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Temperature programmed desorption of Bi on Ni(100)

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The temperature programmed desorption (TPD) spectra of Bi from Ni(100) are characterized by a large shift of the desorption maximum to lower temperatures with increasing coverage. Similar behavior is observed for the desorption of Bi from other metal substrates. Analysis of the desorption of Bi from Ni(100) was performed to determine the kinetic order of desorption and the energetics of the Bi-Ni interaction. We find that Bi desorption is described well by first-order kinetics with a strong coverage dependence of the activation energy of desorption E_d . The value of E_d varies from 70 kcal mol⁻¹ at low Bi coverage to 57 kcal mol⁻¹ for monolayer Bi coverage. We discuss the possible role of Bi₂ in the desorption process and also report the effect of coadsorbed oxygen on the Bi TPD spectrum and the Bi-Ni interaction.

I. INTRODUCTION

The thermal desorption of thin Bi films on oriented metal substrates has been observed for Pt(111),^{1,2} Ni(111),³ and Ni(100).⁴ In all cases, the temperature programmed desorption (TPD) spectra of Bi from these substrates are characterized by irregular peak shapes with a large shift of the peak maximum to lower temperature with increasing Bi coverage. One model used to explain the irregular peak shape assumes that the activation energy for desorption, E_d , decreases with increasing Bi coverage due to lateral, Bi-Bi repulsive interactions. The well-known desorption of the Bi dimer, Bi₂, from bulk Bi⁵ implies that second-order processes leading to the desorption of the dimer could also be important in Bi desorption from other metal substrates. The observed Bi TPD spectra could, in principle, be due to the kinetic order of the Bi desorption process changing as a function of Bi coverage. It is possible that the Bi desorption would follow first-order kinetics at low coverage due to the desorption of Bi atoms from the substrate. At higher coverages, Bi dimer desorption, following second-order kinetics, competes with first-order atomic Bi desorption and causes the observed shift of the TPD peak maximum toward lower temperatures. We have studied the desorption of Bi from Ni(100) and have attempted to analyze the Bi TPD data to determine the kinetic order of desorption and the energetics of the Bi-Ni interaction.

II. EXPERIMENTAL

These experiments were carried out in a ultrahigh vacuum (UHV) chamber, which has been previously described.⁶ The base pressure during these experiments was typically 4×10^{11} Torr. The Ni(100) was cleaned prior to deposition of Bi by reduction in H₂ at 1200 K. The Bi was deposited on the clean Ni(100) by means of a collimated vapor-deposition source.⁷ The Bi was deposited on the surface at rates of between 0.1 and 0.25 monolayer (ML) min⁻¹. The crystal temperature during dosing was held at 500 K. The TPD spectra were obtained using a quadrupole mass spectrometer (QMS) tuned to detect Bi⁺ (209 amu) and a linear temperature ramp of 5 K s⁻¹. Temperature was monitored us-

ing a chromel-alumel thermocouple. Observation of a $c(2 \times 2)$ low-energy electron diffraction (LEED) pattern coincident with a well-defined break in the Auger electron spectroscopy (AES) uptake plot allows assignment of the saturation monolayer coverage of Bi.⁴ The $c(2 \times 2)$ Bi monolayer structure corresponds to an absolute surface coverage of 0.5 ML, referenced to the Ni(100) surface atom density (1 ML = 1.61×10^{15} atoms cm⁻²). Monolayer coverages can be formed by deposition at 500 K of a thick Bi film and subsequent heating to 750 K. Previous work has also shown that the thin Bi film grows via a Stranski-Krastanov (layer-plus-island) growth mode.^{4,8}

III. RESULTS

The Bi TPD spectra in Fig. 1 show two distinct desorption features. At low coverage, only a single peak at 1300 K is observed. As the coverage increases, this becomes broader and ultimately forms an irregularly shaped peak with a small maximum at 1040 K. At a coverage assigned from LEED of

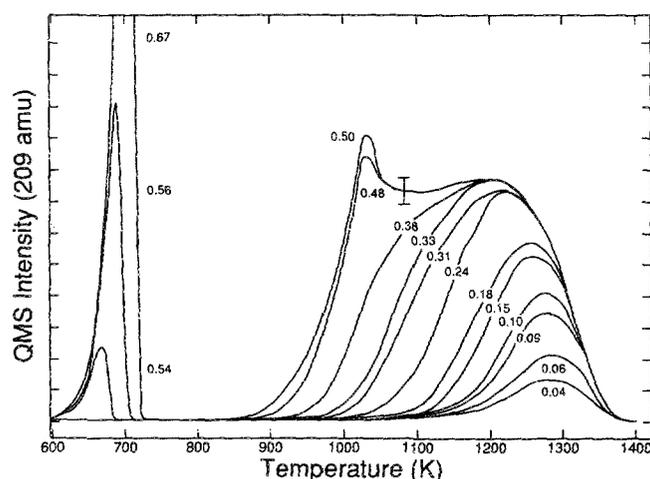


FIG. 1. Experimental TPD spectra of Bi/Ni(100). The labels indicate the surface Bi coverage in ML. The ramp rate was 5 K s⁻¹.

0.5 ML, the high temperature desorption feature is unaffected by increasing coverage. This feature represents desorption from the stable $c(2 \times 2)$ Bi monolayer coverage on Ni(100). Higher coverages result in the growth of a zero-order desorption peak between 600 and 700 K and corresponds to the formation of a multilayer Bi structure. The zero-order desorption peak has $E_d = 48 (\pm 2)$ kcal mol⁻¹, consistent with the sublimation enthalpy of bulk Bi ($\Delta H_{298}^0 = 49.5$ kcal mol⁻¹).⁵ The multilayer can be removed by heating to 750 K, leaving only the chemisorbed monolayer $c(2 \times 2)$ -Bi structure.

Observations of the shape of the desorption features and the shift of the desorption rate maximum can be used to begin analysis of the desorption kinetics. The Bi TPD peak temperature is roughly constant for coverages up to about 0.2 ML. For low surface coverages, the invariance of the peak maximum to increasing coverage and the shape of the peak are indicative of first-order desorption kinetics. As the coverage is increased further, the peak temperature begins a dramatic shift toward lower temperature and the shape of the peak becomes irregular. The low coverage spectra can be simulated using first-order desorption kinetics with constant E_d and preexponential (ν_1). For first-order desorption kinetics, the observed shift of the desorption peak maximum to lower temperatures can only be simulated by decreasing E_d and/or increasing ν_1 as the coverage increases.⁹

Shifts of the desorption peak maximum to lower temperature as the coverage is increased are also characteristic of second-order desorption kinetics. The irregular peak shape and the shift of the desorption maximum toward lower temperature in the experimental Bi TPD could be caused by competing first-order and second-order processes. If this were the case, the first-order process, producing gas phase Bi atoms, would be dominant at low coverage and the second-order process, producing gas phase Bi dimers, would begin to compete as the surface coverage is increased. The shape of the experimental Bi TPD spectra could indicate the presence of a second-order desorption process above 0.2 ML. The presence of gas phase Bi dimers could be confirmed by observation of Bi_2^+ ions during the desorption. Unfortunately, the mass range of the mass spectrometer used for the TPD studies (300 amu) does not allow direct observation of Bi_2^+ (418 amu).

A change from first- to second-order desorption kinetics might also be expected to cause nonlinearity in the plot of Bi TPD peak area with Bi deposition time. The plot of TPD area versus deposition time is linear to within experimental uncertainty (10%), as shown in Fig. 2. An examination of the known kinetics of desorption of bulk Bi offers some insight into how large a change in the TPD uptake plot would be expected if a change in the kinetic order of the desorption occurred. The thermochemistry and ionization cross sections of Bi have previously been investigated.⁵ For the sublimation of bulk Bi, the rate of desorption of Bi_2 is greater than that of Bi atoms at 834 K. As the desorption temperature increases, the ratio of Bi_2 to Bi decreases and approaches unity around 1100 K.¹⁰ At 70 eV, the cross section for formation of Bi^+ from Bi_2 is reported to be 1.54 times the cross section of Bi.⁵ This data can be used to simulate a plot of

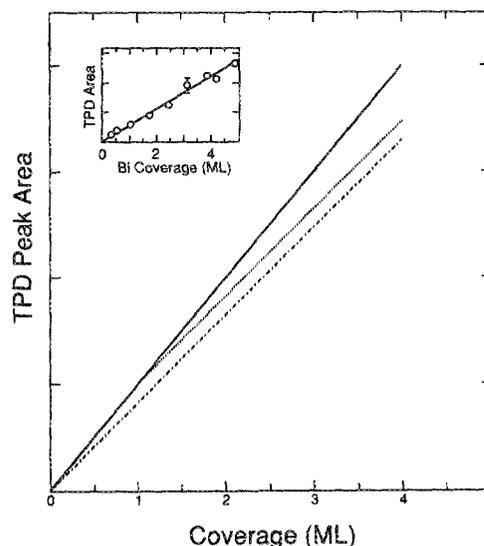


FIG. 2. Plot of the expected TPD area vs surface coverage based on the known desorption kinetics and ionization cross section of Bi. The inset shows the actual experimental uptake. Atoms only (—), atoms and dimers after 1 ML (···), and atoms and dimers (---).

TPD peak area versus surface coverage, as shown in Fig. 2. Within our experimental error, desorption of only Bi atoms is indistinguishable from desorption of both atoms and dimers. The plot clearly shows that monitoring only Bi^+ cannot distinguish between a second-order process producing Bi_2 and purely first-order, atomic desorption. Thus, the linear plot of TPD area versus deposition time we observed cannot be used to rule out competing first- and second-order desorption processes.

We have recently discussed methods of analysis of TPD spectra that can be used to determine the kinetic order of desorption.^{11,12} Application of these methods can determine the kinetic order of the Bi desorption.¹³ The curvature of plots of $[\ln(d\Theta/dt) - n \ln(\Theta)]$ versus $1/T$ was used to determine the order of the desorption kinetics. Fig. 3 shows plots of $[\ln(d\Theta/dT) - n \ln(\Theta)]$ versus $1/T$ for several Bi coverages. Information about the kinetic order of the desorption is obtained by observation of only the low coverage curves. We begin our analysis of the Bi TPD spectra by careful investigation of the spectra obtained at low Bi coverages ($\Theta_{\text{Bi}} < 0.2$ ML). For $\Theta_{\text{Bi}} = 0.15$ ML, the linearity of the plot for $n = 1$ and the upward curvature of the plot for $n = 2$ are both indicative of first-order desorption kinetics. Several low coverage spectra were used to determine the values of the kinetic parameters in the low coverage limit ($\Theta_{\text{Bi}} \rightarrow 0$). This analysis produced values of $n = 1$, $E_d = 70 (\pm 4)$ kcal mol⁻¹ and $\nu_1 = 7.5 \times 10^{10} (\pm 1)$ s⁻¹. This method unambiguously determines the values of n , E_d , and ν_1 in the limit of low coverage.

The Bi TPD spectra at higher coverage were modeled assuming that the values of n and the preexponential^{14,15} were both constant for all values of T and initial Bi coverage. The data for $n = 1$, shown in Fig. 3, were used to calculate the functional form of E_d required to simulate the experimental

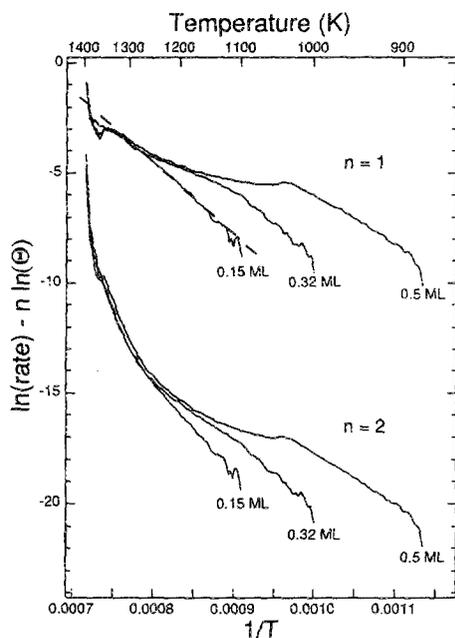


FIG. 3. Plot of $[\ln(d\Theta/dt) - n \ln(\Theta)]$ vs $1/T$ for Bi/Ni(100) TPD. The labels indicate the surface Bi coverage in ML. The dashed line is the best fit to the low coverage data and represents $E_d = 70 \text{ kcal mol}^{-1}$ and $\nu_1 = 7.5 \times 10^{10} \text{ s}^{-1}$.

spectra with $\nu_1 = 7.5 \times 10^{10} \text{ s}^{-1}$ (the value in the low coverage limit). The functional form of E_d required to reproduce the Bi TPD is shown in Fig. 4. As a check of our analysis, we applied the method of Falconer and Madix¹⁶ and calculated values of E_d consistent with the plot in Fig. 4 and a constant value of ν_1 . The coverage dependence of E_d exhibits a sharp change in slope at 0.4 ML and could not be expressed as a

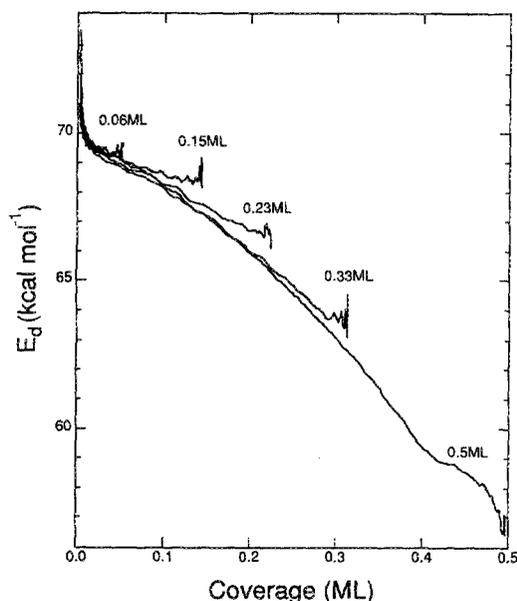


FIG. 4. Calculated first-order, coverage dependent E_d for Bi/Ni(100). The preexponential is held constant at $7.5 \times 10^{10} \text{ s}^{-1}$.

single smooth function. For use in the modeling, the coverage dependence of E_d was fit using two expressions:

$$E_d(\Theta_{\text{Bi}} < 0.412) = 70.0 - 12.8\Theta_{\text{Bi}} - 33.8\Theta_{\text{Bi}}^2,$$

$$E_d(\Theta_{\text{Bi}} \geq 0.412) = 21.3 + 184\Theta_{\text{Bi}} - 226\Theta_{\text{Bi}}^2,$$

where E_d is in kcal mol^{-1} . Simulated TPD spectra created using these expressions and $\nu_1 = 7.5 \times 10^{10} \text{ s}^{-1}$ are shown in Fig. 5. The simulations match the experimental TPD curves extremely well. The cusp that occurs in the Bi TPD spectra at 1000 K is caused by an abrupt change in slope of the plot of E_d versus Θ at 0.4 ML. The subtle change in the slope of E_d versus Θ_{Bi} at 0.4 ML is much smaller than the error associated with our initial determination of E_d in the low coverage limit (approximately 4 kcal mol^{-1}). Yet, simulations that ignore the subtle change in slope fail to accurately duplicate the shape of the experimental spectra. The plot in Fig. 4 can be approximated within the 4 kcal mol^{-1} uncertainty by a simple linear change in E_d with Θ_{Bi} . The result of a simulation assuming such a linearly varying E_d is shown in Fig. 6. This simulation does not match the experimental spectra very well indicating that small inaccuracies in the determination of functional form of E_d will cause poor simulations of experimental spectra. This example stresses the importance of simulation for validating kinetic parameters extracted from TPD spectra.

The effect of oxygen coadsorption on Bi TPD was also investigated. The two spectra shown in Fig. 7 are for Bi desorption from clean Ni(100) and from Ni(100) that had been pre-exposed to 0.5 L O_2 at 500 K prior to desorption. This O_2 exposure forms oxygen adatoms at the surface with $\Theta_{\text{O}} < 0.05 \text{ ML}$.¹⁷ Both Bi TPD spectra are for $\Theta_{\text{Bi}} = 0.7 \text{ ML}$, which corresponds to a chemisorbed Bi ML plus 0.2 ML of additional Bi coverage. The presence of oxygen causes large changes in the Bi TPD spectrum and in the Bi-Ni interaction. No O^+ was observed during TPD and the amount of surface oxygen after TPD, as measured by AES, was equal to

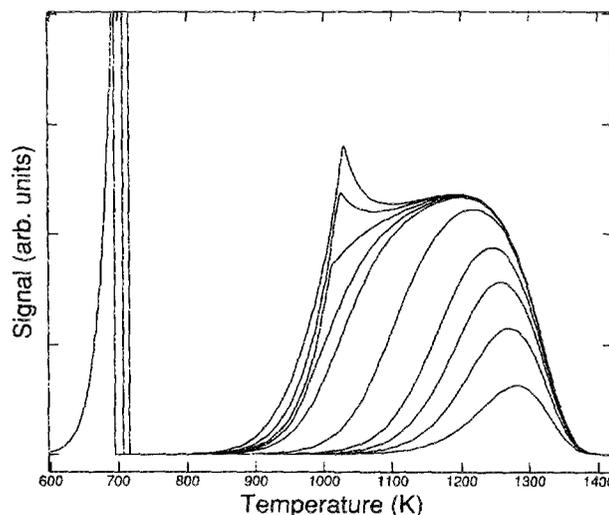


FIG. 5. Simulated Bi/Ni(100) TPD spectra calculated using the coverage dependent, first-order E_d plotted in Fig. 4. Coverages shown are 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.425, 0.45, 0.475, 0.5, 0.55, 0.6, and 0.65 ML.

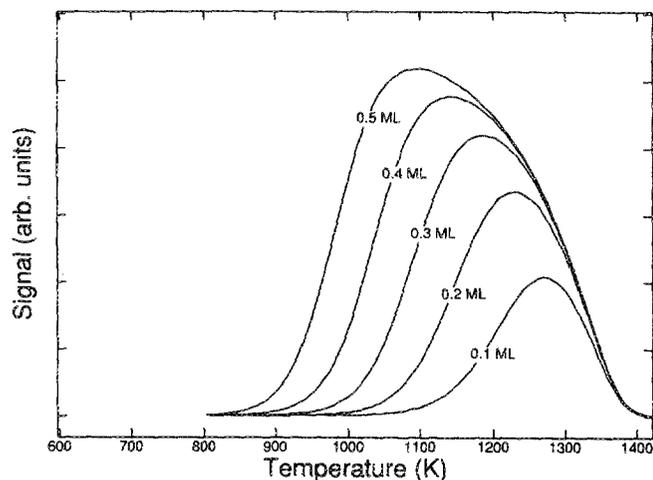


FIG. 6. Simulated Bi/Ni(100) TPD spectra calculated by fitting the curves in Fig. 4 to a single straight line. The spectra were produced with $n = 1$, $\nu_1 = 7.5 \times 10^{10} \text{ s}^{-1}$ and $E_d = 71.2 - 28.3\Theta_{\text{Bi}}$.

the amount present prior to the addition of Bi. In Fig. 7, the high temperature Bi desorption peak areas are identical in the two spectra. Evidently, even though oxygen weakens the Bi-Ni bond, it does not weaken the bond enough at this oxygen coverage to enhance the formation of three-dimensional (3D) Bi crystallites. Oxygen exposure after deposition of Bi on clean Ni(100) was found to have no effect on the Bi TPD spectra. No surface oxygen was detected after exposing a surface with $\Theta_{\text{Bi}} = 0.7 \text{ ML}$ to 10 L of O_2 at 500 K by AES or O_2 TPD.

The spectra shown in Fig. 7 were analyzed to determine the coverage dependence of E_d required to simulate the observed Bi TPD peak shapes. The results are shown in Fig. 8. Coadsorbed oxygen reduces the Bi desorption energy by 7–10 kcal mol^{-1} and thus weakens the Bi-Ni interaction compared to clean Ni(100).

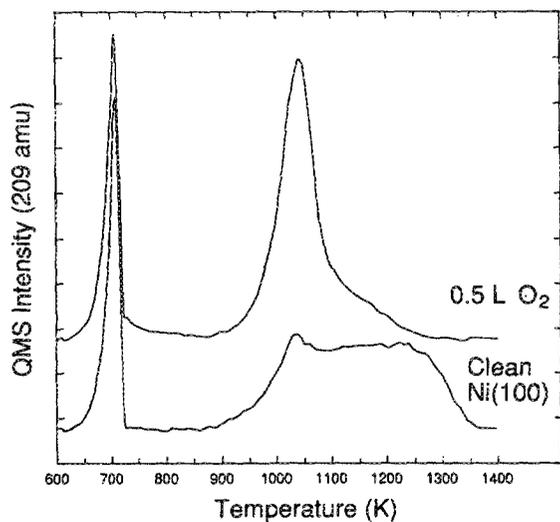


FIG. 7. Experimental Bi/Ni(100) TPD showing the effect of oxygen exposure on the experimental peak shape $\Theta_{\text{Bi}} = 0.7 \text{ ML}$.

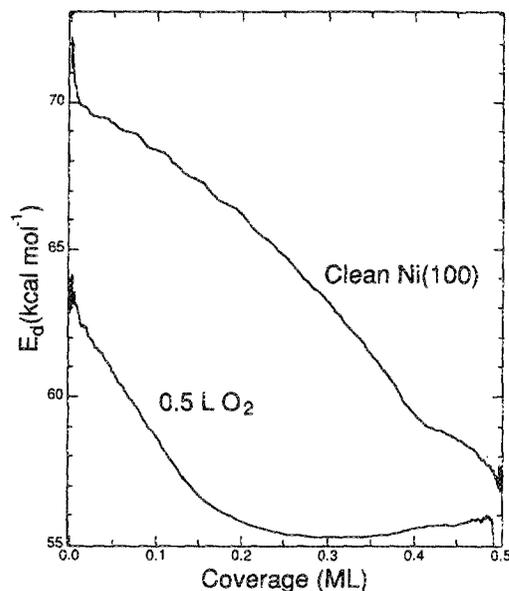


FIG. 8. The coverage dependent, first-order E_d calculated from the spectra in Fig. 7 and assuming a preexponential of $7.5 \times 10^{10} \text{ s}^{-1}$.

IV. DISCUSSION

We were able to successfully model the observed Bi TPD spectra with a coverage dependent E_d using the assumption that the kinetic order and the pre-exponential factor were constants. At low Bi coverage, a first-order process controls the Bi desorption kinetics. Analysis of Bi TPD spectra at higher coverages produces a set of parameters that accurately simulate the experimental data and is consistent with the kinetic parameters determined in the low Bi coverage limit.

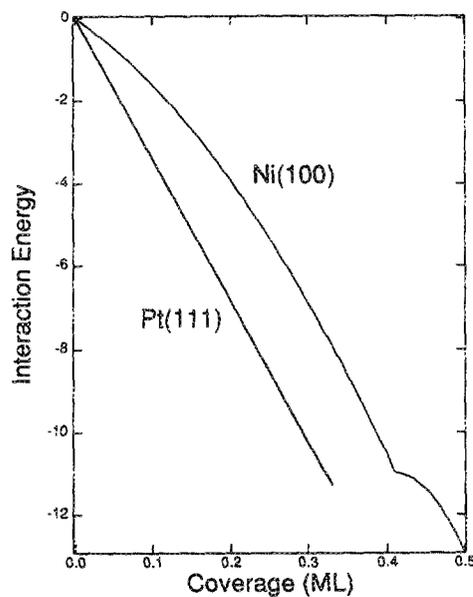


FIG. 9. Plot of the interaction energy for Bi/Ni(100) and Bi/Pt(111) in kcal mol^{-1} .

Direct comparison of the experimental spectra of Fig. 1 with the simulated spectra shown in Fig. 5 illustrates the quality of the calculated parameters. However, our analysis of TPD data obtained only at one heating rate does not produce a unique set of parameters and variation of the kinetic order and/or preexponential factor are not unambiguously excluded. TPD data taken over a wide range of linear heating rates or with a mass spectrometer capable of detecting Bi_2^+ (418 amu) is required to better determine the coverage dependence of the kinetic parameters.

Theoretical treatments of the thermal desorption of weakly perturbing adsorbates (such as Xe) have indicated that adsorbate-adsorbate interactions are the source of the observed coverage dependence in the activation energy for desorption in these systems.^{14,18} The strength of the adsorbate-substrate interaction is responsible for the magnitude of E_d at low surface coverage, E_d^0 . As adsorbate atoms are added to the surface, E_d is altered by a coverage dependent interaction energy, $\alpha(\Theta_{\text{ads}})$, such that $E_d = E_d^0 + \alpha(\Theta_{\text{ads}})$. Therefore, $\alpha(\Theta_{\text{ads}}) = 0$ when $\Theta_{\text{ads}} = 0$.

The small difference in electronegativity between Bi and many transition metal substrates implies that only minimal electron withdrawal occurs when Bi is adsorbed to the surface. This means that the presence of Bi bonded to a substrate atom should only weakly perturb neighboring substrate atoms. The short-range effect of the Bi adsorbate on the substrate means that it is unlikely that through-bond interactions would cause the observed lateral Bi repulsive interactions. Should the Bi-Bi through-space interactions be dominant, one would expect that the functional form of the coverage dependence of the activation energy would be similar on different substrates. The magnitude of the interaction energy we observe for Ni(100) is in very good agreement with the results for Bi on Pt(111),¹ as shown in Fig. 9. This implies that the Bi-Bi repulsive interactions are largely independent of the substrate and should be similar on other metal surfaces.

The experimental Bi TPD spectra are irregularly shaped and exhibit cusps at high coverage that are separate from the multilayer desorption. The cusps observed on Ni(100) are similar to those observed on Pt(111),² Pt(100),¹⁹ and Ni(111).³ Such cusps are inconsistent with a smoothly decreasing E_d due to lateral repulsive interactions.^{9,18} We note that the cusps present in the Bi TPD spectra from clean Ni(100) occur at the same temperature as the peak maximum caused by coadsorbed oxygen (see Fig. 7). The cusps that occur in the TPD spectra of Bi on metal surfaces could be due to (1) an abrupt change in the slope of the coverage dependence of E_d , perhaps due to a two-dimensional structural phase transition, (2) overlapping first- and second-order desorption features, or (3) the presence of very small amounts of contamination on the surface. The presence of the similar cusps in the spectra from several metal surfaces is also an indication that the dynamics controlling the desorption may be determined by Bi-Bi interactions with only a small involvement by the substrate. The Bi-substrate interaction is most important in determining the magnitude of E_d .

V. CONCLUSIONS

Analysis of the desorption of Bi from Ni(100) for small surface coverages of Bi show that the desorption follows first-order kinetics. The TPD spectra of Bi from Ni(100) has been modeled using first-order desorption kinetics with a coverage dependent activation for desorption E_d and constant preexponential factor ν_1 . E_d was shown to vary from 70 kcal mol⁻¹ at low Bi coverage to 57 kcal mol⁻¹ for the monolayer $c(2 \times 2)$ Bi coverage. Lateral Bi-Bi interactions are in large part responsible for the change in E_d with Bi coverage and play an important role in the dynamics of Bi desorption. Small amounts of coadsorbed oxygen adatoms cause changes in the Bi TPD spectra. This results from a reduction in the strength of the Bi-Ni bond and a change in the shape of the coverage dependence of E_d .

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