of the chemisorbed layer.

It is obvious from the preceding discussion that the rate constants characterizing $I''$ will be strongly dependent on $\theta$ under these circumstances and even on the spatial distribution of chemisorbed molecules at constant $\theta$. This is somewhat against the spirit of the used equations, in which the main coverage dependence is assumed to be explicitly given; and the rate parameters are supposed to be essentially coverage independent. The complication arising is similar to the problem of defining an "order" of desorption.[3] To maintain such an approach, more separate precursor states would have to be introduced, one for each local configuration, which is not sensible. We have to accept the considerable coverage dependence of the rate parameters, therefore.

For the coverage range $0.2 < \theta < 0.33$, then, both intrinsic precursors can contribute, so that we have to use the full model of Fig. 4. The formal treatment leads to rather complicated equations; it is briefly outlined in Appendix B. As shown there, it has the following properties:

(i) For small coverages ($\theta < 0.2$) identical results to those from the simplified model are obtained; especially Eq. (6) is found again to hold. This must be so, of course, because of the equivalence of assumptions.

(ii). For coverages $0.2 < \theta < 0.33$, only terms containing ratios of rate constants involving $I'$ are important (apart from directly coverage dependent terms). These ratios determine the onset of deviations from linearity; this causes the considerable temperature dependence found.

(iii) At $\theta > 0.33$ only a single intrinsic precursor remains ($I''$) so that an equation similar to Eq. 3 is again valid, but now with strongly changed relations between the various rate constants. In particular, $k_d'$ can be comparable to $k_d''$ because of the barrier between $I''$ and C. Consequently, $s$ is dependent on $T_s$ and reduced to values which depend on the rate constants of $I''$. A fit of the measured $T$ dependences for $0.33 < \theta < 0.5$ by varying $E_d - E_a$ and the ratio of the corresponding preexponentials gave satisfactory results for $T_s > 200$ K with $E_d - E_a = 7$ kJ/mol, i.e., for a barrier height close to the zero potential energy (corresponding to infinite separation). Below 200 K contributions from the extrinsic precursor lead to deviations. Their magnitude leads to a value of $\alpha_e$ which is somewhat smaller than that estimated above.

(iv) Because of the coverage-dependent properties of $I''$, no attempt was made to fit the region $\theta > 0.5$; qualitatively similar arguments pertain. It is likely that the strong decrease of $s$ around $\theta = 0.6$ is connected to a moving-up of the barrier between $I''$ and C caused by the increase of the compression necessary for adsorption. The compression of the $2\sqrt{3} \times 2\sqrt{3} - R$ 30° LEED structure (Ref. 8); see, however, (Ref. 21) is an indication that the lateral interactions now dominate the layer. Such a compressed layer [for a possible structural model sees Fig. 5(c)] can take up further molecules, but an increasing number of adsorbed molecules has to relax which will lead to increasing activation and consequently small $s$, as found. If the model of Fig. 5(c) is correct, then sites marked $c$ would be the candidates for further adsorption and therefore for the location of $I''$ under these conditions. The coverage for the corresponding layer with $c$ sites filled is 0.66 which is close to the observed saturation coverage of 0.68. Even if only half the $c$ sites are filled, considerable relaxation, or concentration fluctuations, are necessary for further adsorption, so that the very small $s$ values in this range become understandable. It appears also possible that the saturation point is determined by the barrier moving through zero, leading to overall activated adsorption; as the $C$ layer becomes reversible itself, this ends adsorption. High pressure adsorption would be necessary to check this.

## V. DISCUSSION

The analysis of our results in terms of a general precursor model has shown that the main features of the results can be explained semiquantitatively if additional information on the coverage-dependent properties of the chemisorbed layer is used to tailor the model. In view of the many parameters involved it did not appear sensible to aim for a quantitative fit of the data. In this section we examine the physical reality of the formal precursors that were used in the model; some of their properties have inevitably been discussed already in Sec. IV.

As regards the prevalent adsorption mechanism, we can distinguish three main coverage ranges. At $\theta < 0.2$, the adsorption process is formally described by paths via intrinsic precursors $I'$ and (unenclosed) $I''$ which are indistinguishable in this range. The temperature independence of $s_0$ shows that these precursors are *not* separated from the chemisorbed state by an activation barrier, and suggests that the precursors are thermally decoupled from the surface. On the other hand the coverage dependence found is very different from that expected for direct adsorption into allowed sites. Above $\theta = 0.2$, more and more "$I''$ sites" become enclosed by chemisorbed molecules, especially as they form $\sqrt{3}$ islands, and for such precursors chemisorption is only possible by migration to the rim of the island (via states similar to extrinsic precursors $E$), or by fluctuations or compression of the underlying chemisorbed layer, both processes requiring considerable activation. At $\theta = 0.33$, paths via $I'$ have become totally exhausted, and the only path left is via (enclosed) $I''$, with the difference that chemisorption becomes increasingly difficult because of the compression of the layer, and with $E$ acting as possible additional reservoir at low temperatures.

The most straightforward interpretation of a precursor model as that used is the identification of precursor states with weakly bound states in definite sites and possibly configurations. Such states could clearly serve as reservoirs for additional adsorption. They should be separated from the chemisorbed states by an activation barrier[22] and have the possibility to equilibrate with the surface. In these terms, our (uniform) low coverage precursor would *not* be a precursor. $I''$ at medium to high coverages, on the other hand, can be viewed as such a classical precursor: it has a site defined by the enclosed empty site and the enclosing chemisorbed molecules, is separated from chemisorption by the activation energy necessary to compress the layer (temporarily at $\theta < 0.33$ or permanently above 0.33), and is most probably already oriented with the C end towards the enclosed Ru site as this should lead to closest approach and optimum bonding. The extrinsic precursor $E$ which does contribute at low temperatures has a less well-defined site, in particular at low coverages. It is likely to be a "second layer" species which would then most likely be oriented parallel to the surface and rotating in this plane. It could be seen as a (vibrationally and rotationally) excited state of $I''$; the migration of $I''$ would proceed as a "flop" $I''$-$E$-$I''$.

However, such a restrictive definition of precursors is not necessary. They could also be viewed more as dynamical entities, without profound change of the formal treatment. We shall examine such a concept for the low coverage case.

A possible explanation for this range can be found with the following picture. When a (rotating) CO molecule approaches the surface, it feels an attractive as well as a directional force. The latter tries to stop the rotation and to direct the C end to the optimal site (on top of a Ru atom). At low rotational excitations, this process will be efficient and may be successful at first attempt. More strongly rotating molecules will bounce and can be trapped into a state tumbling on the surface to give additional chemisorption chances. This trapping is not an equilibrium capture, but is due to conversion of energy from the normal to the parallel component; it is thus the classical equivalent of selective adsorption.[23] Overall, we shall expect that sticking should be the more probable the lower the rotational excitation. Indeed, desorbing NO molecules have been shown by laser-induced fluorescence to be rotationally considerably colder than the surface from which they desorb,[24] as is expected from microscopic reversibility, if this picture is correct. Also, the postulated tumbling motion across the surface has been seen in molecular dynamics simulation of CO adsorption.[25] Such effects could be checked by variation of $T_s$; this is planned for the future.

Such a picture explains all features of our observations at low coverage. For a weakly rotating molecule, the potential curve will lead smoothly into the chemisorbed state for $I'$; for $I''$, a redirection in the $xy$ plane to a neighboring $I'$ site is necessary in addition (or one bounce more), but this will leave the potential curve in terms of the reaction coordinate smooth. Such processes are really *direct* adsorption, and the redirection explains the observed $(1-\theta)$ dependence. If this is the prevalent path, then it is not very appropriate to speak of an intrinsic percursor in this range. On the other hand, if the orientational force and connected coupling (vibrational and, possibly, electronic) for transfer of energy and momentum to the surface is not strong enough to make the direct path preferred, the trapped molecule bouncing around on the surface could be viewed as the precursor, even though it is kept from chemisorbing only by dynamics, not by a barrier. It appears likely in our case that the first picture is more appropriate, as the bouncing molecule *should* feel the surface temperature so that the $T_s$ independence of $s_0$ would be difficult to understand, and as some influence of $\theta$ on it would be expected. The formal precursor treatment is applicable to both, as direct adsorption results as a limiting case.

We conclude that in the low coverage regime chemisorption proceeds via direct adsorption following directional forces, or via a dynamical precursor, with the former being somewhat more likely. At higher coverages, an intrinsic precursor (in the classical sense) becomes rate determining, whose properties change drastically with coverage and distribution of the chemisorbed layer; it can be viewed as an oriented, weakly chemisorbed state trying to squeeze in between chemisorbed molecules. At low temperatures, an extrinsic precursor which is likely to be a physisorbed molecule above the chemisorbed layer, also contributes. Generalizing, we want to stress that the applicability of the formal precursor treatment does not neccesitate the existence of classical precursors, and that for molecular adsorption intrinsic precursors are likely to be of dynamic nature at low coverages, while they may become real through interactional effects at higher coverages.

## VI. SUMMARY

Careful, detailed measurements of the sticking coefficients of CO on the basal Ru(001) plane as functions of coverage and surface temperature have been made, using continuous work function monitoring and correcting for reflection from the counterelectrode. Clear connections to the structural properties of the adlayer have been found. The main features of the results are:

(1) $s_0$, the sticking coefficient at $\theta=0$, is equal to 0.7 in the entire temperature range 100–400 K.

(2) For $0<\theta<0.2$ and $T_s>200$ K, $s$ drops proportional to $(1-\theta)$.

(3) Above $\theta=0.23$, $s$ drops sharply for $T_s>200$ K up to $\theta=0.36$ where the decrease becomes weaker; a second strong decrease sets in around $\theta=0.45$, leading to $s<10^{-2}$ above $\theta=0.55$.

(4) For $T_s<200$ K the initial decrease is weaker and the first strong decrease less pronounced. At $T_s=100$ K the weakly decreasing part leads up to $\theta=0.5$ and only one strong decrease above that coverage follows.

The results can be understood in terms of direct and precursor-mediated adsorption. Up to $\theta=0.2$ and $T_s>200$ K, direct adsorption with participation of *all* uncovered sites is the most likely explanation; the fact that the interactionally blocked next neighbor sites *do* contribute can be understood from a consideration of the likely adsorption path. However, adsorption via a "dynamical precursor" (molecules temporarily trapped above the surface plane by selective adsorption) cannot be ruled out.

At higher coverages, true intrinsic precursors, i.e., oriented weakly chemisorbed molecules above empty sites not accessible for chemisorption and separated from accessible sites by chemisorbed molecules, become important for sticking. The properties of these precursor molecules change strongly with chemisorption coverage; in particular there is a drastic difference between $\theta$ below and above total filling of the $\sqrt{3}$ structure as permanent compression of the layer is necessary above that coverage. The transition is smeared out, however, probably because of nonequilibrium effects between terraces. At very high coverages ($\theta>0.61$), adsorption can only proceed by fluctuations in the compressed layer; therefore $s$ drops below $10^{-2}$.

The contributions of extrinsic precursors (physisorbed molecules on top of the chemisorbed layer which can be considered as vibration-rotational excitations of the intrinsic precursor in the strongly anharmonic potential, forced by the blocking of the ground state, and which also serve as transition states in the migration of the intrinsic precursor) smears out the various structures at $T_s<200$ K and leads to a weak linear coverage dependence up to $\theta=0.5$ at $T_s=100$ K.

The improved sticking coefficient data and the developed concepts for the mechanism of adsorbate interactions make the derivation of a new structural model for the $2\sqrt{3}$ structure possible, in which only six instead of seven CO molecules per unit cell are contained and which consists of three domains of a $2\sqrt{3}$

$\times\sqrt{3}R\,30°$ chain structure.

As a generalization of the consideration of precursor contributions, it is suggested that intrinsic precursors in the classical sense are expected to exist for molecular adsorption only at coverages high enough for strong interactional effects to occur. At zero coverage, only dynamical precursors or direct adsorption paths are likely to exist. Vertical interactions, i.e., influences of the properties of the chemisorbed layer on the transient species occurring during adsorption, are thus important for adsorption kinetics, and explain the influence of changes in the chemisorbed layer (e.g., phase transitions) on sticking.

## ACKNOWLEDGMENTS

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## APPENDIX A: COVERAGE CALIBRATION, INFLUENCE OF THE VIBRATING CAPACITOR ON ADSORPTION, AND ABSOLUTE STICKING COEFFICIENT AT ZERO COVERAGE

For the $\Delta\phi(\theta)$ calibration shown in Fig. 1 and Eq. (1) and used for the evaluation of the results, the coverage prepared by some dose was characterized by the $\Delta\phi$ value induced by it; then the crystal was moved 5 mm in front of the quadrupole aperature and a desorption spectrum was obtained by heating the crystal linearly with 5 K/s. The rise in partial pressure was digitally recorded and the desorption spectrum was integrated after subtraction of the small background (which was always less than 3% of the maximum desorption rate; as it pumped down slowly, it was set proportional to the amount already desorbed). The deviations from linearity for $\Delta\phi > 440$ mV (Fig. 1) became also obvious in comparing thermal desorption spectra monitored by the partial pressure rise and by $\Delta\phi$ changes (see Ref. 12).

For the $\Delta\phi(\theta)$ calibration the exact doses used for a certain coverage were unimportant. For the main purpose of this work, determination of accurate $s$ values, exact doses to the crystal have to be known, of course. To achieve this, the shielding effect of the crystal by the counterelectrode positioned in front of it during continuous $\Delta\phi$ measurements has to be eliminated. Even for a counterelectrode mainly consisting of a thin grid, this effect is not negligible, especially as it is coverage dependent, i.e., changes during an adsorption run. The advantage of simple and continuous coverage measurements with the vibrating capacitor is thus partly compensated by the necessity of a more complicated evaluation of adsorption runs. On the other hand, this shielding offers a possibility to evaluate high striking coefficients absolutely, as shown in the following.

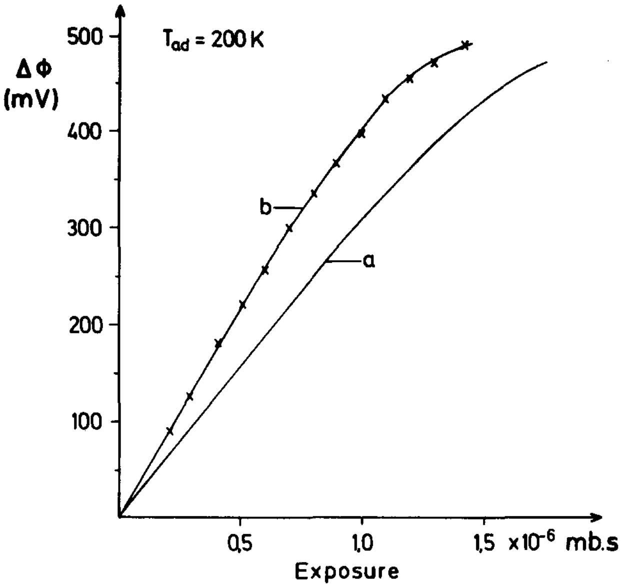

FIG. 6. Shielding effect of the vibrating counterelectrode: Work function changes as function of exposure at $T_{ad} = 200$ K. Curve *a*: full shielding (minimum distance sample electrode). Curve *b*: no shielding (counter-electrode removed during dosing).

As the ratio of the radius of the capacitor electrode to its distance from the crystal is about 1 : 10 we assume as a first approximation an infinitely extended sample and reference electrode. This is not a bad approximation, as the small lateral losses of once or multiply reflected particles are partly compensated by molecules arriving at the surface at high angles without passing the electrode. Also, spatial inhomogeneties of the shielding effect of the electrode (which consists of a wire ring covered with a thin grid[14]) are neglected for the moment. So the electrode is assumed to shield a constant fraction $x$ of the incoming gas flux $F$. The same happens to the reflected flux $F(1-x)[1-s(\theta)]$. If the contributions of all orders of reflections are summed up, the result for the sticking coefficient is

$$s(\theta) = \frac{\dot{N}(\theta)(1-x)}{F(1-x) - x\dot{N}(\theta)}\,, \tag{A1}$$

$\dot{N}$ is the number of molecules actually adsorbing per unit time and area. If the shielding factor of the electrode is well known, an absolute determination of the sticking coefficient without pressure calibration can be obtained by comparison of measurements with and without hindering of the incoming gas flux. At constant coverage the sticking coefficient without shielding is given by $\dot{N}_0/F$. Elimination of $F$ from Eq. (A1) yields

$$s = (\dot{N}_0/\dot{N} - 1)(1-x)/x\,. \tag{A2}$$

An example for the application of this equation can be shown using the data of Fig. 6, where two $\Delta\phi$ vs exposure curves, taken at $T = 200$ K, are plotted. Curve *a* corresponds to full shielding (counterelectrode in place throughout the adsorption run), curve *b* was measured pointwise without any influence of the electrode on the impinging gas flux. To achieve the latter condition, the crystal was moved away from the counter electrode for dosing so that the gas flow was unimpeded.

After completing a certain dose, the crystal was moved back in front of the vibrator to measure the induced $\Delta\phi$. To check the relative coverage in both cases, the crystal was finally moved in front of the quadrupole and a thermal desorption spectrum taken and integrated as described above. From the known geometry of the electrode the average shielding factor was calculated to be 37%. Putting this factor together with the ratio of the initial slopes of curves *a* and *b* into Eq. (A2) gives a sticking coefficient at zero coverage $s_0$ of 0.66. As exposures were reproducible to better than 5% and the $\Delta\phi$ values are accurate to less than 1 mV the uncertainty of *s* would be expected to be of the order of 5%. However, a somewhat larger error can be introduced by the nonhomogeneity of the electrode and therefore the gas flux, and the neglected edge effects. A small systematic shift to higher values is expected because neglecting these factors overestimates the shielding. Therefore we use $s_0 = 0.7$ (±0.06) in the following as the probable absolute values (the relative error, as judged by the reproducibility, was about 2% to 3%). This determination was consistent with direct determination using the pressure reading. In fact, for this particular measurement the two values coincided even better (+1/−3%), which must be accidental.

## APPENDIX B: FORMAL KINETIC MODEL FOR INTERMEDIATE TO HIGH COVERAGES

The model according to Fig. 4 contains the two intrinsic precursors $I'$ and $I''$. In the range $0.2 < \theta < 0.33$ they will both contribute. Confining ourselves to $T_s > 200$ K where the contribution of the extrinsic precursor is negligible, we only have to account for the exclusion of sites by *C*. We use the nomenclature of Fig. 4. The probabilities of finding precursor states $I'$ and $I''$ are given by

$$F' = 1 - n\theta;\quad F'' = (n-1)\theta;\quad F' + F'' = 1 - \theta\ , \tag{B1}$$

where *n* is the average number of sites excluded by adsorption of one aditional chemisorbed molecule ($n = 7$ for $\theta = 0$, $n = 3$ for $\theta = 0.33$, with a gradual change-over depending on the distribution of islands of chemisorbed molecules). The average probabilities $F'_m$ that a precursor $I'$, in moving, moves to $I''$, and $F''_m$ for the reverse process are given by

$$F'_m + F''_m = 1;\quad F'_m = (n-1)\theta/(1-\theta);\quad F''_m = (1 - n\theta)/(1-\theta)\ . \tag{B2}$$

The adsorption probabilities $F'_a$ and $F''_a$ are set = 1 as chemisorption is possible from any intrinsic precursor (with different rate constants, of course); $\alpha' = \alpha''$ is assumed for reasons given above. We then get for the sticking coefficient:

$$S = \alpha \cdot \frac{k'_a(1-n\theta)(k''_d + k''_a + k''_m) + k''_a(n-1)\theta(k'_d + k'_a + k'_m)}{\left[k'_d + k'_a + k'_m\dfrac{(n-1)\theta}{1-\theta}\right]\left[k''_d + k''_a + \dfrac{k''_m(k'_d + k'_a)\dfrac{1-n\theta}{1-\theta}}{k'_d + k'_a + k'_m\dfrac{(n-1)\theta}{1-\theta}}\right]}\ . \tag{B3}$$

For small coverages this model and the one previously used give identical results for $T_s > 200$ K, as it must because we make equivalent assumptions: For chemisorption from $I'$ and migration from $I''$ to $I'$ (and vice versa) fast compared to all other rate constants we again get Eq. (6).

For coverages $\theta > 0.2$, however, we are now able to describe the deviations from the $(1-\theta)$ dependence of *s* and the now appreciable temperature dependence.

As $k''_m$ and $k'_m$, taken as averages, decrease with increasing coverage, we must now assume

$k'_a \gg k'_m,\ k'_d,\ k''_m,\ k''_d,\ k''_a$. This gives

$$s = \alpha \cdot \frac{(1-n\theta)(k''_d + k''_a + k''_m) + k''_a(n-1)\theta}{k''_d + k''_a + k''_m\dfrac{1-n\theta}{1-\theta}}\ . \tag{B4}$$

Near $\theta = 0.33$, $n = 3$:

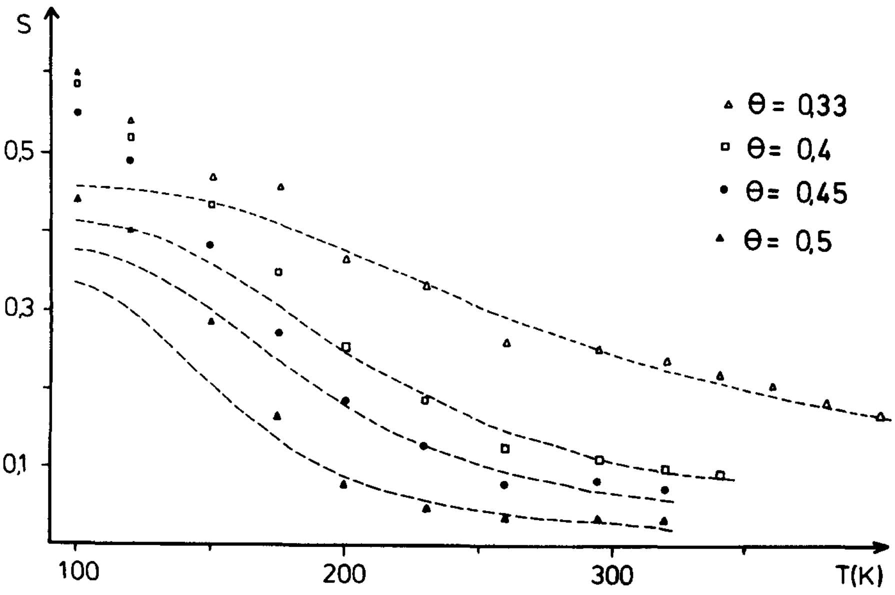

FIG. 7. Fit of the experimental temperature dependences of *s* at fixed coverages above 0.33, to Eq. (B5) (first term). The calculated values (dashed curves) must necessarily lie above the experimental points for $T < 200$ K as the influence of the extrinsic precursor has been neglected in the calculation.

$$s = \alpha \cdot \frac{(1-\theta)k_a'' + (1-3\theta)(k_d'' + k_a'')}{k_d'' + k_a'' + k_m'' \dfrac{1-3\theta}{1-\theta}} \; . \qquad \text{(B5)}$$

As expected, only the ratios of rate constants from $I''$, apart from the directly coverage dependent terms, now determine the adsorption probability. As essentially every molecule arriving in $I'$ is chemisorbed, $I'$ is only contained in the directly coverage dependent terms. Depending on the ratio of $k_m''$ to the other rate constants of $I''$ the onset of deviations from the $(1-\theta)$ dependence of $s$ shifts in coverage.

On approaching $\theta = 0.33$ the second term of Eq. (B5) goes to zero as no $I'$ precursor sites are available any more. Indeed at this coverage there is again a situation with only a single intrinsic precursor ($I''$) and we therefore get an equation similar to Eq. (3), but now the assumption $k_a'' \gg k_d''$ is not valid because of the activation energy necessary for chemisorption. Consequently $s$ is now temperature dependent and reduced to values which depend on the ratio of the rate constants of $I''$. Indeed the experimental data of $T_s > 200$ K show a second region of slow decrease with $\theta$ in this range. However, this region is reached at about 0.36, i.e., at 10% higher coverage than expected, and the point of inflection of this plateau moves to lower coverages at higher temperatures. This seems to suggest that even at 340 K areas with local concentrations below and above 0.33 coexist during the adsorption process. This is probably due to the existence of terraces (of about 150 Å width[10]) which equilibrate only slowly with each other. Second, the $\theta$ dependence of the second plateau is somewhat steeper than $(1-\theta)$ at all $T_s > 200$ K. This can be explained by variations of the (average) rate constants with coverage or by the appearance of "new" precursor states, as discussed.

Around $\theta = 0.33$ there is essentially only one precursor state and assuming as a first approximation that its properties do not change much up to $\theta = 0.5$ we tried to fit the measured temperature dependences for $0.33 < \theta < 0.5$ by varying the difference of activation energies $E_d - E_a$ and the ratio of $(k_d'')_0$ to $(k_a'')_0$ using the first term of Eq. (B5). This is possible for $T_s > 200$ K with a single value of $E_d - E_a$ of 7 kJ/mol. This means that for $\theta > 0.33$ the adsorption from $I''$ to $C$ takes place via an activation barrier which is only a few kJ below the value for infinite separation. Figure 7 compares values calculated with these assumptions with the experimental results for fixed $\theta$. Below 200 K the calculated curves must necessarily lie below the experimeltal values because the influence of the extrinsic precursor, which is no longer negligible, has not been included in the calculation. The difference at 100 K between theoretical curves and measured points is somewhat smaller than expected from our former estimate of $\alpha_e$. The ratio of the preexponentials of the rate constants $(k_d'')_0$ to $(k_a'')_0$ is found to change from 15 : 1 at $\theta = 0.33$ to 200 : 1 at $\theta = 0.5$. This can be understood by the assumption that a favorable site for chemisorption at $\theta > 0.33$ has no molecules as neighbors which have already been shifted from the $\sqrt{3}$ sites (Fig. 5). Then the number of favorable $I''$ sites decreases more rapidly than $\sim(1-\theta)$, so that an additional decrease becomes noticeable in $(k_a'')_0$.

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[21] It is interesting to note here another consequence of our results. Our measurements show clearly that the optimal coverage for the "$2\sqrt{3} \times 2\sqrt{3} - R\ 30°$" structure is smaller than the value of 0.58 which was assumed in a previously published model (Ref. 8) because in that work a constant sticking coefficient up to this coverage had been assumed. Our data show that, even at 100 K, $s$ decreases slightly from $\theta = 0$ on, and a sharp decrease sets in before $\theta = 0.5$. We therefore conclude that the optimal coverage for this LEED structure is $\theta = 0.5$ and the unit mesh of this structure contains only six molecules instead of seven. A possible model for this structure based on this finding and compatible with other aspects of this work is shown in Fig. 5(c).

[22] Such an activation barrier is formed most clearly in dissociative adsorption. In molecular adsorption, a barrier can derive from interactional effects at sufficiently high converages, as in our case. It should be noted that even at zero coverage the existence of a barrier is not excluded here; it could derive from a necessity of rehybridization of the system for formation of the chemisorption bond.

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