The effect of lateral interactions on the thermal desorption of N_2 from Ni(100)

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We have investigated the desorption of N_2 from Ni(100) using thermal desorption spectroscopy (TDS). A modified Polanyi–Wigner equation has been used to obtain the desorption energy and the preexponential factor, both of which depend on the coverage of the adsorbate. We show that there is a large lateral interaction among the adlayer molecules when N_2 goes down as ordered $c(2\times2)$ on Ni. In addition, the overlayer ordering, in the thermal desorption process, is observed to affect the thermal desorption spectra.

I. INTRODUCTION

The interaction of molecular nitrogen on Ni(100) has been the focus of several studies.[1–3] It has been observed that the adsorption of N_2 on Ni(100) at 84 K results in the formation of either an ordered $c(2\times2)$ (with an average domain size of 34 Å) or a disordered $c(2\times2)$ (with an average domain size of 17 Å).[2] Since the disordered $c(2\times2)$ N_2 overlayer is a nonequilibrium phase, probing the energetics of this phase cannot be accomplished using equilibrium techniques that have been applied to the study of ordered $c(2\times2)$ overlayers. We have, therefore studied the effects of the precursor state and lateral interactions for N_2 on Ni(100) using thermal desorption spectroscopy (TDS).

Ordering (as well as other phase changes) occurring during the thermal desorption process has a profound effect upon thermal desorption spectra, as we shall demonstrate for N_2 on Ni(100). The adlayer lateral interactions between adsorbed N_2 molecules influence the apparent heat of adsorption of N_2 on Ni(100).

II. EXPERIMENTAL

The experiments were carried out in a ultrahigh vacuum system equipped with low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The thermal desorption experiments were undertaken at constant heating rates β following adsorption of ordered or disordered overlayers of N_2. By adsorbing at 85 K, N_2 forms a disordered overlayer with an average domain size of 17 Å as determined by LEED, as is described in detail elsewhere.[2] Ordered overlayers were formed by annealing the Ni(100) surface, repeatedly in an ambient N_2 background, between 120–130 K. These ordered overlayers have an average domain size of 34 Å or larger as determined by LEED.[2] In this paper, we have assumed that the ordered $c(2\times2)$ structure corresponds to a coverage of 8.05×10^{14} molecules/cm^2 at saturation ($\theta=0.5$).

The Ni(100) crystal was cleaned by repeated Ar$^+$ ion bombarment and annealing to 700 K, and was ascertained to be clean by AES following each experiment. The temperature was determined by a calibrated chromel–alumel thermocouple.

III. THEORY

In thermal desorption spectroscopy an adsorbate is desorbed from the surface by heating the substrate. The gaseous desorption products are detected by a mass spectrometer. The rate of desorption (r) can be described by the Polanyi–Wigner (PW) equation[4–25]

$$r = -\frac{d\theta}{dt} = \nu(\theta)\theta^{\,n}\exp\left[\frac{-E_d(\theta)}{RT}\right], \qquad (1)$$

where θ is the adsorbate coverage, $\nu(\theta)$ is the theta dependent preexponential factor, n is the order of desorption kinetics, $E_d(\theta)$ is the coverage dependent desorption energy, R is the gas constant, and T is the temperature. Several approaches have been taken to solve the rate parameters ν and E_d. Simplified methods of analysis have been proposed by Redhead[26] and Chan–Aris–Weinberg (CAW)[27] formula. For a first order reaction, the Redhead formula can be used to calculate E_d when a choice is made on the value of the preexponential. The usual choice is 10^{13} s^{-1}, although in the literature values between 10^{10} and 10^{22} s^{-1} have been reported.[20]

The disadvantage of CAW analysis is that the desorption parameters E_d and ν are obtained as a function of initial coverage θ_0 (at time $t=0$) and not of the actual coverage θ. The dependence of E_d and ν on θ_0 and not on θ is possibly an unwarrented assumption though when E_d and ν are coverage independent, the CAW formulas should give correct values. Unfortunately for many overlayers, E_d and ν do depend
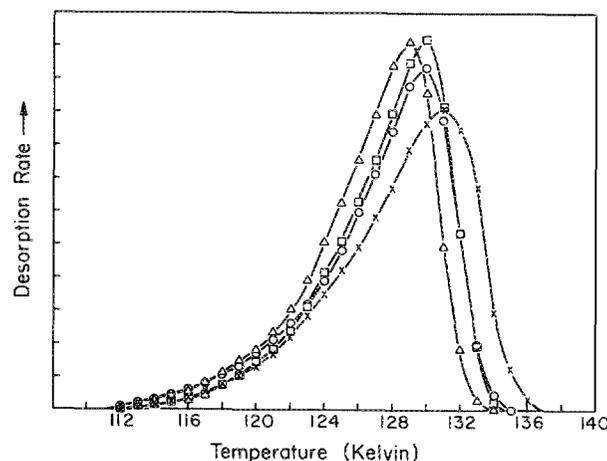

FIG. 1. Normalized thermal desorption spectra for N_2 on Ni(100). These spectra correspond to the saturated overlayer of the disordered $c(2\times2)$ N_2 for different heating rates, $\beta = 0.9(\triangle)$, $1.4(\square)$, $3(\bigcirc)$, $5.3(\times)$ K/s. These have been normalized so that they correspond to the same coverage (integrated intensity under thermal desorption spectra) of ~0.42 (see text).
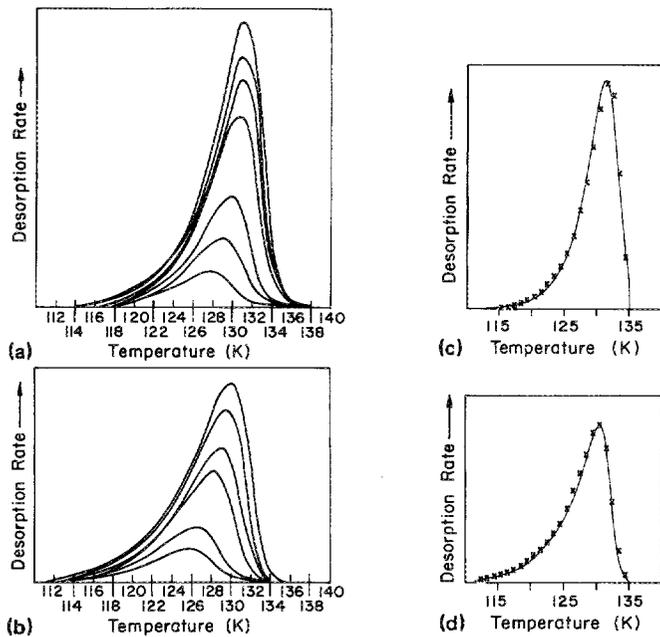
FIG. 2. (a) Thermal desorption spectra for N_2 from an ordered $c(2\times2)$ on Ni(100) and (b) where N_2 forms a disordered $c(2\times2)$ on Ni(100). (c) The experimental data (x) is compared with theoretical models for the saturated overlayer thermal desorption spectra for ordered N_2 adlayer and (d) for the disordered adlayer. The heating rate is $\beta = 3$ K/s.

FIG. 4. Desorption energy $E_d(\theta)$ plotted as a function of coverage for the N_2 in a disordered $c(2\times2)$ overlayer on Ni with $\beta = 0.9(\triangle)$, $1.4(\square)$, $3(\times)$, $5.3(+)$ K/s. We have also plotted $E_d(\theta)$ for the ordered overlayer ($\bigcirc$) and the isosteric heat of adsorption ($\blacksquare$). $\theta_{max} = 0.5$, the saturation coverage for the ordered overlayer.

on coverage, θ. More complete analysis methods have been proposed by King,[12] Bauer,[20] and Habenschaden and Küpper.[23] We have used the modified PW thermal desorption model,[28] in which lateral interactions between the adsorbed particles, manifest themselves by coverage-dependent desorption parameters:

$$E_d(\theta) = E_0 + \Delta E(\theta),   (2)$$

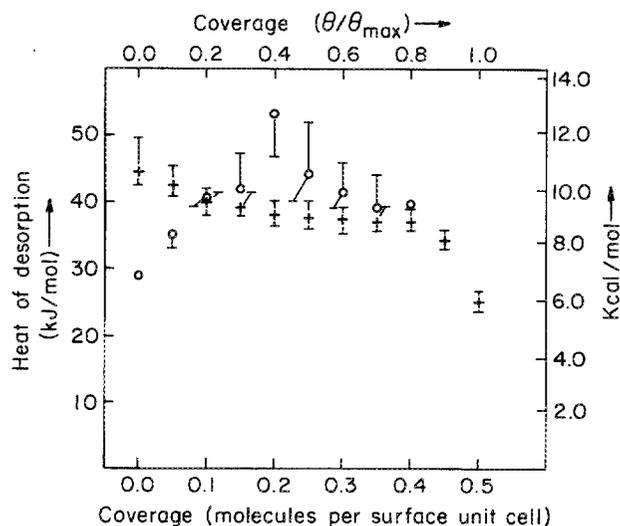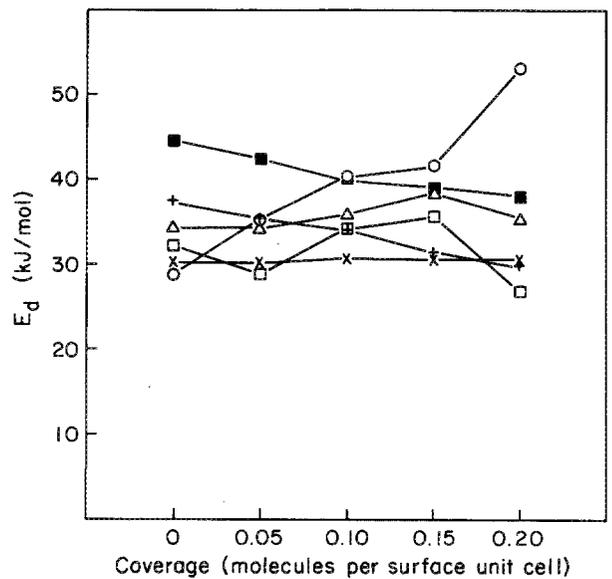$$\ln \nu(\theta) = \frac{\Delta E(\theta)}{RT_c} + \ln \nu_0,   (3)$$

where E_0 is the desorption energy at zero coverage, ν_0 is the preexponential frequency factor at zero coverage, ΔE is the coverage dependent part of the desorption energy, and T_c is the compensation effect temperature. We will assume that the lateral interactions are pairwise and that the desorption occurs statistically. Then $E_d(\theta)$ is given by[29,30]

$$E_d(\theta) = E_0 - W\theta.   (4)$$

The interaction energy W is negative for attractive interactions and positive for repulsive interactions. Using Eqs. (1), (3), and (4), we get the modified PW equation[28]

$$r = \nu_0 \theta^n \exp\left(\frac{-E_0}{RT}\right) \exp\left[\frac{-\Delta E(\theta)}{RT - RT_c}\right].   (5)$$

FIG. 3. Heat of desorption $E_d(\theta)$ is plotted, as a function of coverage ($\bigcirc$) for the ordered adlayer of N_2 on Ni(100) ($\beta = 3$ K/s). Also shown is the isosteric heat of adsorption, q_{st} (+). $\theta_{max} = 0.5$, the saturation coverage for the ordered overlayer.
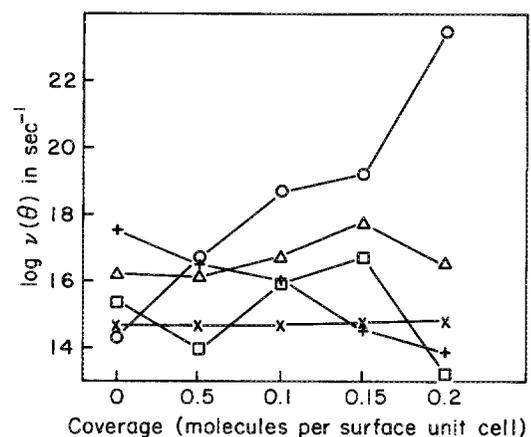

FIG. 5. Log $\nu(\theta)$ plotted as a function of coverage. Results are shown for N_2 adsorbed in disordered $c(2\times2)$ overlayers on Ni(100) with $\beta = 0.9(\triangle)$, $1.4(\square)$, $3(\times)$, $5.3(+)$ K/s. The results for the ordered case ($\bigcirc$) are also shown. $\theta_{max} = 0.5$, the saturation coverage for the ordered overlayer.

TABLE I. The values of E_0 (from PW and CAW), W, ν_0 (from PW and CAW), and T_c for various heating rates, β are listed. These values are for disordered layers of N₂ on Ni(100). The average error bars have also been indicated. W is negative for attractive interactions and positive for repulsive interactions.

β (K/s)	E_0 (PW) (kJ/mol)	E_0 (CAW) (kJ/mol)	W (kJ/mol)	ν_0 (PW) (s⁻¹)	ν_0 (CAW) (s⁻¹)	T_c (K)
0.95	34.3 ± 2.8	46.38	+5.2 ± 10.4	(1.7 ± 0.7)×10¹⁶	3.0×10¹⁸	146.9 ± 41.8
1.4	32.2 ± 8.2	46.11	+2.8 ± 28.5	(2.3 ± 0.5)×10¹⁵	2.5×10¹⁹	126.5 ± 12.8
3.0	30.3 ± 0.6	38.86	−0.88 ± 1.9	(4.9 ± 2.3)×10¹⁴	2.5×10¹⁶	579.7 ± 375.0
5.35	37.6 ± 0.7	36.53	+15.8 ± 1.6	(3.6 ± 0.5)×10¹⁷	3.1×10¹⁵	107.9 ± 1.5

This equation can be used to illustrate the effect of pairwise interactions and a constant preexponential factor on the shape of thermal desorption spectra, and is often successful in describing thermal desorption data.[31] In the case where the desorption takes place through a precursor, Eq. (5) can be modified[32,33] to

$$r = \nu_0 \left(\frac{\theta^*}{1 - \theta^*} \right)^n \exp\left(\frac{-E_0}{RT} \right) \exp\left[\frac{-\Delta E(\theta^*)}{RT - RT_c} \right]. \quad (6)$$

Here θ^* is the relative coverage which is equal to 1 at saturation coverage. We have not distinguished between an extrinsic or intrinsic precursor state.

IV. THERMAL DESORPTION RESULTS AND ANALYSIS

For the disordered $c(2\times2)$ N₂ overlayer (domain size 17 Å) with the considerable adlayer lattice defect density, we have taken thermal desorption data at four different heating rates ($\beta = 0.9$, 1.4, 3.0, and 5.3 K/s). Figure 1 shows the spectra for the saturated overlayers obtained at these heating rates. In order to compare relative coverages and energetics, both the ordered and disordered overlayers were characterized at the same heating rate ($\beta = 3$ K/s), as shown in Figs. 2(a) and 2(b). Following background subtraction, the ordered and disordered overlayer thermal desorption spectra have been compared, and we have been able to assign a satu-
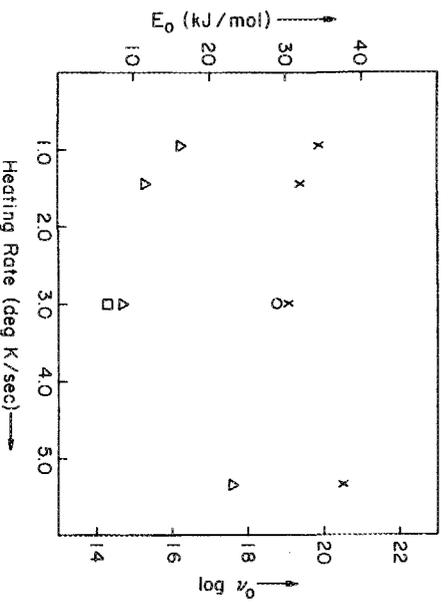
ration coverage of 0.42 to the disordered overlayer (assuming a saturation coverage of 0.5 molecules/surface Ni atom for the ordered N₂ overlayer).

In analyzing our thermal desorption spectra, we have assumed that desorption occurs through a mobile precursor state. This is based upon isothermal adsorption curves[2] which exhibit a constant sticking coefficient (~ 1) for N₂ adsorption at 85 K characteristic of an extrinsic mobile precursor state. The analysis of our data without a precursor state is not observed to qualitatively alter the results significantly. Nonetheless the fit of the model to the data is substantially better at higher coverages assuming desorption through a precursor state than without.

N₂ adsorbs on Ni(100) molecularly, under our experimental conditions, with the molecular axis normal to the surface.[3] For this reason, we have also assumed in our analysis that the order of desorption (n) is equal to one, as has been assumed elsewhere,[32] and have applied Eq. (6) accordingly.

From our coverage dependent thermal desorption spectra, as shown in Fig. 2, Arrhenius plots were constructed and the desorption energy $E_d(\theta)$ has been calculated. This has been done on the basis of Eq. (6) by plotting $\ln(R)$ vs $1/T$. The variation in $E_d(\theta)$ for the ordered overlayer is plotted in Fig. 3 and compared with the isosteric heat of molecular N₂ adsorption, q_{st}.[2] The error bars for $E_d(\theta)$ have been calculated according to a jack knife indicator.[34]

For the disordered $c(2\times2)$ molecular overlayer, the calculated heat of desorption is generally observed to vary with the coverage and heating rate as shown in Fig. 4. A PW analysis of the thermal desorption data for the disordered overlayer indicates that over a wide range of coverages $E_d(\theta)$ is larger for smaller heating rates, β. While the heat of desorption is coverage dependent, the preexponential frequency factor, $\nu(\theta)$, is only observed to be strongly coverage dependent for the ordered overlayer (Fig. 5).

The coverage independent parameters T_c, E_0, W, and ν_0 [using Eq. (6)] have been calculated and are summarized in Table I. In general, the heat of desorption at zero coverage, E_0, varies little with heating rate or order of the overlayer as seen in Fig. 6. The difference between the ordered overlayers as opposed to the disordered overlayers is that the disordered overlayers have a weakly repulsive in plane interactions, while the ordered overlayers have a strongly attractive interactions between adsorbed N₂ molecules as given by the value of W (see Table II). The results of analysis of the data by the CAW approach[27] are also shown (in Tables I and II)

E₀ (kJ/mol) ——

FIG. 6. Desorption energy E_0 has been plotted as a function of heating rate, β for both ordered (○) and disordered (×) overlayers of N₂ on Ni(100). Also plotted is log ν_0 as a function of heating rate, β. This too, is shown for ordered (□) and disordered (△) adlayers of N₂ on Ni(100).

TABLE II. The values of E_0 (from PW and CAW), W, v_0 (from PW and CAW) and T_c. These values are for ordered layers of N_2 on Ni(100). The average error bars have also been indicated. W is negative for attractive interactions and positive for repulsive interactions.

β (K/s)	E_0 (PW) (kJ/mol)	E_0 (CAW) (kJ/mol)	W (kJ/mol)	v_0 (PW) (s^{-1})	v_0 (CAW) (s^{-1})	T_c (K)
3.0	28.8 ± 3.3	40.95	-55.3 ± 15.4	$(2.0 \pm 0.6) \times 10^{14}$	2.1×10^{17}	137.3 ± 3.7

for comparison and give consistantly higher values for E_0 than does the PW model.

V. DISCUSSION

As has been assumed for equilibrium studies,[2] our results indicate that N_2 on Ni(100) adsorbs into a single site. This conclusion is based upon observing only the single feature in the thermal desorption spectra and the linear variation in $\ln(R)$ versus $1/T$ plots.[25] Angle-resolved photoemission studies[3] are also consistent with a single molecular N_2 adsorption site.

A comparison of thermal desorption results for the ordered N_2 overlayer with earlier equilibrium studies[2] show that the desorption energy, for coverages $> \theta = 0.1$, is larger than the equilibrium heat of adsorption (Fig. 3). This may indicate an activation barrier to desorption. The activation barrier $[E_{act} = E_d(\theta) - q_{st}]$, is ~6 kJ/mol at $\theta = 0.25$. Such an activation barrier is consistent with the existence of a precursor state observed earlier.[2] The lower heat of desorption as compared to q_{st} at low coverages, is a common artifact of thermal desorption spectroscopy and has been observed before[32] for N_2 on Ni(110).

We have noted that the saturation coverage of the disordered $c(2\times2)$ overlayer is some 84% of the ordered overlayer, indicating that a large number of defects are frozen into this disordered overlayer, consistent with previous LEED results.[2] A large drop in the equilibrium heat of adsorption can be associated[2] with the completion of the overlayer and formation of antiphase domain boundaries. By freezing into the overlayer similar defects, the differential entropy of the adsorbed layer,[2] $\bar{S}_{ad} = \Delta S + S_g^0$, remains large for a wider coverage range since defects are not avoided or forced to growing domain edges. Effectively, the pairwise interactions are lost, and lateral interactions are substantially reduced, with large defect densities.

This decrease in lateral attractive interaction energies is observed. For the ordered overlayers our results suggest that the overlayer has strongly attractive pairwise interactions (Table II) while the disordered overlayers have slightly repulsive interactions overall, in the overlayer, as indicated by the value of W (Table I). The overall increase in $E_d(\theta)$ for the disordered overlayer with decreasing heating rate, β, supports this observation as well. Ordering does occur during the thermal desorption process and the smaller the β, the more ordering will occur during thermal desorption and annealing of overlayer. Ordering effectively reduces the defect density resulting in a larger attractive lateral interaction term W and greater $E_d(\theta)$, as is observed (Fig. 4). The CAW method of analysis results in E_0 values that also reflect this increasing $E_d(\theta)$ (Tables I and II).

The hybridization of molecular N_2 orbitals to form bands has been observed for molecular N_2 adsorbed on Ni(100).[3] Such hybridization, as evidenced by strong dispersion of the bands, does indicate a strong lateral attraction between N_2 molecules on Ni(100) as observed in this work. We have also used the PW model, taking in account the presence of lateral interaction, to calculate theoretical desorption spectra that fit our experimental curves quite well [Figs. 2(c) and 2(d)]. The same model with no mobile precursor did not give as good a fit for high coverages.

In conclusion, we have determined that there are strong lateral interactions for the ordered N_2 overlayers on Ni(100). This lateral interaction is strongly attractive and is about 55 kJ/mol ($40 < |W| < 70$ kJ/mol). A softening of the vibrational mode and an increase in the differential entropy associated with the antiphase domain boundaries[2] is observed in general with an increasing defect density in a molecular N_2 overlayer.

We have observed that for the nonequilibrium phase of a disordered $c(2\times2)$ N_2 overlayer on Ni(100), the heating rate for thermal desorption profoundly influences the results and apparent energetics of N_2 interactions in the adsorbed overlayer.

ACKNOWLEDGMENTS

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