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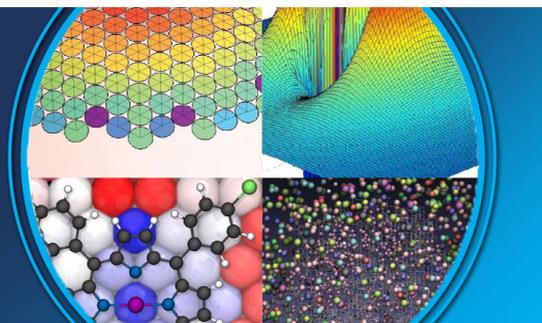
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PERSPECTIVES



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

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A variety of methods [temperature programmed desorption via pressure rise and via work function changes ( $\Delta\phi$ ); isothermal desorption via  $\Delta\phi$ ; quasiequilibrium measurements via isobars monitored by  $\Delta\phi$ , in combination with sticking coefficients] has been used to obtain detailed data on the coverage dependence of the adsorption equilibrium and desorption kinetics for CO on the basal Ru(001) face. While the deviation from reversibility varies strongly over these methods, no significant influence of the degree of irreversibility on the results has been found. Desorption energies and isosteric heats are constant at 160 kJ/mol for  $0 < \theta < 0.2$ , then rise slowly up to 175 kJ/mol at  $\theta = 0.33$ , where they fall abruptly to 120 kJ/mol and more gradually at higher coverage. The "first order" frequency factor (Arrhenius preexponential normalized by the coverage) is  $10^{16} \text{ s}^{-1}$  at  $\theta = 0$ , rises precipitously, especially in the range  $0.2 < \theta < 0.33$ , to  $10^{19} \text{ s}^{-1}$  at  $\theta \approx 0.33$ , where it drops abruptly to  $\approx 10^{14} \text{ s}^{-1}$ . The main conclusions drawn are: (1) The dependence on coverage of the desorption energies and preexponentials can be understood in terms of the equilibrium statistical mechanics of the chemisorption layer, governed by lateral adsorbate-adsorbate interactions. In particular, the high preexponentials and their strong increase close to  $\theta = 0.33$  are due to strong localization in the adlayer. (2) No strong influence of precursor kinetics exists in desorption. (3) Possible dynamic effects have constant influence throughout the range of measurements and can be described by the behavior of the sticking coefficient. These conclusions are discussed in connection with other recent findings.

## I. INTRODUCTION

In part I of this work<sup>1</sup> detailed measurements for the dependences of the sticking coefficient of CO on Ru(001) on coverage and surface temperature have been reported and discussed in terms of the structural properties of the chemisorbed layer (which in turn are defined by lateral interactions) and the influence of chemisorption coverage on the existence and properties of precursor states (vertical interactions). Here we report the results of detailed coverage and temperature dependent measurements of desorption kinetics and equilibrium for the same system, obtained with a variety of independent methods which serve to check each other's results and differ considerably in their distance from reversibility. The main results have been published before in short form together with an abridged discussion.<sup>2</sup> Here we give experimental and interpretational details and improve the evaluation and interpretation by drawing on the results of paper I.<sup>1</sup>

From the earliest days of kinetic and equilibrium measurements on adsorption layers it has been realized that the derived parameters—enthalpies and entropies of adsorption, and activation energies and preexponentials of desorption—will, in general, be coverage dependent, expressing the energetics and statistics of lateral interactions. For instance, Taylor and Langmuir<sup>3</sup> have given detailed coverage dependent data for Cs/W as early as 1933. Nevertheless, a large fraction of publications on these topics neglects this dependence. While the coverage dependence of the adsorption energy is more often observed, there are only relatively few publications where the coverage dependence of the desorption preexponential is considered in detail (e.g. see below). Also,

while well-known statistical mechanical arguments lead to the expectation of high desorption preexponentials from localized adsorption, and some reports of preexponentials up to  $10^{16} \text{ s}^{-1}$  for unimolecular desorption existed in the literature prior to Ref. 2, only recently very high values and strong coverage dependences have been reported. Furthermore, the possible influences of intermediate states (precursors) and of dynamic effects on desorption—questions which have found considerable interest recently—can be examined using our data.

## II. EXPERIMENTAL

### A. Experimental equipment

The experiments were done in a standard stainless steel UHV chamber, pumped by an ion getter pump and a titanium sublimation pump. The base pressure was about  $5 \times 10^{-11}$  mb. At a later stage an additional oil diffusion pump was installed which made it possible to reduce the base pressure to  $1 \times 10^{-11}$  mb. The chamber was equipped with LEED/Auger optics, a quadrupole mass spectrometer QMG 111 (Balzers) and a vibrating capacitor. Details of this type of vibrating capacitor are described in Ref. 4. It is operated in a self-compensating circuit by using a lock-in amplifier. The main advantages over other designs are short time constants ( $< 20$  ms), high accuracy for the measured work function changes (0.1 mV at 1 Hz bandwidth), low noise level (1 mV rms undamped), and the possibility to heat the sample during measurement. The electrode of this capacitor consisted of a small ring, 4 mm in diameter, made of 0.25 mm tungsten wire. A fine grid of stainless steel (optical transmission 80%) was spanned over

the ring, and the assembly covered with tin oxide so that there were no work function changes on the electrode by gas adsorption at pressures up to  $10^{-4}$  mb. In order to precisely calibrate work function changes against coverage<sup>1</sup> the quadrupole, used for the reported  $\Delta p$  measurements, was replaced by a Balzers QMG 311 with glass shield around the ionization chamber.<sup>5</sup> The crystal was prepared as reported previously.<sup>1</sup> It could be resistively heated and cooled with liquid nitrogen down to 80 K. An electronic temperature controller allowed the temperature to be held constant to better than 0.1 K. The temperature could be linearly swept up and down at heating rates between 0.01 and 50 K/s.

## B. Experimental procedures and evaluation

### 1. General

Kinetic and equilibrium measurements of gas adsorption on surfaces necessarily require a possibility to monitor the momentary coverage on the surface as a function of conditions (temperatures of gas and surface, ambient pressure, and possibly other parameters). For temperature programmed desorption (TPD)<sup>6</sup> via pressure rise ( $\Delta p$ -TPD) which to date is the most used method to determine desorption kinetics,<sup>7-9</sup> the ambient base pressure is usually negligibly small and one measures the change in coverage by monitoring the partial pressure rise  $\Delta p$  in the vacuum chamber caused by desorbing gas from the surface, and establishing a mass balance. The actual coverage at any given instance is then obtained by integration of parts of such desorption spectra. There are numerous methods to evaluate such measurements<sup>6-14</sup> some of which can be used to extract coverage dependent parameters (see in particular Refs. 9-14). The disadvantages of this method are the limitations of usable heating rates, the possible interactions of the gas molecules with walls, pumps, and pressure measuring devices (reversible adsorption-desorption, displacement, and reactions) which can lead to disturbances, and—for single crystal samples—the fact that contributions from differently oriented parts of the crystal (mainly the rim) and from the crystal mounting are difficult to be clearly separated from desorption from the well ordered sample regions. All these effects limit the obtainable resolution which in turn degrades the accuracy of the derived kinetic parameters. Most of these problems can be overcome by using a shielded quadrupole mass spectrometer which only allows molecules desorbing from the central part of the crystal to enter the ionization chamber of the QMS.<sup>5</sup>

A much greater variety of information is offered by measuring directly the changing coverage. In this way not only TPD is possible, but measurements of sticking coefficients, isothermal desorption (ID), and equilibrium measurements with the gas phase can be done as well. Isothermal desorption has been done quite early as well as more recently by several workers using different coverage parameters<sup>15,16</sup>; as  $\Delta p$  cannot be used here, this mode of measurement is not widespread. Measurements of equilibrium (or rather quasiequilibrium; see below) isosters also go back to Langmuir<sup>3</sup>; they are frequently used for coverage-dependent enthalpy determinations.

For many systems a precise and flexible tool to record coverages is given by the work function change  $\Delta\phi$  which is often related uniquely to coverage and big enough to give a precise measure of coverage. For determination of isosteric heats,  $\Delta\phi$  is the usual coverage parameter; for macroscopic single crystals this method has been introduced by Tracy and Palmberg.<sup>17</sup>

$\Delta\phi$  is also an excellent coverage monitor for isothermal desorption.<sup>16</sup> To our knowledge, the application of  $\Delta\phi$  in TPD measurements was introduced by us.<sup>2,5,18</sup> For CO on Ru(001) the saturation coverage of  $\Theta_s = 0.68$  (relative to Ru surface atoms) corresponds to  $\Delta\phi = 780$  mV, and the exact coverage dependence is well known. Therefore the quasiequilibrium and most kinetic measurements described below were done using  $\Delta\phi$ . For comparison,  $\Delta p$ -TPD with the improved method<sup>5</sup> was also done.

### 2. Desorption experiments

The Arrhenius equation, the basic ansatz for all desorption experiments, can be rewritten (for molecularity<sup>14,19</sup> as CO is only molecularly adsorbed on Ru(001)<sup>20</sup> as

$$-E_{\text{eff}}/kT_s = \ln r_d - \ln r_{d0} = \ln r_d - \ln [N_{\text{ad}} k_{01}(\Theta, T_s)], \quad (1)$$

where  $r_d$  is the rate of desorption and  $r_{d0}$  its nonexponential part,  $N_{\text{ad}}$  is the surface density of adsorbate, and  $k_{01}$  the normalized preexponential.<sup>19</sup> As the relevant temperature throughout this work is the surface temperature, we omit the suffix  $s$  in the following and simply write  $T$  for the variable. The gas temperature was always about 295 K. The effective desorption energy  $E_{\text{eff}}$  is not necessarily equal to the binding energy  $E_B$ , even for nonactivated adsorption, as desorption occurs irreversibly and precursor influences are possible.<sup>1,14,21,22</sup> A comparison to the results of measurements in (or close to) equilibrium with the gas phase is therefore instructive and discrepancies in the results or their absence can give further insight into the desorption mechanism. In some recent theoretical work, where the microscopic details of the excitation process by phonons for a desorbing particle are studied,<sup>23</sup> systematic deviations from the Arrhenius law are found, but these become obvious only if large temperature ranges are observed. For sticking coefficients varying not too abruptly with  $T$  the Arrhenius law is well fulfilled over limited temperature ranges and the deviations of the effective desorption energies from the barrier height are of the order  $kT$ . Measuring tolerances are of the same magnitude so that these deviations would be difficult to detect.

With the assumption that for a small range of temperature—a variation of typically 10% of the absolute temperature at constant coverage is experimentally possible— $k_0$  is essentially independent of temperature (see also discussion) the slope of the logarithmic straight line,  $\ln r_d$  vs  $1/T$ , at constant coverage  $\Theta$  (desorption isoster) gives  $E_{\text{eff}}$  and the extrapolation  $1/T \rightarrow 0$  the preexponential factor. This kind of evaluation requires the knowledge of  $r_d$  and of the remaining coverage on the surface simultaneously. Both can easily be determined

by  $\Delta\phi$  measurements, whereas in  $\Delta p$  measurements the latter can be found only by back integration which is much more problematic because of the reasons mentioned above.

Many evaluations of desorption experiments have assumed a constant order of desorption, i. e., that the coverage-dependent part of  $r_d$  is contained totally in a term  $N^x$  where  $x$  is an integer and constant<sup>10</sup>;  $E_{\text{eff}}$  and  $k_0$  should then be essentially coverage independent, at least over certain ranges (for certain states). Generally speaking, however, both  $k_0$  and  $E_{\text{eff}}$  have to be expected to be coverage dependent, as stressed above, possibly even strongly, and it is the main aim of our work to obtain exact coverage dependences of these parameters. It is necessary for this to have extensive data of  $r_d$  as functions of  $\Theta$  and  $T$ . One possible way to obtain such data sets is to change  $T_s$  stepwise to a certain value where the chosen initial coverage is unstable, and then to follow  $r_d(\Theta)$  at constant  $T_s$ ; with different  $\Theta_0$  and  $T$  values a large data field can be obtained.<sup>16</sup> Such *isothermal desorption runs* would be very difficult if not impossible by  $\Delta p$  measurements. A change in desorption rates at constant coverage can also be achieved in *temperature programmed* desorption by changing either the initial coverage at constant heating rates<sup>11</sup> or by varying the heating rates at constant initial coverage.<sup>10,13</sup> The implicit assumption for all these evaluations is that at equal residual coverage and temperature there always exists the same state on the surface, independent of heating rates, i. e., there is internal equilibrium on the surface. This also means that the shape of desorption curves is independent of heating rates. A special case of the latter method is considered by Falconer and Madix who use the temperature of the desorption maximum  $T_p$  and vary the heating rates  $\beta$ .<sup>12</sup> A plot of  $\ln \beta/T^2$  vs  $1/T$  gives again a straight line with slope  $E_{\text{eff}}$ . In order to get  $k_0$  in the same way as described above one must additionally assume here that  $E_{\text{eff}}$  is only slowly varying with coverage.<sup>18</sup> This method can be easily applied also to  $\Delta p$ -TPD as here the background is no severe problem. The measurement via  $\Delta\phi$  is again more advantageous, however, as limitations of heating rates are avoided in this way.<sup>2,18</sup>

*Use of  $\Delta\phi$  as coverage indicator.* The calibration curve  $\Delta\phi(\Theta)$  obtained in adsorption<sup>1</sup> can be checked directly by desorption to exclude any temperature or shielding effects. If  $\Delta\phi$  varies linearly with coverage as is *exactly* correct up to  $\Theta=0.33$  in this system, the rate of adsorption or desorption is simply proportional to  $d(\Delta\phi)/dt$  which can be obtained by direct electronic differentiation of the lock-in output. Figure 1 shows comparisons of TPD spectra for medium and high coverages, obtained in the way just described (dashed) and via the partial pressure rise  $\Delta p$  (full lines) using the shielded quadrupole mass spectrometer. These curves were only adjusted for equal peak maxima. A background of less than 3% of the maximum desorption rate was subtracted in the  $\Delta p$  plots, which was assumed to be proportional to the amount already desorbed. This seems to slightly overestimate the influence of the background and leads to a too sharp cutoff at the high temperature end of the  $\Delta p$  spectra. These spectra corroborate

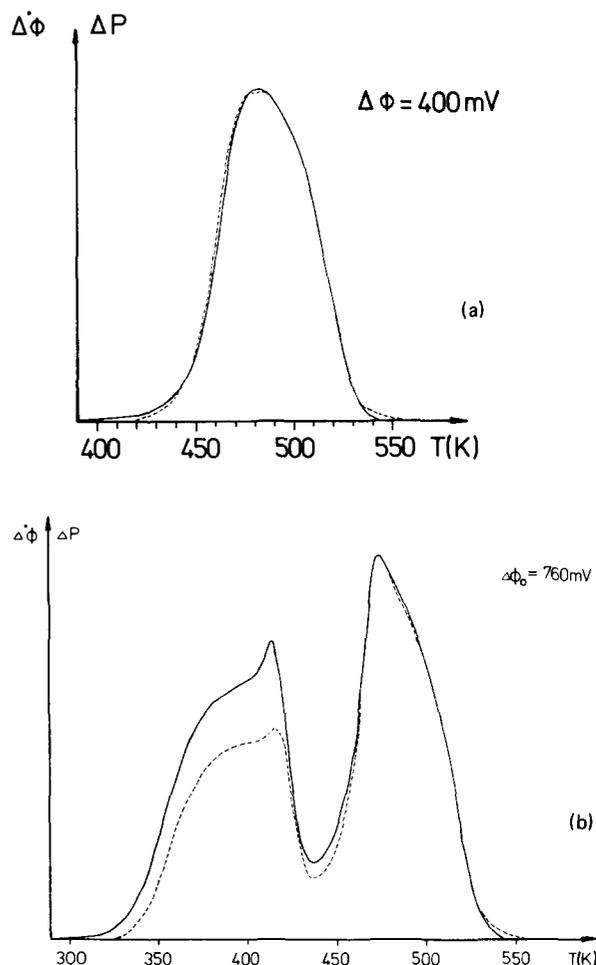


FIG. 1. Comparison of thermal desorption spectra obtained via partial pressure rise ( $\Delta p$ -TPD; full lines) and work function change ( $\Delta\phi$ -TPD; dashed lines) for two initial coverages corresponding to (a)  $\Theta \approx 0.30$ ; (b)  $\Theta \approx 0.68$  (saturation).

the strict proportionality of  $\Delta\phi$  and  $\Theta$  up to  $\Theta=0.33$ , even when the temperature is changing. Clear deviations are found at higher coverages. These findings are consistent with the  $\Delta\phi$  vs coverage calibration<sup>1</sup> and were used as additional information for this calibration there. Correction of the data for the different  $\Theta - \Delta\phi$  relation in this range<sup>1</sup> fully accounts for this effect, so that no measurable influence of the changed temperature on the  $\Delta\phi$  measurements exists in this range either (see also below, Sec. IIB 3). The exact conformity of the high temperature peaks in these spectra (within a tolerance of  $\pm 1$  K on the temperature axis) also shows that shielding effects by the vibrating counterelectrode (positioned about 0.2 mm before the sample surface)<sup>1</sup> have no measurable influence. This can be exactly correct only for measurements in equilibrium with the gas phase as there equal numbers of gas particles are reflected from both sides of the electrode. Under desorption conditions, where the ambient pressure is negligible, the electrode reflects a fraction  $x$  of the desorbing flux which can stick again on the surface with probability  $s$ ; the measured desorption rate could thus be reduced. The results of Fig. 1 and similar others show that this is not

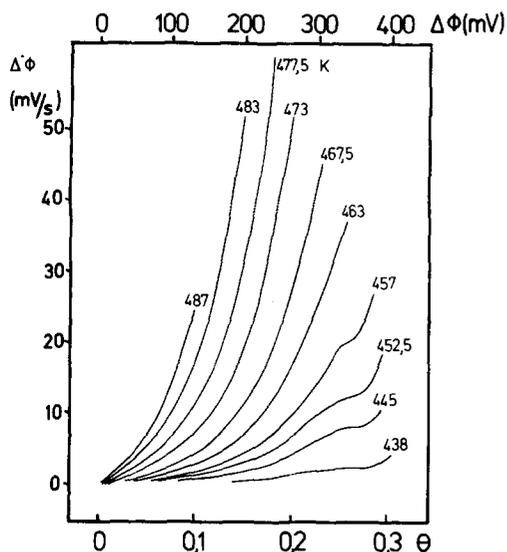


FIG. 2. Isothermal desorption traces at various temperatures for the regime below  $\Theta = 0.30$ . In time, the curves are run through from right to left.

the case. Closer examination (see Appendix A) explains this finding.

**Procedures for isothermal desorption.** Ideally the crystal should be heated stepwise and without overshoot to a temperature which should then be maintained constant during the desorption measurement. As this is, of course, not possible, the following procedure was adopted. After adsorption of about 0.6 of a monolayer at  $150 < T < 250$  K for the investigation of the coverage range  $\Theta < 0.33$ , or of a saturation layer at  $T_{\text{ad}} < 170$  K for higher coverages, the crystal was linearly heated to the desired desorption temperature with 35 K/s in the former and with 25 K/s in the latter cases in order to avoid large overshooting. Typically after 2 s, when the temperature had reached its end value to better than 0.2 K, the measurement was started and  $d(\Delta\phi)/dt$  against  $\Delta\phi$  was recorded. Desorption rates between 0.2 and 20 mV/s (corresponding to about  $2 \times 10^{-4}$  to

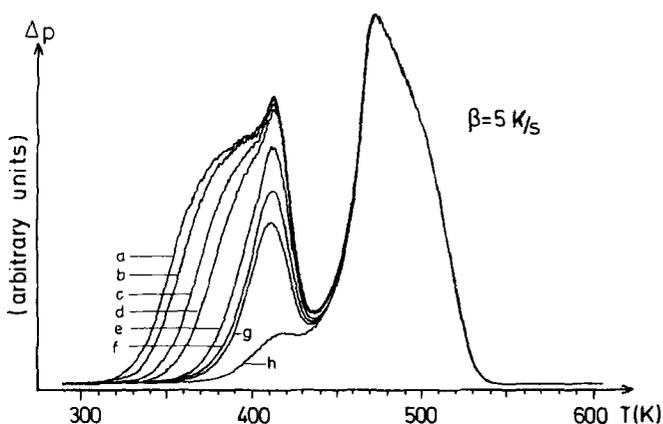


FIG. 3.  $\Delta p$ -TPD traces for various initial coverages of (a) 0.66; (b) 0.63; (c) 0.58; (d) 0.54; (e) 0.49; (f) 0.45; (g) 0.43; (h) 0.38.

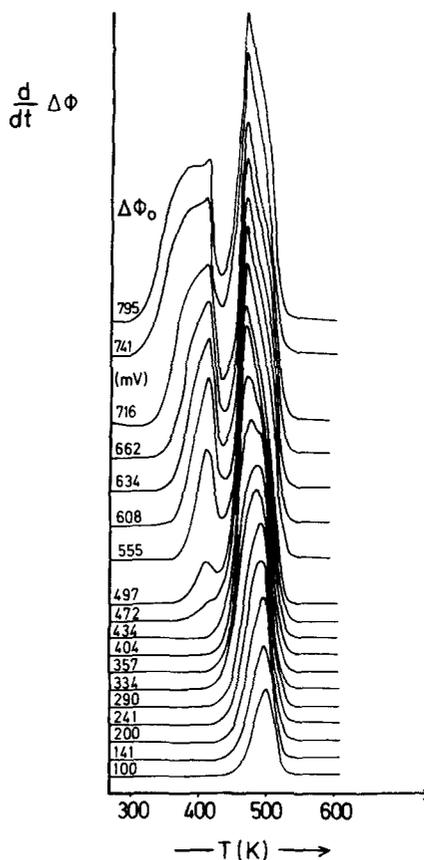


FIG. 4.  $\Delta\phi$ -TPD traces for various initial coverages given by the initial  $\Delta\phi$  value.

$2 \times 10^{-2}$  monolayer/s) could be measured to better than 3%–5%. A set of such curves for  $\Theta < 0.33$  is shown in Fig. 2. The evaluation is then done by cuts at constant  $\Theta$  and plots of desorption isosters, according to Eq. (1). The desorption energy can always be taken directly from the slope; the  $k_0$  value obtained from the intercept has to be corrected in the range where the  $\Delta\phi - \Theta$  relation is no longer strictly linear. The correction can be avoided if  $\ln[d(\Delta\phi)/\Delta\phi \cdot dt]$  is plotted against  $1/T$ , as the nonlinearity of  $\Delta\phi(\Theta)$  then cancels out.

**TPD; variation of initial coverage.** Starting with many different coverages, TPD spectra were taken either via  $\Delta p$  according to Ref. 4, or via  $d(\Delta\phi)/dt$ . Figures 3 and 4 show examples for such sets of spectra. For isosteric evaluation of  $\Delta p$  data, the residual coverage has to be obtained in each point by integration over the rest of the trace; in the  $\Delta\phi$  mode, the  $\Delta\phi$  values can be recorded simultaneously with their time derivative. In both cases, curves of  $\ln[\Theta/(d\Theta/dt)]$  as a function of  $\Theta$  can be constructed, with  $T$  as parameter (see Fig. 5), as suggested before by Bauer.<sup>11</sup> Vertical cuts yield again desorption isosters, from which  $E_{\text{eff}}(\Theta)$  and  $k_0(\Theta)$  are taken as above.

**TPD; variation of heating rates.** The special case of Ref. 12 was used. As many measurements with one initial coverage are necessary to obtain one  $E - k_0$  pair, this type of evaluation was used for two different coverages only; for both,  $\Delta\phi$  and  $\Delta p$  measurements were

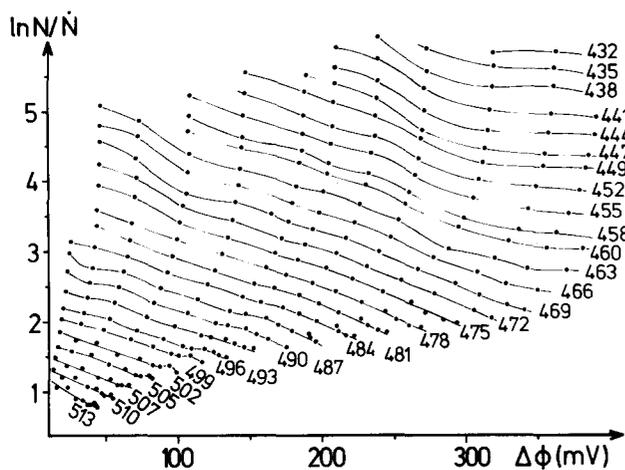


FIG. 5. Desorption isotherms (Ref. 11) obtained from TPD via the procedures described in the text. Parameter: Surface temperature.

carried out. For  $\Delta p$ , the unshielded mass spectrometer was used. Because of the limitations imposed by the background (here about 20% of the desorption maximum at  $\beta = 5$  K/s), and the pumping speed, the usable range of  $\beta$  was only between 0.2 and 20 K/s. In  $\Delta\phi$  runs, these limitations do not exist, and rates from 0.05 to 50 K/s were applied. Figure 6 shows a plot of  $\ln \beta/T_p^2$  vs  $1/T$  for such a series, from which  $E_{eff}$  and  $k_0$  are obtained according to Ref. 12. Curve sets obtained by  $\beta$  variation can also be evaluated isothermally (see above and<sup>13</sup>); this has not been done here.

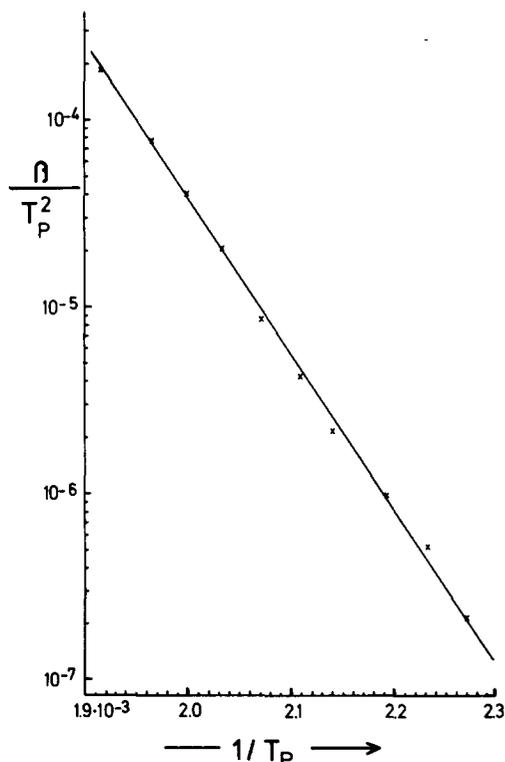


FIG. 6. Evaluation of TPD peak temperatures according to Ref. 12, for a  $\Delta\phi$ -TPD series.

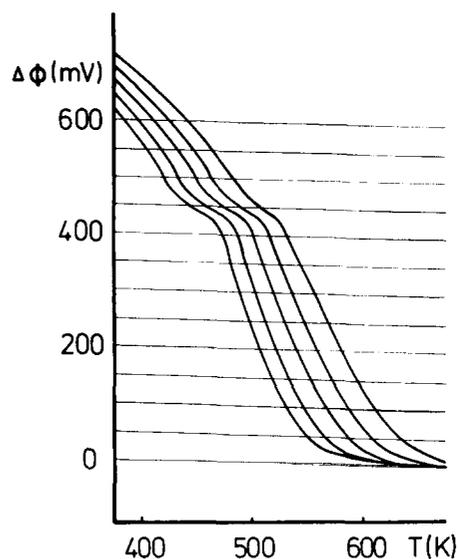


FIG. 7. Quasiequilibrium isobars monitored via  $\Delta\phi$ . The thin lines show the temperature dependence of  $\phi$  for which a correction is applied in evaluation.

### 3. Equilibrium with the gas phase

The determination of isosteric heats by variation of  $T$  and  $p$  such that a certain coverage  $\Theta$  is maintained under reversible conditions, and application of the Clausius-Clapeyron (or Vant' Hoff) equation to these data goes back to Langmuir<sup>3</sup> and has been introduced to single crystals by Tracy and Palmberg.<sup>17</sup> To our knowledge, none of the many applications of this procedure has been done under real equilibrium conditions, i. e., for  $T_g = T_s$ , but the varied temperature was always  $T_s$ , while  $T_g$  was held constant at room temperature. Thus, only a steady state or quasiequilibrium is attained. However, it can be shown that the effect on the determined enthalpy is negligibly small under normal conditions.<sup>24</sup> Also, the difference between enthalpies and internal energies for this case is of order  $kT$  and therefore negligibly small.<sup>24</sup> We can therefore directly compare these almost reversible with irreversible (activation) energies; if strong influences of precursors exist, then deviations between these energy values should be found.<sup>14,22</sup>

The usual procedure ( $T_s$  varied;  $T_g$  constant) was therefore used here as well. At constant pressures between  $1.3 \times 10^{-6}$  and  $1.3 \times 10^{-4}$  mb, the sample temperature was varied slowly and work function changes were monitored continuously. The attainment of steady state was checked by comparison of runs with upwards or downwards variation of  $T$ ; heating or cooling rates of 0.5 K/s were slow enough to eliminate any hysteresis. Examples for the resulting isobars are shown in Fig. 7 which also displays the temperature-induced change of  $\phi$  of the clean surface as base lines. In the evaluation, a correction for it was applied.

From the isobars (Fig. 7), isosters were constructed by vertical cuts and plotting  $\ln p$  vs  $1/T$  according to Clausius-Clapeyron's equation. The quasiequilibrium isosteric heat which is equal to the equilibrium  $E_B$  to an accuracy of the order  $kT$  (see above) is obtained

from the slope. If the sticking coefficient  $s$  is known in the range of isobaric measurement and does not vary too strongly with temperature there, one can calculate  $k_0$ —which is thus assumed to be constant over the temperature range involved—by equalization of the rates of adsorption and desorption as has been done by many authors since Langmuir<sup>3,25</sup>:

$$k_0 = s p [(2\pi m k T)^{1/2} N_{ad}]^{-1} \exp(E_B/kT). \quad (2)$$

Our sticking coefficient measurements<sup>1</sup> were necessarily carried out at lower temperatures (100–400 K, as compared to 350–650 K for the equilibrium runs). However, for  $\Theta < 0.3$  the temperature dependence of  $s$  is zero or weak, so that the low temperature values can be used directly with confidence; for higher coverages, the curves of Fig. 3 of Ref. 1 were extrapolated to measuring temperatures. Average values for those  $T$  ranges were then used for calculation of  $k_0$ .

### III. RESULTS

The results derived from all these measurements and evaluations are collected in Fig. 8. The effective desorption energies,  $E_{eff}$  (open symbols), and the isosteric heats of adsorption (full circles) are shown in Fig. 8(a), whereas Fig. 8(b) shows the corresponding preexponential factors. Despite some scatter in the data both within one single method and between the various types of measurements they all show the same behavior. Near  $\Theta = 0$ ,  $E_{eff}$  or  $E_B$  are about  $160 \pm 6$  kJ/mol. This value is constant up to  $\Theta = 0.2$  where it starts to rise; it finally reaches an average value of 175 kJ/mol at  $\Theta = 0.33$ . However, measurements at exactly this coverage with acceptable accuracy were possible only in equilibrium with the gas phase; the increase of binding energy is most pronounced there. [In the TPD runs a rate minimum obtains there, so that the corresponding values are especially inaccurate; besides, some smearing out seems to occur, as for the sticking coefficients (see Ref. 1).] At this coverage there is a sharp jump of  $E_{eff}$  and similarly of  $E_B$  down to  $\sim 120$  kJ/mol. Up to saturation coverage a further slight decrease to an end value of 110 kJ/mol is observed. The values of  $E_B$ , measured in quasiequilibrium with the gas phase, lie for  $\Theta < 0.25$  slightly below, for  $\Theta > 0.3$  above the results for  $E_{eff}$ . This does not seem to be caused by precursor effects as this behavior is directly coupled to  $k_0$  so that the rates of desorption seem to be equal in equilibrium and in nonequilibrium measurements.

The preexponential factor behaves similarly but in a more pronounced way. It rises with coverage from the beginning; from  $k_0 \approx 2 \times 10^{16} \text{ s}^{-1}$  it increases to about  $1 \times 10^{19} \text{ s}^{-1}$  at  $\Theta = 0.33$ , falling to values around  $10^{14}$  at higher coverages, with a tendency to increase again near saturation coverage.

Accuracy, as judged from linear regression analysis, was best for isothermal desorption and equilibrium measurements. Here the tolerances are  $\pm 5$  kJ/mol for  $E_{eff}$  and  $E_B$ , and  $\pm$  half a power of 10 for  $k_0$ , but possibly up to a factor of 2 larger for higher coverages where  $s$  had to be extrapolated. The TPD data have much higher uncertainties ( $\pm 10$  kJ/mol and  $\pm 1$  order of magnitude,

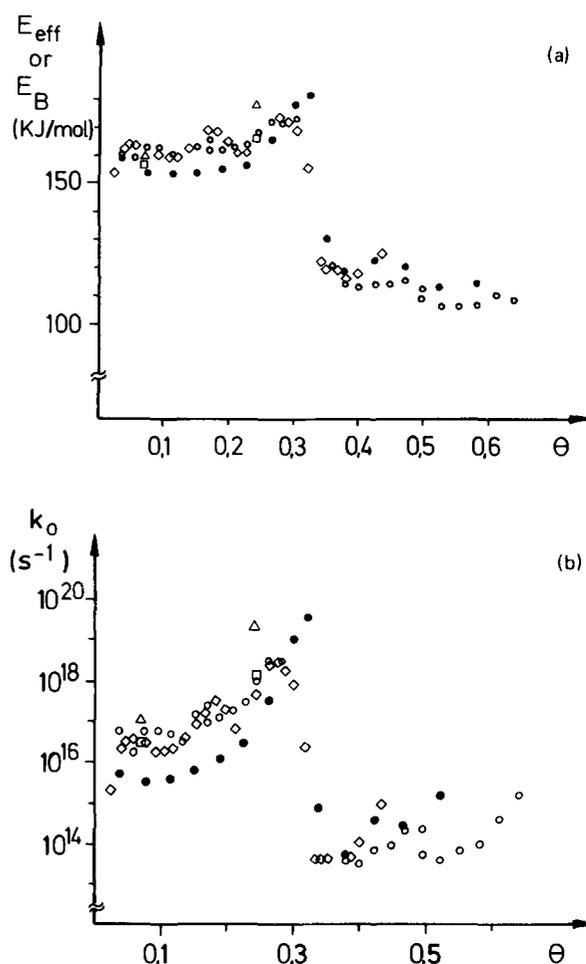


FIG. 8. Compilation of the results for (a) energies and (b) normalized preexponentials of desorption, as function of coverage. Full circles:  $E_B$  from quasiequilibrium data, and  $k_0$  from entropies and sticking coefficients; open symbols: effective desorption energies and preexponentials (circles: isothermal desorption; diamonds:  $\Delta\phi$ -TPD evaluated via desorption isosters; triangles and squares: from peak temperatures in  $\Delta\phi$  and  $\Delta p$ -TPD).

respectively) for several reasons. Firstly, the  $T$  values are known to only  $\pm 0.25$  K; where the peak temperatures are used these are precise only to  $\pm 1.5$  K. Secondly, the desorption rates could not be varied as much in TPD at constant heating rate as in ID, especially at high coverages. These values were not used therefore at  $\Theta > 0.5$ . For TPD via variation of heating rates the high uncertainty in peak temperature cannot be compensated by a variation of the desorption rate by three orders of magnitude and has therefore about the same error bars.

We conclude that no systematic differences can be derived for the results obtained with different degrees of approach to equilibrium, from the strongly irreversible situation of the initial state of ID, via the various heating rates of TPD, to the reversible quasiequilibrium measurements. This also proves that  $(\Theta, T)$  are sufficient to characterize the state of the layer, i.e., that *internal equilibrium* in the layer was always reached irrespective of the mode of measurement.

## IV. DISCUSSION

### A. Comparison to other work

When the first account of this work appeared<sup>2</sup> the measured preexponentials were very high compared to most values published previously. There had been a number of reports of high values,<sup>11,18</sup> and from early on, theoretical considerations had shown that these should be expected for desorption from immobile layers.<sup>25</sup> However, the prevalent view was that of normal preexponentials of  $10^{13} \text{ s}^{-1}$  for unimolecular desorption, and in particular no such strong increases with coverage as found by us had been seen before. Meanwhile similar results have been found for the system CO/Ni(111).<sup>26</sup> The present results differ from those in Ref. 2 only in that greater care has been applied to take into account all possible disturbances and correct for them, and in that more accurate sticking coefficients have become available.<sup>1</sup> All this shows that our results are trustworthy within the given error limits which in turn lends credibility to other reports of high preexponentials of molecular desorption (see the papers cited in Refs. 2 and 26) and suggests that the frequent reports of normal preexponentials (of about  $10^{13} \text{ s}^{-1}$ ) may partially be due to inadequate data collection and/or evaluation. Specifically, conclusions from TPD peak shapes or widths are not considered trustworthy, in particular if obtained via standard  $\Delta p$  measurements with their many sources of distortion and broadening. To give an example: our own early TPD measurements for the present system<sup>27</sup> were of (normal) low quality as well and would not have warranted quantitative conclusions, if considered from the present state of development. We suggest that the situation may be similar in many other reported cases. As a preexponential has to be assumed to deduce desorption energies from TPD peaks, many such energies in the literature are probably too low by about 25% or more.

In our preliminary report,<sup>2</sup> we used transition state theory (TST)<sup>28</sup> for the discussion of the measured preexponentials. However, this treatment does contain some ambiguities, in particular with respect to the interpretation of the transition state. It is advantageous, therefore, to use a simple treatment balancing rates of adsorption and desorption which leads to identical results. The independence of our results of the degree of irreversibility can then be used to draw further conclusions about the mechanisms involved, in particular about the possible role of precursor states.<sup>22</sup>

### B. Energetics and structure

Before discussing this briefly, we want to examine the connection between the existing structural information on this system, known from LEED<sup>27,29-31</sup> and vibrational spectroscopy,<sup>32,33</sup> and our results. According to the cited work, a  $\sqrt{3} \times \sqrt{3} R 30^\circ$  structure grows from  $\Theta \approx 0.08$  on and reaches its maximum intensity and stability at  $\Theta = 0.33$ ; a further increase of  $\Theta$  quickly destroys it. Vibrational spectra<sup>32,33</sup> and LEED-IV analysis<sup>31</sup> have shown that on-top sites are occupied at the superstructure maximum. This means that a rather strong repulsive interaction between CO molecules on

next neighbor (NN) sites prevents their filling. The jump in binding energy found at  $\Theta = 0.33$  gives a lower limit for the strength of this interaction. According to the model advanced in Ref. 1, one additional adsorbed molecule at  $\Theta > 0.33$  has to occupy a site in the center of three molecules in  $\sqrt{3}$  configuration which are shifted apart by the repulsive interaction; probably further relaxation in the neighborhood occurs as well. This leads to the fast destruction of the  $\sqrt{3}$  structure above  $\Theta = 0.33$ . In any case, the molecules do *not* sit on NN sites in the resulting configuration, so that the full NN repulsive interaction does not take effect; on the other hand, the molecules chemisorbed originally have been shifted from their optimal sites which weakens their surface bonds. The jump of about 55 kJ/mol in the isosteric heat at  $\Theta = 0.33$  gives the sum of all these effects. If for simplicity we consider only the three next neighbors of the newly adsorbed molecule to be shifted [see Fig. 7(b) of Ref. 1], then the pairwise repulsive interaction in the shifted state amounts to about 18 kJ/pair. The NN repulsion is certainly considerably higher than that, as seen from the fact that adsorption ceases at  $\Theta \approx 0.68$ , i. e., still far from occupation of NN sites. The finding that isosteric heats and desorption energies are indistinguishable within the error limits shows that upon desorption the leaving molecule can pick up the energy gained when the neighbor molecules snap back into optimal sites. The rise in binding energy between  $\Theta = 0.2$  and 0.33 must be due to an attractive interaction between NNN (near-next neighbors at distance  $a\sqrt{3}$ ). Indeed island formation in adsorption at low temperatures<sup>27,29,30,33,34</sup> is indicative of this. At the high desorption temperatures the order is destroyed up to  $\Theta \approx 0.2$ ; above that coverage a second order transition maintains partial order even up to the measurement temperatures used here, and around  $\Theta = 0.33$  the order is maintained rigidly up to desorption.<sup>29</sup> Indeed the rise of  $E$  starts exactly at the coverage where the phase boundary of the order-disorder transition begins to rise sharply in a temperature vs coverage plot.<sup>29</sup> As the energetic and kinetic measurements sense an average over all configurations, the attractive interaction is gradually turned on with increasing coverage: an increasing part of the desorbing molecules are forced to desorb from configurations with many neighbors in  $\sqrt{3}$  distances and therefore with higher binding energy. At  $\Theta = 0.33$ , desorption occurs from a completely ordered layer. Considering only next neighbor interactions, the pairwise attractive energy at distances  $a\sqrt{3}$  becomes about 2.5 kJ/pair. As there may be contributions from further correlated molecules beyond the first  $\sqrt{3}$  spacing, as well as three-body forces, this estimate constitutes an upper limit.

### C. Preexponentials of desorption and statistics of the chemisorbed layer

We now turn to a consideration of the influence of the statistics of the chemisorbed layer on equilibrium and desorption kinetics and focus on an interpretation of the experimentally found high preexponentials and their strong coverage dependence. Under equilibrium or stationary conditions, the rates of adsorption and desorp-

tion must cancel. The preexponential of desorption is then given by an equation similar to Eq. (2) which can be rewritten as

$$k_0(\Theta) = s(\Theta) (v_g/4) (N_g/N_{ad}) \exp(E_B(\Theta)/RT_s), \quad (2a)$$

where  $v_g = (8kT_g/\pi m)^{1/2}$  is the mean velocity in the gas phase,  $N_g$  and  $N_{ad}$  are the particle concentrations in gas (per volume) and surface (per area), and  $s$ ,  $k_0$ ,  $E$  are assumed roughly  $T$  independent over the range of observation. For truly reversible situations ( $T_s = T_g = T$ ), the quantity  $N_g/N_{ad}$  can be obtained from statistical mechanics; it will always be of the type

$$N_g/N_{ad} = (Q_g/Q_{ad}) f(\Theta) \exp(-E_B/RT), \quad (3)$$

where  $Q_g$  and  $Q_{ad}$  are the single particle partition functions in gas and adsorbate, and  $f(\Theta)$  contains the statistics of the layer. For a localized, oriented adsorbate (no translations or rotations excited in the layer), and negligible internal vibrational excitation in the molecule in gas or layer, we have

$$\begin{aligned} k_0(\Theta) &= s(\Theta) (v_g/4) (q_t^3 q_r / q_v) f(\Theta) \\ &= s(\Theta) (kT/h) (q_t^2 q_r / q_v) f(\Theta), \end{aligned} \quad (4)$$

where  $q_t$  is the partition function per translational degree of freedom,  $q_r$  that for rotation of the gas molecule, and  $q_v$  that for the soft vibrations of the adsorbate (frustrated translations and rotations). For our cases of quasiequilibrium ( $T_s \neq T_g$ ) and of irreversible desorption, this treatment is not strictly applicable. However, our experimental results show no significant influence of the various degrees of deviation from reversibility. We therefore feel justified to use this treatment even there with the only correction to use the appropriate temperature ( $T_s$ ,  $T_g$ ) in each term. In effect, this corresponds to the assumption that the rates of adsorption and desorption under irreversible conditions are equal to those under reversible but otherwise identical conditions (i. e., for desorption: for the same  $T_s$  and  $N_{ad}$ ). Similar treatments have been used by several authors before.<sup>14,26,35</sup> Equation (2a) is very similar<sup>2</sup> to the expression for  $k_0$  derived for *irreversible* desorption from TST<sup>28</sup> for certain assumptions, except that the latter does not contain the sticking coefficient.<sup>36</sup>

The simplest approximation is to assume that the layer can be described by an ideal lattice gas. While this will be a bad assumption for appreciable coverages because of the well-known strong interactions in this system, it is acceptable for high dilution, i. e., for  $\Theta \rightarrow 0$ . The equilibrium between ideal gas and ideal lattice gas is described by<sup>37,38</sup>

$$N_g/N_a = (Q_g/Q_a) [\alpha/N_s(1-\alpha\Theta)] \exp(-E_B/RT), \quad (5)$$

where  $\alpha$  is the number of metal atoms which form a site. At  $\Theta = 0$  every metal atom can be an adsorption site ( $\alpha = 1$ ), so that we get

$$k_0(0) = s(0) (kT/h) (q_t^2 q_r / q_v) (1/N_s) \quad (6)$$

with  $N_s$  as the number density of Ru surface atoms.

With the gas phase values calculated for  $T_g = 300$  K,  $k_0(0) \approx 8 \times 10^{16} / q_v$  ( $s^{-1}$ ) (the higher value given in Ref. 2 stems from the use of  $T_s$  instead of  $T_g$  in  $q_t, r$ , consistent

with TST). Comparison to the experimental value suggests that  $q_v$  is of the order 10. Estimates using values derived from data for metal carbonyls<sup>39</sup> as well as from theoretical estimates<sup>40</sup> for the soft vibrations which are of importance (e. g., energies of the frustrated translations are expected to lie in the range 50–100  $\text{cm}^{-1}$ ) lead to values between 10 and 40 (at  $T_s = 450$  K), which is on the high side. The most probable explanation is that there is also a contribution from the change of the surface phonon spectrum by adsorption. To account for this, a factor ( $q_{s,c}/q_{s,a}$ ), the quotient of the partition functions for surface phonons on the covered and the clean surface, has to be included in Eq. (6). Indeed, the adsorption induced increase of the surface Debye temperature, found experimentally,<sup>29</sup> suggests a shift of the surface phonon spectrum towards bulk behavior, i. e., a stiffening, by adsorption of CO. In view of the remaining uncertainties, more detailed calculations and consideration are not appropriate. In particular, the explicit extraction of the temperature dependences of the  $q$ 's<sup>26</sup> does not appear necessary; not only do they cancel to a large degree for most assumptions, but the experimental accuracies for both the  $E$  and  $k_0$  values are too small to recognize the difference. It has become clear, however, that  $k_0(0)$  values between some  $10^{15}$  and  $10^{17} \text{ s}^{-1}$  can be obtained depending on the details of the adsorbate modes, making the estimates compatible with experiment. The increase over the normal value of  $10^{13}$  assumed often is seen to come from the reduction of mobility in the adsorbed phase in agreement with expectations.<sup>25</sup>

In order to explain the  $\Theta$  behavior of  $k_0$ , we have to consider the statistics of the layer. For a noninteracting lattice gas with constant  $N_s$  sites,

$$k_0(\Theta) = \frac{s(\Theta)}{s(0)} k_0(0) \frac{1}{1-\Theta}$$

would result<sup>37,38</sup> and a divergence at  $\Theta = 1$  could occur if not canceled by  $s(\Theta)$ . In our case the obvious existence of strong NN repulsion seen in the stability of the  $\sqrt{3}$  structure and in the  $E(\Theta)$  dependence suggests as a first approximation to set  $\alpha = 3$  in Eq. (5). This would lead to a divergence at  $\Theta = 1/3$ , and indeed  $k_0$  does rise strongly there. However, for low coverages, each adsorbed molecule blocks seven metal atoms ( $\alpha = 7$ ), and in between the number of adsorption sites varies in a complicated manner depending on the configurations in the layer. On the other hand, repulsion at  $\Theta > 0.33$  is not infinite leading to additional adsorption. This does not take place on NN sites, however, but leads to compression of the layer; therefore a lattice gas model is not adequate for  $\Theta > 0.33$ . But even for  $\Theta < 0.33$ , no simple description can be given, as no exact solutions exist for the statistics of interacting particles in two dimensions, except for  $\Theta = 0.5$ .<sup>37</sup> Approximations must be used, therefore.

The Bragg-Williams approximation is of no use here as it does not consider entropy changes. The quasi-chemical approximation (QCA)<sup>37</sup> is more useful. However, the usual QCA only treats next neighbor pairs exactly; it would lead to a divergence at  $\Theta = 0.5$  and is thus not useful in our case. A reduction of the numbers

of adsorption sites, as proposed by Zhdanov,<sup>41</sup> leads to the same difficulties as for the noninteracting lattice gas. A better representation is possible with a generalized QCA<sup>42</sup> which uses an enlarged basic unit of sites treated exactly, so that the actual symmetry and interactions can be accounted for, at least in principle. If only NN-repulsive interactions are considered, a triangle is sufficient as basic cell on a hexagonal lattice. Results of this calculation for a pairwise NN repulsion of 20 kJ have been obtained in Ref. 42. For  $\Theta < 0.33$ , the agreement between experiment and calculation was acceptable, although the increase of  $k_0$  was too small. This is partly due to the fact that the real NN repulsion must be much higher than that derived from the step in our  $E(\Theta)$  curve (see above), and to neglect of attractive interactions. Improvement would be possible by changes in both cases, although calculations with attractive interactions would be considerably more complicated.

Even though lattice gas models break down for  $\Theta > 0.33$ , qualitatively the same arguments can be applied there. Above  $\Theta = 0.33$ , the localization of adsorbate should strongly decrease as the surface bond is weakened and mobility thus increased in the slightly compressed layer. Also,  $s$  is now strongly coverage (and temperature) dependent and decreases by two orders of magnitude between  $\Theta = 0.33$  and 0.6. Both effects lead to a decrease of  $k_0$ , as observed. On the other hand, localization becomes strong again upon approaching saturation which should lead to a strong increase of  $k_0$  towards saturation. The observations give an indication for such an effect although by far not as strongly as for  $\Theta \rightarrow 0.33$ . While the measurements are much less accurate above  $\Theta = 0.5$  so that firm conclusions are difficult, it is well possible that part of the increase is indeed cancelled by the decrease of  $s$  which is not known with sufficient accuracy in this range.

#### D. Precursor influences and dynamic effects

In Sec. IVC we have used a treatment based on equalization of rates so that considerations of the paths of adsorption and desorption did not enter but only the two states in equilibrium (at least in principle) with each other—chemisorbed layer at  $\Theta$  and gas phase at  $p$ —were of importance. This treatment effectively splits the rate of desorption into an equilibrium term (determined by the equilibrium statistics of the layer) and the term  $s(\Theta, T)$  which can contain dynamic effects (i.e., effects of deviations from thermalization during reaction,<sup>35,43</sup>) as well as effects caused by particular reaction paths (e.g., precursor influences<sup>22</sup>). Recent state-resolved desorption and scattering measurements in similar systems<sup>44–46</sup> have shown the existence of dynamic effects, and the discussion of our sticking data<sup>1</sup> has indicated precursor as well as dynamic effects. We have to discuss the compatibility of these findings, therefore.

We begin with precursor effects. The analysis of sticking coefficients for the present system<sup>1</sup> has shown that adsorption kinetics is most likely to be governed by direct adsorption up to  $\Theta \approx 0.2$ , in agreement with the results reported here. At higher coverages, however,

precursors (intrinsic throughout the  $T$  range, extrinsic only at  $T < 200$  K) contribute importantly in adsorption.

Nevertheless, the measurements reported here did not yield a significant difference between equilibrium and desorption energies,  $E_B$  and  $E_{eff}$ , at any coverage. [In fact, the most obvious difference of the sets of measurements occurs in the region below  $\Theta \approx 0.2$ , see Fig. 7(a), where a precursor influence can be excluded; also, the difference is in the wrong direction. This shows that it is due to systematic influences in the experimental procedures, not to a true physical difference.] The main difference between the sticking measurements of Ref. 1 and the present equilibrium and desorption measurements concerns the range of surface temperatures (100–400 K for adsorption, vs 350–650 K for equilibrium and desorption). An influence of the extrinsic precursor on the latter can therefore be discounted right away. The intrinsic precursor  $I''$  (adsorbed above empty chemisorption sites blocked interactionally), however, should also constitute the preferred path of desorption, at least above 1/3 coverage. For  $k_d'' \gg k_a''$  (see Ref. 1 for the nomenclature and details of the model) which is fulfilled the better the higher  $T_s$ , the measured desorption energy should then be equal to the energy of the transition state between chemisorbed state and precursor,  $E_{eff} = E_D < E_B$ .<sup>14</sup> Such a difference between  $E_B$  and  $E_{eff}$  has been reported recently for Xe/W by Opila and Gomer<sup>47</sup>; it has not been seen here. However, the difference  $E_B - E_D = E_d - E_a$ , the energetic difference between the transition state between  $C$  and  $I''$ , and the gas phase, was determined to be about 7 kJ/mol in Ref. 1, so that it would barely be visible with our accuracy. Our data are consistent with such an interpretation ( $E_B$  is slightly higher than  $E_{eff}$  for  $\Theta > 0.3$ , and if a systematic error is assumed which makes  $E_B$  always somewhat too low, as suggested by the low coverage comparison, about the correct difference results) but in view of the comparable errors we do not place confidence on this. Whether a molecule desorbed from the chemisorbed state  $C$  to the precursor  $I''$  is again fully accommodated in the latter—which is assumed in this treatment—or not cannot be decided from our data. The latter would be a true dynamic effect; it would bring us back to direct desorption for the medium to high coverage range as well. We shall address these questions more generally in the following.

This takes us to the discussion of dynamic effects. Our discussion of sticking at low coverage<sup>1</sup> has suggested that adsorption is more probable for low rotational excitations. According to microscopic reversibility, desorbing particles (strictly speaking only under reversible but most likely also under irreversible conditions) should then be rotationally cool. Indeed, such an effect has been seen for NO thermally desorbing from Ru(001)<sup>44</sup> (the findings of rotationally selective molecular beam scattering at surfaces<sup>45</sup> may be less relevant here because of the much higher energies used which may change the collision dynamics thoroughly). In fact, very recently the same authors<sup>46</sup> even reported *translationally* cold desorbing molecules for the same system. Such effects may be present for high coverages also: if desorbing CO passes through  $I''$  quickly, its orientation could be preserved. All these effects are contained

in the sticking coefficient. As long as  $s$  is large and not strongly changing with  $T$  and  $\Theta$ , this would *not* show up in desorption measurements or their comparison to reversible measurements. We conclude from this that the agreement of data taken in irreversible and reversible (equilibrium) measurement situations does *not* imply an equilibrium situation (in terms of distribution over states), nor can the latter be implied from high and roughly constant sticking coefficients.

## V. SUMMARY AND CONCLUSIONS

Measurements of desorption kinetics as functions of surface temperature and coverage have been conducted with several independent methods (isothermal desorption via  $\Delta\phi$  changes; temperature programmed desorption via  $\Delta p$  and  $\Delta\phi$ , using changes of initial coverages and of heating rates) and evaluated in Arrhenius fashion to yield desorption energies  $E_{\text{eff}}$  and preexponentials  $k_0$ . Quasiequilibrium measurements via  $\Delta\phi$  have been used to derive isosteric heats  $E_B$  and corresponding  $k_0$  values for the reversible situation have been extracted using sticking coefficients extrapolated to measurement temperatures. No significant difference between the sets of parameters obtained via irreversible or via almost reversible measurements was found.

The coverage dependence of the binding or desorption energy correlates well with the interactions in this adsorbate system known from other measurements. From a value of about 160 kJ/mol at zero to low coverage, the energy rises to about 175 kJ/mol between  $\Theta=0.2$  and 0.33, due to attractive interactions which are made effective by a second order phase transition. At  $\Theta=0.33$ ,  $E$  drops sharply to 120 kJ/mol due to strong repulsive interactions which exclude occupation of nearest neighbor sites and lead to compression of the  $\sqrt{3}$  layer; at the highest attainable coverage, a value of 110 kJ/mol is approached.

The preexponential of desorption is about  $10^{18} \text{ s}^{-1}$  at zero coverage, rises first slowly and then very sharply with coverage to above  $10^{19} \text{ s}^{-1}$  at  $\Theta=0.33$ , where it falls stepwise to about  $10^{14} \text{ s}^{-1}$ . There may be a second increase above  $\Theta=0.5$ , but results are less certain there. The results are well explained by the equilibrium statistical mechanics of the layer and in particular by the strong decrease of the layer's phase space by localization in the region of the ordering transition. ( $0.2 < \Theta < 0.33$ ). An exact description is made difficult by the necessity to take account of interactions of more than two molecules, but semiquantitatively the behavior is well understood.

Possible dynamic effects are included in the sticking coefficient in this treatment. It is shown that the presence of such effects, due to the kinematics of adsorption/desorption processes, is very probable; this is supported by recent state-resolved measurements in a similar system. Also, our failure to detect influences of precursors on the desorption kinetics, even though sticking data show these to exist, can be understood.

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## APPENDIX A: INFLUENCE OF THE VIBRATING COUNTERELECTRODE ON THE DESORPTION RESULTS

As mentioned in Sec. IIB2, the reflection of desorbing particles by the vibrating electrode reduces the desorption rate  $r_d$  to a value  $r'_d$  which depends on the (coverage and temperature dependent) sticking probability  $s$ . If spatial inhomogeneities of the electrode and changes of gas temperature by reflection (in general  $T_s \neq 300 \text{ K}$ ) are neglected, the change of the rate in terms of the reflected fraction  $x$  is given by

$$r'_d = r_d(1-x)/[1-x+s(\Theta, T_s)] \quad (\text{A1})$$

Depending on  $s$ , the actual desorption rate  $r'_d$  varies between  $r_d(1-x)$  at  $s=1$  and  $r_d$  at  $s=0$ . As long as  $s$  does not change appreciably with temperature, a constant reduction of  $r_d$  results for fixed  $\Theta$ , so that the semilogarithmic desorption isosters are simply shifted parallel, leaving  $E_{\text{eff}}$  constant and changing only  $k_0$  by a factor of less than two. This is the case for  $\Theta < 0.3$  where  $s$  varies very slowly with  $T$ .<sup>1</sup> The effect is thus negligible in this range, in agreement with the conclusion from comparing  $\Delta p$ - and  $\Delta\phi$ -TPD curves (Fig. 1). At higher  $\Theta$ ,  $s$  is smaller than 0.2 at desorption temperatures so that the change of  $r_d$  by the temperature dependence of  $s$  becomes smaller than 3% over the experimental range used. For high coverages the effect becomes even smaller because of the very small  $s$  values. Therefore, corrections for the effect of the counterelectrode on the gas flux are not necessary here, contrary to the situation in adsorption kinetics.<sup>1</sup>

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