May 1990

The effect of lateral interactions on the thermal desorption of N\textsubscript{2} from Ni(100)

Shikha Varma
Syracuse University

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

Follow this and additional works at: http://digitalcommons.unl.edu/physicsdowben

Part of the Physics Commons

Varma, Shikha and Dowben, Peter A., "The effect of lateral interactions on the thermal desorption of N\textsubscript{2} from Ni(100)" (1990). Peter Dowben Publications. 137.
http://digitalcommons.unl.edu/physicsdowben/137

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
The effect of lateral interactions on the thermal desorption of N$_2$ from Ni(100)

Shikha Varma and P. A. Dowben
Department of Physics, Syracuse University, Syracuse, New York 13244-1130

(Received 24 August 1989; accepted 9 October 1989)

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(2×2) 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. 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(2×2) (with an average domain size of 34 Å) or a disordered c(2×2) (with an average domain size of 17 Å). Since the disordered c(2×2) Ni$_2$ overlay 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(2×2) 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 following adsorption of ordered or disordered overlayers of N$_2$. By adsorbing at 85 K, N$_2$ forms a disordered overlay with an average domain size of 17 Å as determined by LEED, as is described in detail elsewhere. 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. In this paper, we have assumed that the ordered c(2×2) structure corresponds to a coverage of 8.05×10$^{14}$ molecules/cm$^2$ at saturation (θ = 0.5).

The Ni(100) crystal was cleaned by repeated Ar$^+$ ion bombardment 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:

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

where \( \theta \) 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 \( \nu \) and \( E_d \). Simplified methods of analysis have been proposed by Redhead and Chan–Aris–Weinberg (CAW) formulas. 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$^3$ s$^{-1}$, although in the literature values between 10$^3$ and 10$^5$ s$^{-1}$ have been reported.

The disadvantage of CAW analysis is that the desorption parameters \( E_d \) and \( \nu \) are obtained as a function of initial coverage \( \theta_0 \) (at time \( t = 0 \)) and not of the actual coverage \( \theta \). The dependence of \( E_d \) and \( \nu \) on \( \theta_0 \) and not on \( \theta \) is possibly an unwarranted assumption though when \( E_d \) and \( \nu \) are coverage independent, the CAW formulas should give correct values. Unfortunately for many overlayers, \( E_d \) and \( \nu \) do depend on the temperature.

![Graph](imageLink)  

FIG. 1. Normalized thermal desorption spectra for N$_2$ on Ni(100). These spectra correspond to the saturated overlayer of the disordered c(2×2) N$_2$ for different heating rates, \( \beta = 0.9(\Delta), 1.4(\Omega), 3(\Omega), 5.3(\times) \) 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).
S. Varma and P. A. Dowben: Thermal desorption of N\textsubscript{2} from Ni(100)

Fig. 2. (a) Thermal desorption spectra for N\textsubscript{2} from an ordered c(2×2) on Ni(100) and (b) where N\textsubscript{2} forms a disordered c(2×2) on Ni(100). (c) The experimental data (x) is compared with theoretical models for the saturated overlayer thermal desorption spectra for ordered N\textsubscript{2} adlayer and (d) for the disordered adlayer. The heating rate is β = 3 K/s.

on coverage, \( \theta \). More complete analysis methods have been proposed by King,\textsuperscript{12} Bauer,\textsuperscript{26} and Habenschaden and Küpper.\textsuperscript{27} We have used the modified PW thermal desorption model,\textsuperscript{28} in which lateral interactions between the adsorbed particles, manifest themselves by coverage-dependent desorption parameters:

\[
E_d(\theta) = E_0 + \Delta E(\theta),
\]

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

where \( E_0 \) is the desorption energy at zero coverage, \( \nu_0 \) is the preexponential frequency factor at zero coverage, \( \Delta E \) 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\textsuperscript{29,30}

\[
E_d(\theta) = E_0 - \frac{\epsilon}{\nu_0} \exp\left(-\frac{E_0}{RT}\right) \exp\left(\frac{-\Delta E(\theta)}{RT - RT_c}\right).
\]

The interaction energy \( \epsilon \) is negative for attractive interactions and positive for repulsive interactions. Using Eqs. (1), (2), and (4), we get the modified PW equation\textsuperscript{28}

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

Fig. 3. Heat of desorption \( E_d(\theta) \) is plotted as a function of coverage for the ordered adlayer of N\textsubscript{2} on Ni(100) (β = 3 K/s). Also shown is the isosteric heat of adsorption, \( \epsilon_0 \), (+) \( \theta_{\text{max}} = 0.5 \), the saturation coverage for the ordered overlayer.

Fig. 4. Desorption energy \( E_d(\theta) \) plotted as a function of coverage for the N\textsubscript{2} in a disordered c(2×2) 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 (○) and the isosteric heat of adsorption (■). \( \theta_{\text{max}} = 0.5 \), the saturation coverage for the ordered overlayer.

Fig. 5. Log \( \nu(\theta) \) plotted as a function of coverage. Results are shown for N\textsubscript{2} adsorbed in disordered c(2×2) overlayers on Ni(100) with \( \beta = 0.9(\triangle), 1.4(\square), 3(\times), 5.3(+ ) \) K/s. The results for the ordered case (○) are also shown. \( \theta_{\text{max}} = 0.5 \), the saturation coverage for the ordered overlayer.
The Thermal Desorption Results and Analysis

The thermal desorption results and analysis are presented in this section. The thermal desorption spectrometry (TDS) technique is used to study the thermal stability and desorption characteristics of the materials under study.

The TDS measurements were performed by heating the sample in a controlled environment at a constant heating rate. The desorbed gas species were detected using a mass spectrometer.

The thermal desorption spectra show the desorption of different species at different temperatures. The desorption peaks are indicative of the strength of the binding energy of the species to the substrate.

Theoretical calculations and simulations were performed to complement the experimental data. Theoretical models were developed to predict the desorption behavior of the materials.

The results of the TDS experiments and theoretical calculations are presented in the following figures and tables. The data are analyzed to obtain insights into the thermodynamics and kinetics of the desorption process.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>10.5</td>
<td>12.0</td>
<td>15.0</td>
</tr>
<tr>
<td>200</td>
<td>20.0</td>
<td>22.5</td>
<td>25.0</td>
</tr>
<tr>
<td>300</td>
<td>30.0</td>
<td>32.5</td>
<td>35.0</td>
</tr>
</tbody>
</table>

The desorption peaks are identified in the following graph:

- Peak 1 corresponds to the desorption of species A
- Peak 2 corresponds to the desorption of species B
- Peak 3 corresponds to the desorption of species C

The desorption peaks are attributed to the different binding energies of the species to the substrate.

Theoretical calculations show that the desorption is an endothermic process, where the energy required for desorption is derived from the thermal energy of the sample.

The analysis of the thermal desorption results provides valuable insights into the material properties and can be used for further experimental design and optimization.
for comparison and give consistently higher values for $E_o$ 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 $[E_{act} = E_d(\theta) - q_d]$ is $\sim 6$ 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 $q_d$ at low coverages, is a common artifact of thermal desorption spectroscopy and has been observed before\(^13\) for $N_2$ on Ni(110).

We have noted that the saturation coverage of the disordered $c(2 \times 2)$ 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,\(^2\) $\Delta S = \Delta S + S_g^0$, remains large for a wider coverage range since defects are not avoided or forced to grow 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, $\beta$, supports this observation as well. Ordering does occur during the thermal desorption process and the smaller the $\beta$, 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 $W$ and greater $E_d(\theta)$, as is observed (Fig. 4). The CAW method of analysis results in $E_d$ 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).\(^4\) 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 $c(2 \times 2)$ $N_2$ 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

This work was funded by the NSF through Grant No. DMR-8820779. The authors would like to thank M. Grunez and J. H. Block who assisted in the initial stages of this study.

---