

## Rapid Communications

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### Unusual coverage dependence of a sticking coefficient: N<sub>2</sub>/Ru(001)

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A very unusual  $s(\Theta)$  dependence has been observed for adsorption of molecular N<sub>2</sub> on Ru(001). It is interpreted as being due to interactional effects between two different types of adsorption states.

There are a number of detailed investigations of the coverage dependence of the sticking coefficient,  $s$ , for well-defined surface layers (see, e.g., Refs. 1–3). In most of these cases,  $s$  stays constant with increasing coverage or drops gradually or sharply. This behavior is understood in terms of precursor-mediated or direct adsorption or the transition from one to the other. Only in a few cases [e.g., oxygen on W(110) (Ref. 3)], an increase of  $s$  with  $\Theta$  has been observed which is explained by a lower reflection coefficient (i.e., better accommodation) for the incoming particle on top of an adsorbate, compared with the clean surface.<sup>3</sup>

In the course of a program to investigate experimentally<sup>4,5</sup> and theoretically<sup>6</sup> the adsorption of molecular nitrogen on group VIII metals and to compare it with the well-known adsorption behavior of the isoelectronic CO, we have studied the system N<sub>2</sub> on Ru(001) which is of interest because of our detailed knowledge of CO on Ru(001). We have found that the detailed nature of the formed layer depends strongly on adsorption temperature between 78 and 110 K which expresses itself in an unusual dependence of the sticking coefficient on coverage at 78 K:  $s$  stays constant with increasing coverage over a certain coverage range, but then suddenly increases to almost twice that value, to decrease roughly linearly with further increase of coverage. We do not know of a similarly sharp increase of  $s$  with  $\Theta$  in a well-defined adsorbate layer (the sharp increases of  $s$  with  $\Theta$  found for oxygen adsorption on evaporated Ni films<sup>7</sup> are probably caused by reconstruction of the mixed layers). The investigations were carried out with TPD (temperature-programmed thermal desorption), ESD (electron-stimulated desorption) of ions and neutrals,  $\Delta\phi$  (work-function change), and LEED

(low-energy electron diffraction) measurements, under well-controlled uhv and surface conditions. For experimental details see Ref. 8. Here we concentrate on the TPD measurements.

After adsorption at 78 K, TPD spectra [Fig. 1(a)] show two main peaks,  $\gamma$  and  $\delta$ , each of which has a

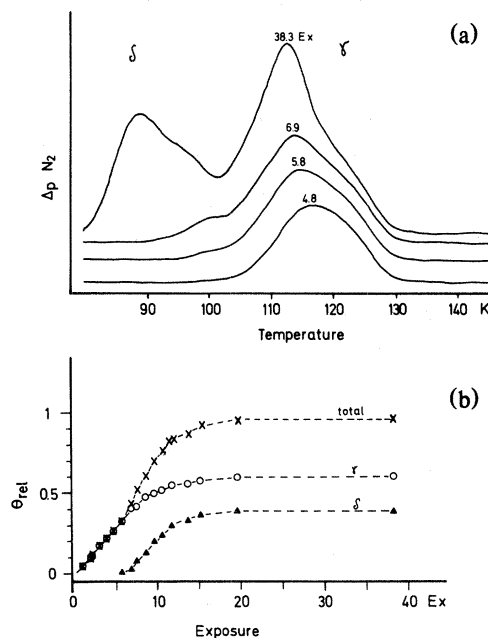


FIG. 1. (a) TPD spectra from N<sub>2</sub> layers on Ru(001) after various exposures [1 Ex = 10<sup>-14</sup> cm<sup>-2</sup> (Ref. 9)] at a crystal temperature of 78 K. Note the appearance of the  $\delta$  state around 6 Ex. (b) Relative amounts desorbed in  $\gamma$ ,  $\delta$ , and  $(\gamma + \delta)$  as a function of exposure at 78 K, obtained from spectra such as in (a).

shoulder at the high-temperature side. The  $\gamma$  peak alone comes in at exposures up to 6 Ex [1 Ex =  $10^{14}$  collisions/cm<sup>2</sup> (Ref. 9)], with the peak temperature shifting from 124 to 113 K with increasing coverage, while the  $\delta$  peak fills at higher doses and has a peak temperature of 100 to 88 K. The two peaks are well separated so that their individual coverages can be determined. If the total coverage is obtained from integrated TPD spectra as a function of coverage, then an increase of slope is found at the coverage where the  $\delta$  state starts to fill [Fig. 1(b)]; differentiation leads to the total sticking coefficient  $s_T$  which is shown as a function of relative coverage in Fig. 2 and exhibits the unusual behavior mentioned in the Introduction. [The fat black line corresponds to the slope of the straight line through the experimental points of Fig. 1(a); the individual points are obtained from the slopes of three-point regression lines. This procedure tends to accentuate the errors in the low coverage regime and smears out the shape in the transition region between  $\Theta = 0.4$  and 0.5. Examination of Fig. 1(b) suggests that the actual change of  $s_T(\Theta)$  is more discontinuous.] A breakdown of the total amount adsorbed into the contributions of  $\gamma$  and  $\delta$  shows the reason: While the partial sticking coefficient (or better: differential coverage change)  $s_\gamma$  stays constant up to the coverage where  $\delta$  begins to fill and decreases markedly only at higher coverage so that the total sticking is almost doubled, only to decrease at higher  $\Theta$ .

This sudden opening of the  $\delta$  channel must mean that a critical condition must be developed in the layer to make  $\delta$  possible. ESD and  $\Delta\phi$  measurements show that  $\gamma$  and  $\delta$  are separate individual states coexisting in the full layer, and are *not* caused by interactional effects alone (as in the case for CO

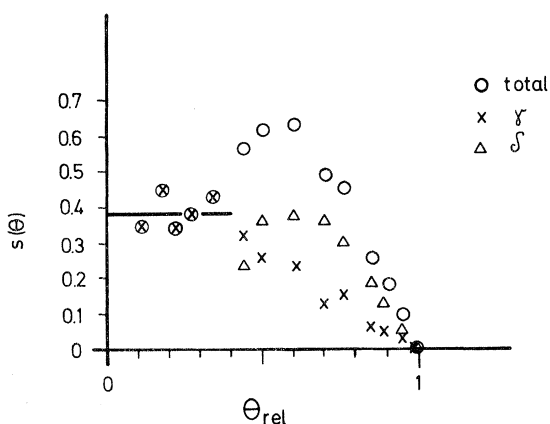


FIG. 2. Total sticking coefficient,  $s_T$ , and partial sticking coefficients,  $s_\gamma$  and  $s_\delta$ , as functions of coverage at 78 K, obtained from the data of Fig. 1(b). The procedure to obtain the individual points (see text) tends to exaggerate deviations and to smooth out sudden changes.

on Ru where the full layer contains only one homogeneous binding state). The binding energy for  $\delta$  is about  $\frac{2}{3}$  of that of  $\gamma$ , as shown by detailed evaluation of the TPD spectra.<sup>8</sup> The  $\gamma$  state is shown by LEED to be ordered into a  $\sqrt{3}$ -type structure, whose development depends strongly on the adsorption temperature. In fact, not only the order, but also the amount of  $\gamma$  (and indirectly of  $\delta$ ) depend on adsorption temperature: If adsorption is carried out at 90–100 K, the LEED pattern is much more intense, the saturation coverage of  $\gamma$  is increased, and the  $\delta$  state is practically suppressed, even if the 90-K layer is cooled to 78 K and exposed to N<sub>2</sub> once more. Working at temperatures where  $\delta$  is not stable on the surface (above 90 K), a disorder-order transition has been found in the  $\gamma$  layer at the coverage at which the  $\delta$  channel would open at lower temperature, with a very weak temperature dependence of the ordering coverage. CO preadsorption strongly suppresses the  $\gamma$  state.

Our present interpretation of these findings<sup>8</sup> is the following: The  $\gamma$  state is chemisorbed N<sub>2</sub> bound upright on top of Ru atoms in a  $\sqrt{3}$ -type superstructure, like CO.<sup>10</sup> At an adsorption temperature of 78 K, the order of this layer is rather imperfect, and above an absolute coverage of about 0.16 (equivalent to  $\Theta_{\text{rel}} = 0.4$ ) many faults and vacancies surrounded by  $\gamma$  molecules are formed. In these voids  $\delta$  molecules are adsorbed (possibly, but not necessarily, in a horizontal configuration<sup>11</sup>) whose binding energy is only about  $\frac{2}{3}$  of that of  $\gamma$ , but is considerably higher than that of a similar state on the clean surface, due to attractive interactions between  $\gamma$  and  $\delta$ . The  $\delta$  molecules then block the total filling of the  $\gamma$  layer. If adsorption is carried out at slightly higher temperature so that the  $\gamma$  layer is mobile enough to anneal out faults during adsorption, the  $\delta$  state is blocked. This elimination of  $\delta$  is not only due to its low desorption temperature, but—as shown by the redosing experiment after cool down of such a layer to 78 K—mainly to the fact that now no space is available for  $\delta$ -N<sub>2</sub>. This shows that a  $\delta$  molecule does not fit between  $\gamma$  in  $\sqrt{3}$  array. On the other hand, about two  $\delta$ 's can be accommodated for one missing  $\gamma$  in a faulty layer. This would be consistent with two  $\delta$  molecules lying in the void left by one  $\gamma$  missing in a  $\sqrt{3}$  layer, but there is no proof for such a configuration. The  $\delta$  molecules could also be bound in the region between  $\sqrt{3}$  islands meeting out of step. The parallel between the ordering coverage in  $\gamma$  and the opening of the  $\delta$  adsorption channel may be due to the appearance of a large number of  $\gamma$ -surrounded vacancies at that coverage.

This model would still make it possible that the total sticking coefficient would not change drastically when the  $\delta$  state starts to fill. This would be the case if  $\gamma$  and  $\delta$  would be formed alternatively from the

same precursor (a decrease of the reflection coefficient should lead to gradual changes of  $s_T$  only). The fact that  $s_\gamma$  stays constant up to and somewhat above the critical coverage for  $\delta$  shows that  $\delta$  forms from that part of precursor molecules which are redesorbed at lower coverages.

The simplest explanation is that the binding energy of a hypothetical  $\delta'$  state (equivalent to  $\delta$  on the clean surface, i.e., without the stabilizing influence of  $\gamma$ ) is so low that it completely desorbs at 78 K, while the stabilizing effect of  $\gamma$  is sufficient to keep  $\delta$  on the surface. It may even be that  $\delta'$  is *identical* to the

precursor.

Many details of this system have yet to be clarified, but the results so far are sufficiently interesting to warrant further investigation.

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