

Application of transition state theory to desorption from solid surfaces: Ammonia on Ni(111)

Antonio Redondo,^{a)} Yehuda Zeiri,^{b)} John J. Low,^{c)} and William A. Goddard III

Arthur Amos Noyes Laboratory of Chemical Physics,^{d)} California Institute of Technology, Pasadena, California 91125

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We have used transition state theory to derive analytical expressions for the rates of desorption of atoms and molecules (diatomic as well as polyatomic) from solid surfaces. Realistic forms for the three dimensional adsorbate-surface interaction potentials are employed, including surface corrugation. Using potential parameters from a combination of experiment and *ab initio* calculations we have applied the rate expressions to evaluate the temperature programmed desorption spectra of NH₃ from Ni(111). Comparing these curves to the experimental spectra leads to a bond energy of $D_0 = 21.0-3.7\theta$ kcal/mol, where θ is the fraction of saturation coverage.

I. INTRODUCTION

Although transition state theory¹ (TST) has been applied to rate processes for numerous gas phase reactions there are few examples²⁻⁴ in which TST has been applied to desorption from solid surfaces. The TST rate of desorption is given by

$$R = \frac{kT}{h} \frac{f^*}{f} \exp\left(-\frac{E}{kT}\right), \quad (\text{I. 1})$$

where k is the Boltzmann constant, T is the absolute temperature, f^* and f are the partition functions for the activated complex and the adsorbed particle, respectively, and E is the activation energy for desorption. The main difficulty with TST concerns the definition of the transition state for the desorbing species. The most common choice is to assume that the transition state is located at an infinite adsorbate-surface separation. For example, Garrison and Adelman² have derived, using the TST approach, an expression for the one dimensional desorption rate of an atom from a solid surface (motion of the adparticle restricted to the direction normal to the surface). In their derivation they assumed an activated complex located at an infinite distance from the substrate, thus, the partition function at this configuration corresponds to a free atom moving in a direction normal to the surface. The rate expression obtained was

$$R = \frac{\Omega_0}{2\pi} \exp\left(-\frac{D_e - 1/2\Omega_0}{kT}\right), \quad (\text{I. 2})$$

where Ω_0 and D_e are the stretch frequency and binding energy associated with the adsorbate-surface interaction potential. This leads to preexponential factors in the range $10^{12}-10^{13} \text{ s}^{-1}$. On the other hand, Menzel and co-workers³ used the TST approach to explain the large preexponential factors obtained for the desorption rate of CO from metal surfaces.⁵ The rate expression derived yields a preexponential factor of the order of 10^{18}

s^{-1} which is 10^2-10^3 times larger than the experimentally observed values. In some cases it has been assumed⁴ that the ratio of the partition functions appearing in Eq. (I. 1) is approximately equal to one. As a result, considerable discrepancies (2 to 3 orders of magnitude) with experiment have been obtained (for the case of molecular desorption).

In a recent paper⁶ we have used a classical stochastic diffusion theory (CSDT) approach to derive analytic expressions for the rate of desorption of atoms and diatomic molecules from solid surfaces. These results were obtained assuming one dimensional motion of the adsorbate (normal to the surface). For atomic as well as molecular desorption the CSDT expression leads to excellent agreement with experiment. Using the CSDT formalism for a desorbing atom, we obtained a rate expression which is identical to Eq. (I. 2). However, for molecular desorption the expression derived using the CSDT approach was very different from that obtained by Menzel and co-workers.^{3,6}

In the present paper we present a derivation of the expressions for the rate of desorption from surfaces using the TST formalism. In Sec. II we derive the theoretical results for atomic and molecular adsorbates (diatomic and polyatomic) using realistic approximations for the three dimensional interaction potential between the surface and the adsorbate. In Sec. III we apply the results obtained in Sec. II to the desorption of ammonia from Ni(111) surfaces.

II. RATES OF DESORPTION

As pointed out above, the choice of an unambiguous activated complex is of crucial importance. A criterion for the choice of the transition state is given by the variational transition state theory proposed by Horiuti.^{7,1(c)} Here, the activated complex is defined so that the flux at the transition state is an extremum, leading to a nonlinear differential equation for the position of the critical surface. If the potential between the adparticle and the surface increases monotonically from the equilibrium position to infinity, the only solution to the variational equation corresponds to an infinite separation between the adparticle and the surface. There-

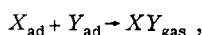
^{a)}Present address: Los Alamos National Laboratory, Group E-11 MS/D429, Los Alamos, NM 87545.

^{b)}Chaim Weizmann Postdoctoral Fellow.

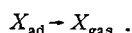
^{c)}Exxon Fellow, 1983.

^{d)}Contribution No. 6854.

fore, application of variational transition state theory leads to the activated complex geometry with the adsorbate infinitely removed from the surface. In addition, we shall assume that the contribution to the partition function from the degrees of freedom of the solid is the same whether the adparticle is close to the surface or infinitely separated from it.² According to CSDT there is a small (10%) effect on Ω_0 due to the coupling of the adsorbate-surface vibration with the surface and bulk phonon spectrum, but we ignore this effect here. It should be pointed out that for the case of associative desorption



the activated complex need not be infinity. Thus, the current theoretical discussion is primarily aimed at the process



A. Rates of atomic desorption

Let us consider an adatom of mass m which is at equilibrium on the surface at a temperature T . The TST expression for the rate of desorption is then given by Eq. (I.1). If we let the z direction be normal to the surface, then the corresponding classical partition function at the transition state is given by

$$f^* = \int dx dy \frac{dp_x}{h} \frac{dp_y}{h} \exp\left(-\frac{p_x^2 + p_y^2}{2mkT}\right) = A \frac{2\pi mkT}{h^2}, \quad (\text{II.1})$$

where p_x and p_y are the components of the momentum parallel to the surface, and A is the total area of the surface.

The partition function for the adatom near the surface is given by

$$f = \int dx dy dz \frac{dp_x}{h} \frac{dp_y}{h} \frac{dp_z}{h} \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mkT}\right) \times \exp\left(-\frac{V(x, y, z)}{kT}\right) = \frac{(2\pi mkT)^{3/2}}{h^3} \int dx dy dz \times \exp\left(-\frac{V(x, y, z)}{kT}\right). \quad (\text{II.2})$$

Here, $V(x, y, z)$ is the interaction potential between the adparticle and the surface. In a typical experimental setup the range of temperatures under which the experiments are performed is such that $kT \ll D_0$, where D_0 is the bond energy, corrected for zero point motion. As a result, the contribution to the partition function due to the interaction potential is appreciable only near the equilibrium position. Thus, we may represent the potential near the surface by the following form:

$$V(x, y, z) = \frac{1}{2} m \Omega_0^2(x, y) [z - z_0(x, y)]^2 + E(x, y), \quad (\text{II.3})$$

where z_0 is the equilibrium distance between the adparticle and the surface, and $E(x, y)$ describes the variation of the potential parallel to the surface (corrugation). Assuming that the surface is periodic in the x and y directions, then, Ω_0 , z_0 , and E will have the same periodicity. Using Eq. (II.3) the integral over z in Eq.

(II.2) leads to

$$f = \frac{m(2\pi kT)^2}{h^3} \int dx dy \frac{\exp[-E(x, y)/kT]}{\Omega_0(x, y)}. \quad (\text{II.4})$$

Now we expand Ω_0^{-1} and $E(x, y)$ in terms of Fourier series,

$$\Omega_0^{-1}(x, y) = \sum_{nm} \Omega_{nm}^{-1} \cos \frac{n\pi x}{a} \cos \frac{m\pi y}{b}, \quad (\text{II.5})$$

$$E(x, y) = \sum_{nm} E_{nm} \cos \frac{n\pi x}{a} \cos \frac{m\pi y}{b}. \quad (\text{II.6.a})$$

where $2a$ and $2b$ are the lattice spacings in the x and y directions, respectively. Since there currently is insufficient information to describe the higher order terms of Eq. (II.6a) (and to keep the problem analytically tractable), we have used only the initial terms of the Fourier series,

$$E(x, y) = -\frac{1}{2} E_x \cos \frac{\pi x}{a} - \frac{1}{2} E_y \cos \frac{\pi y}{b}, \quad (\text{II.6.b})$$

A similar expression has been previously used in surface scattering studies.⁸ In this definition we have assumed that the dissociation energy is measured from the average potential that the particle feels at the surface. Substituting Eqs. (II.5) and (II.6b) into (II.4) we obtain

$$f = A \frac{m(2\pi kT)^2}{h^3} \sum_{nm} \Omega_{nm}^{-1} I_n(E_x/2kT) I_m(E_y/2kT), \quad (\text{II.7})$$

where $I_n(a)$ is the modified Bessel function⁹ of order n . Thus, the final expression for the rate is given by

$$R = \frac{\exp(-D_0/kT)}{2\pi \sum_{nm} \Omega_{nm}^{-1} I_n(E_x/2kT) I_m(E_y/2kT)}. \quad (\text{II.8})$$

For the case of a flat surface Ω_0 and E are independent of x and y , and Eq. (II.8) reduces to Eq. (I.2).

We shall now consider the two limiting cases in which the corrugation is either very small or very large. For small corrugation we have that $E_x \ll 2kT$ and $E_y \ll 2kT$, and we can also assume that Ω_0 is constant. Thus, Eq. (II.8) reduces to

$$R = \frac{\Omega_0}{2\pi} \left[1 + \left(\frac{E_x}{4kT}\right)^2 + \left(\frac{E_y}{4kT}\right)^2 \right]^{-1} \exp(-D_0/kT). \quad (\text{II.9})$$

In this case, the correction due to the corrugation has a minor effect with respect to the rate obtained for a flat surface. On the other hand, when the corrugation is large, i.e., $E_x \gg 2kT$ and $E_y \gg 2kT$ (this is a common situation for chemisorbed systems), the following expression is obtained:

$$R = \frac{(E_x E_y)^{1/2}}{2kT \sum_{nm} \Omega_{nm}^{-1}} \exp[-(D_0 + \frac{1}{2} E_x + \frac{1}{2} E_y)/kT]. \quad (\text{II.10a})$$

The energy expression in the exponential now corresponds to the binding energy with respect to the bottom of the potential. In addition, the preexponential factor is larger than the corresponding prefactor in Eq. (I.2) and is an explicit function of temperature. If one replaces the periodic potential (II.6) with simple harmonic potentials

$$E(x, y) = -\frac{E_x + E_y}{2} + \frac{E_x}{a^2} x^2 + \frac{E_y}{b^2} y^2,$$

with a minimum at the best adsorption site (stretch frequency Ω_0), the resulting desorption rate is

$$R_{\text{harmonic}} = \frac{2\Omega_0(E_x E_y)^{1/2}}{\pi^2 kT} \exp[-(D_0 + \frac{1}{2}E_x + \frac{1}{2}E_y)/kT]. \quad (\text{II. 10b})$$

This expression differs from that of Eq. (II. 10a) by a factor of $\pi^2/4$, due to the difference between the probability distributions for harmonic and sinusoidal potentials.

B. Rates of molecular desorption

The main difference between molecular and atomic desorption is due to two characteristic features of molecular adsorbates. First, molecules have *internal* degrees of freedom which are absent in atomic systems. In addition, molecules exhibit *frustrated rotational* modes (surface-adsorbate bending modes) strongly coupled to the surface but which become pure rotational modes in the activated state. First we consider a diatomic molecule desorbing from a solid surface. The partition function of the activated complex is given by

$$f^* = \int dx dy dr d\vartheta d\varphi \frac{dp_x}{h} \frac{dp_y}{h} \frac{dp_r}{h} \frac{dp_\vartheta}{h} \frac{dp_\varphi}{h} \times \exp\left(-\frac{P^2}{2kT}\right) \exp\left(-\frac{U(r)}{kT}\right). \quad (\text{II. 11})$$

where

$$P^2 = \frac{p_x^2 + p_y^2}{M} + \frac{p_r^2}{\mu} + \frac{p_\vartheta^2}{I} + \frac{p_\varphi^2}{I \sin^2 \theta}.$$

M is the total mass of the molecule, μ is the reduced mass, and I is the moment of inertia. Here x and y refer to the position of the center of mass, while r , ϑ , and φ are the spherical polar (internal) coordinates defined with respect to the center of mass. Since the activated complex corresponds to an infinite surface-molecule separation, the total potential reduces to the internal potential, represented by $U(r)$. In calculating the integrals appearing in Eq. (II. 11), we will assume that the internal potential, $U(r)$, is harmonic, with a frequency ω_i . Within this approximation the partition function at the transition state reduces to

$$f^* = \frac{A}{h^5} \left[\frac{32\pi^4 M (kT)^3 I}{\omega_i} \right]. \quad (\text{II. 12})$$

The partition function for the adsorbed state is given by

$$f = \int dq \frac{dp}{h^5} \exp\left[-\frac{P^2 + p_r^2/M}{2kT} - \frac{V(q)}{kT}\right], \quad (\text{II. 13})$$

where q and p represent the coordinates and momenta both of the center of mass and of the internal degrees of freedom, while $V(q)$ is the three dimensional potential felt by the molecule near the surface. Performing the integral over the momenta we obtain

$$f = \frac{(2\pi kT)^3 M^{3/2} \mu^{1/2} I_r}{h^5} \int dq \sin \vartheta \exp\left[-\frac{V(q)}{kT}\right], \quad (\text{II. 14})$$

where I_r is the moment of inertia associated with the frustrated rotation at the surface.

As in the case of atomic desorption, the main contri-

bution to the partition function arises from configurations near the equilibrium position. Hence, we shall represent the potential $V(q)$, with a form similar to that of Eq. (II. 3) (an alternate description of this potential in terms of two independent bending oscillators is discussed in the Appendix),

$$V(q) = \frac{1}{2} \{ M \Omega_0^2(x, y) [z - z_0(x, y)]^2 + I_r \Omega_r^2(x, y) \vartheta^2 + \mu \bar{\omega}_i^2(x, y) r^2 \} + E(x, y), \quad (\text{II. 15})$$

where Ω_r is the frequency associated with the bending (angle ϑ) motion, and $\bar{\omega}_i$ is the frequency of the internal vibration at the surface. In Eq. (II. 15) we have assumed that the total potential is independent of the azimuthal angle, φ . This is generally a good approximation for binding sites on low Miller index surfaces but would not necessarily be valid for a molecule binding at a step or at a surface defect. The quantities depending on x and y will have the same periodicity as the surface; thus, they can be expanded in terms of the corresponding Fourier series. As in the atomic case, we shall assume that $E(x, y)$ has the first order form given in Eq. (II. 6b). Performing the integrations over z , r , ϑ , and φ we obtain

$$f = \frac{M(2\pi kT)^5}{h^8} \int dx dy \Omega_0^{-1}(x, y) \Omega_r^{-2}(x, y) \times \bar{\omega}_i^{-1}(x, y) \exp\left[-\frac{E(x, y)}{kT}\right]. \quad (\text{II. 16})$$

In deriving this equation one has to evaluate the integral:

$$\int_0^\pi d\theta \sin \theta \exp\left[-\frac{I_r \Omega_r^2(x, y) \theta^2}{2kT}\right].$$

Under typical experimental conditions, $I_r \Omega_r^2(x, y) \pi^2 \gg 2kT$, so that the exponential term decays rapidly and we can extend the limits of integration from zero to infinity. As a result, the integral is given by a confluent hypergeometric series¹⁰ which we can approximate by the first term, leading to Eq. (II. 16).

We will consider now the integrations over x and y . Since each of the frequencies appearing in the integrand of Eq. (II. 16) is a periodic function of x and y , the pre-exponential factor in the integrand can be expanded in terms of a Fourier series,

$$[\Omega_0(x, y) \Omega_r^2(x, y) \bar{\omega}_i(x, y)]^{-1} = \sum_{nm} \Gamma_{nm} \cos \frac{n\pi x}{a} \cos \frac{m\pi y}{b}. \quad (\text{II. 17})$$

Substituting Eqs. (II. 6b) and (II. 17) into Eq. (II. 16) one obtains

$$f = \frac{AM(2\pi kT)^5}{h^8} \sum_{nm} T_{nm} I_n(E_x/2kT) I_m(E_y/2kT). \quad (\text{II. 18})$$

The rate of desorption is then given by

$$R = \frac{I \exp(-D_0/kT)}{\pi kT \omega_i \sum_{nm} I_n(E_x/2kT) I_m(E_y/2kT)}. \quad (\text{II. 19})$$

In the limit of a flat surface this expression reduces to

$$R = \frac{\Omega_0}{2\pi} \left(\frac{2I\Omega_r^2}{kT} \right) \left(\frac{\bar{\omega}_i}{\omega_i} \right) \exp(-D_0/kT). \quad (\text{II. 20})$$

Except for a factor of $\pi/4$ (~ 0.8) this expression agrees

with the corresponding rate obtained from CSDT.⁶ The difference arises from the fact that in the present treatment the integral over the angle ϑ was carried out from zero to infinity, whereas in the CSDT approach we integrate to a maximum bending angle (which was taken to be $\pi/2$). The effect of the internal vibration on the rate of desorption is given by the ratio $\bar{\omega}_i/\omega_i$. In most cases the internal vibrational frequency at the adsorbed state is only slightly different ($\sim 10\%$ – 20%) from the corresponding value for a free molecule. For chemisorbed molecules one often finds that the limit of large corrugation, $E_x \gg 2kT$ and $E_y \gg 2kT$, is satisfied. One then obtains an expression similar to Eq. (II.10). On the other hand, in such a situation one adsorption site is usually dominant (large binding energy) and only the frequencies associated with this site can be measured experimentally. Assuming that these frequencies do not vary appreciably with x and y , (i.e., their Fourier series consist only of the constant term), one obtains the following form for the rate of desorption:

$$R = \frac{\Omega_0}{2\pi} \left(\frac{2\pi I \Omega_r^2 (E_x E_y)^{1/2}}{(kT)^2} \right) \left(\frac{\bar{\omega}_i}{\omega_i} \right) \exp[-D_0 + \frac{1}{2} E_x + \frac{1}{2} E_y]/kT]. \quad (\text{II. 21})$$

A comparison between the atomic and diatomic desorption rates shows that the main difference lies in the additional degrees of freedom of the diatomic molecule (e.g., frustrated rotation and internal vibration). The frustrated rotation is strongly coupled to the surface, so that the total potential which the adsorbed molecule feels has a large component due to this mode. However, the corresponding mode in vacuum is a free rotation. Hence, the ratio of the partition function in Eq. (I.1) leads to a special (and relatively large) contribution to the prefactor.

On the other hand, the internal degrees of freedom contribute to the total potential both at the adsorbed state and in the activated complex. Since the difference between these contributions to the respective partition functions is small, their effect on the preexponential factor appears as the ratio $\bar{\omega}_i/\omega_i$, which is always close to unity. Therefore, for a polyatomic molecule we can treat the contribution of the internal modes to the total interaction potential (at the surface) similarly to that of the internal vibration of a diatomic system [Eq. (II.15)]. Consequently, the rate of desorption of a polyatomic molecule, for the case of a flat surface, is given by

$$R = \frac{\Omega_0}{2\pi} \left(\frac{2I \Omega_r^2}{kT} \right) \prod_i \left(\frac{\bar{\omega}_i}{\omega_i} \right) \exp(-D_0/kT), \quad (\text{II. 22a})$$

where the product is over all the internal degrees of freedom. The corresponding expression for the large corrugation case is

$$R = \frac{\Omega_0}{2\pi} \left(\frac{2\pi I \Omega_r^2 (E_x E_y)^{1/2}}{(kT)^2} \right) \prod_i \left(\frac{\bar{\omega}_i}{\omega_i} \right) \times \exp[-(D_0 + \frac{1}{2} E_x + \frac{1}{2} E_y)/kT]. \quad (\text{II. 22b})$$

As discussed above, the rate expressions for diatomic molecules derived in this section are almost identical to those obtained using the CSDT formalism. In the CSDT approach we assumed that the energy stored in the frustrated rotation could be transformed¹¹ (through the cou-

pling to the surface) into translational kinetic energy, resulting in an increase in the desorption rate (with respect to the atomic case). The agreement between these two methods confirms the validity of this assumption. Therefore, one would expect that a desorbed diatomic molecule has a rotational temperature which is about half of the surface temperature. In general, the rotational temperature of the desorbed molecule would correspond to an energy which is $\approx \frac{1}{2} kT$ less than the corresponding value at the surface; for a polyatomic molecule this is equivalent to a rotational temperature equal to one third that of the surface. This is in excellent agreement with recent experiments by Cavanagh and King,¹² who find that NO desorbing from a clean Ru(001) surface at 455 K exhibits a rotational temperature of 235 ± 35 K (with a Boltzmann distribution).

III. DESORPTION OF AMMONIA FROM Ni(111)

The rate expressions (as obtained from CSDT) presented in Sec. II have been previously applied to both atomic (physisorbed and chemisorbed) and molecular (diatomic) desorption.⁶ In all the systems studied the agreement between the calculated and experimental rates has been excellent. In this paper we will consider the desorption of a polyatomic molecule, namely ammonia, from the Ni(111) surface. Although several temperature programmed desorption (TPD) spectra have been published¹³ for this system, no bond energies have been extracted from the data, probably because of the lack of a quantitative basis for estimating the preexponential factors for the desorption process. In this section we will use the expressions derived in Sec. II to calculate such prefactors. These can then be used to fit the published TPD spectra, and hence, to obtain estimates for the ammonia-surface bond energy, as well as its dependence on coverage.

Most of the internal vibrational frequencies of ammonia on Ni(111) surfaces are known experimentally,^{13(a)} however, neither the molecule surface stretch frequency Ω_0 , nor the frequency of the frustrated rotation Ω_r , have yet been determined in these experiments. Unfortunately, these two frequencies appear in the expression for the preexponential factor [e.g. Eq. (II.22)]. In order to obtain quantitative estimates, we have performed Hartree-Fock calculations for ammonia adsorbed on the three-coordinate site of the Ni(111) surface modeled with a Ni₁₅ cluster (see Fig. 1). Optimizing the geometries with an analytic gradient procedure,¹⁴ we found that the ammonia molecule has C_{3v} geometry with a negligible barrier (< 0.1 kcal/mol) for rotation about the C_{3v} axis. To test the effect of the basis set dependence of the results, the calculations have been performed using several basis sets.¹⁴ We found that the most sensitive quantities are the binding energy, which varied between 10 and 30 kcal/mol, and the equilibrium Ni-N distance (changes by as much as 0.2 Å). Typical values for the geometry parameters with a standard basis set¹⁵ are 2.13 Å for the nearest neighbor Ni-N distance, 1.012 Å for the N-H bond length, and the optimum H-N-H angle was 104.8°. The calculated¹⁵ ammonia-surface stretch frequency was 417 cm⁻¹ while Ω_r was found to be 509 cm⁻¹. The basis set dependence of these frequencies is much weaker than

that of the binding energy (the maximum variation corresponded to a decrease of $\sim 150 \text{ cm}^{-1}$).

Since the variation of the interaction potential parallel to the surface is not known experimentally, and since cluster calculations may not yield accurate values for such potentials, we assumed a flat surface and used Eq. (II. 22) to obtain the preexponential factors. Introducing the experimental frequencies^{13(a)} together with the calculated values for Ω_0 (417) and Ω_r (509) into the expression for the preexponential factor [Eq. (II. 22a)] the rate of desorption is given by

$$R = \frac{\nu_0}{T} \exp\left(-\frac{D_0}{kT}\right), \quad (\text{III. 1})$$

where $\nu_0 = 9.5363 \times 10^{17} \text{ K/s}$. In order to estimate the sensitivity of Eq. (III. 1) upon the calculated values for the frequencies Ω_0 and Ω_r we considered the case where the actual frequencies are overestimated by $\sim 100 \text{ cm}^{-1}$. Using $\Omega_0 = 300 \text{ cm}^{-1}$ and $\Omega_r = 400 \text{ cm}^{-1}$ we found that $\nu_0 = 4.2319 \times 10^{17} \text{ K/s}$, a decrease of only a factor of 2.

To calculate the TPD spectra we solved numerically the Redhead equation¹⁶

$$\frac{d\Theta}{dt} = -\frac{\nu_0\Theta}{T} \exp\left(-\frac{D_0(\Theta)}{kT}\right), \quad (\text{III. 2})$$

where Θ is the coverage. In a previous study^{8(c)} we calculated the variation of D_0 and ν_0 with coverage for the desorption of Xe from W(111). There we found that $D_0(\Theta)$ varies linearly with the coverage, whereas the preexponential factor remains coverage independent. Thus, in the numerical solution of the Redhead equation we assumed that both of these conditions are valid, so that

$$D_0(\Theta) = D_0(0) + \beta\Theta.$$

The solution of Eq. (III. 2) can be used to fit the experimental TPD spectra^{13(b)} by varying $D_0(0)$ and β . We fitted curves (a), (b), and (d) of Fig. 1 in Ref. 13(b) assuming that the corresponding coverages are 0.25, 0.35, and 1.0 monolayers, respectively [these values are consistent with the areas under curves (a) and (b) assuming, as the authors of Ref. 13(b) indicate, that curve (d) cor-

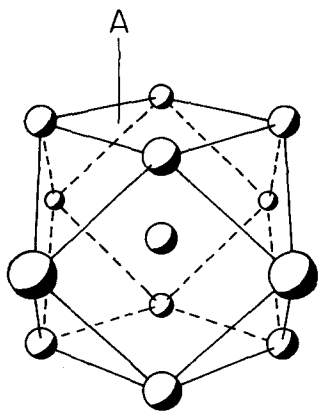


FIG. 1. Ni_{13} cluster used to model the Ni(111) surface.

$\text{Ni}_{13} [4:5:4]$ cluster

TPD spectra of NH_3 on Ni(III)

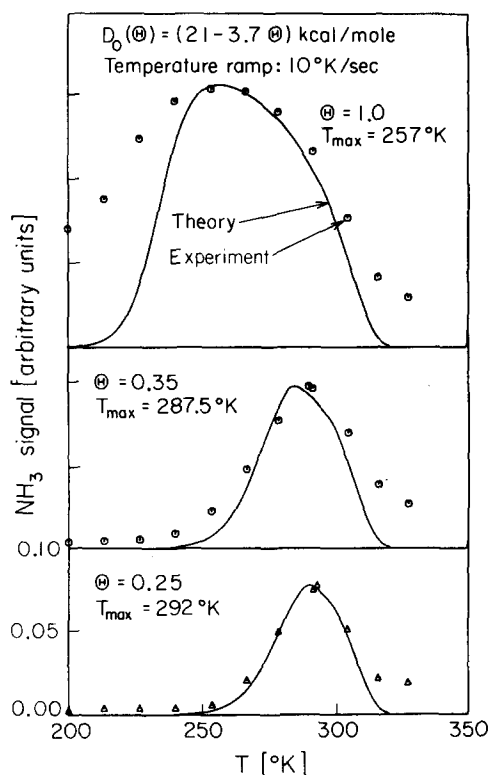


FIG. 2. Calculated TPD spectra. Solid lines: calculated curves; circles and triangles: experimental values [after Ref. 13(b)].

responds to $\Theta = 1.0$]. Using the experimental temperature ramp (10 K/s), the best fit to the TPD curves was obtained for $D_0(0) = 21 \text{ kcal/mol}$ and $\beta = -3.7 \text{ kcal/mol}$. Figure 2 shows a comparison between the calculated TPD curves obtained using these parameters (solid lines) and the experimental points [as taken from Fig. 1 of Ref. 13(b)]. For each coverage the experimental curve was renormalized so that the value at the peak coincided with the calculated maximum height. The fit between the experimental and calculated TPD spectra is excellent for low coverages. At $\Theta = 1.0$ the experimental curve exhibits a shoulder at low temperatures which may be due to desorption from islands of ammonia ice, which are not included in the present calculations. A similar calculation using the ν_0 obtained from the "corrected" frequencies Ω_0 and Ω_r leads to a $D_0(0)$ which is 0.5 kcal/mol smaller. The shift in the TPD peaks to lower temperature (with increasing coverage) as well as the negative sign of β indicate that the lateral interaction between coadsorbed NH_3 molecules is repulsive.^{8(c),13(d)} If one assumes that at saturation coverage ($\Theta = 1.0$) the ammonia molecules adsorb in every other threefold site,¹³ then the average lateral repulsion between two coadsorbed ammonia molecules (at a N-N distance of 2.49 Å is 1.2 kcal/mol (as obtained from the value of β).

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APPENDIX

In this Appendix we discuss an alternate description of the potential (II.15) for a diatomic molecule in the adsorbed state. In particular, we are interested in the possibility of describing the potential of the molecule near the equilibrium position z_0 in terms of two independent bending modes (which will be represented by harmonic oscillators), say one on the xz plane and the other along the yz plane. For simplicity, we shall restrict the discussion to the case of a flat surface. Thus, the contribution to the total potential due to these two frustrated rotations would be

$$V_{fr} = \frac{1}{2} I_r \Omega_r^2 (\vartheta_x^2 + \vartheta_y^2) \approx \frac{1}{2} I_r \Omega_r^2 (\sin^2 \vartheta_x + \sin^2 \vartheta_y) \\ = \frac{1}{2} \mu \Omega_r^2 (x_i^2 + y_i^2), \quad (\text{A1})$$

where x_i and y_i refer to the internal coordinates. Neglecting the internal degree of freedom, Eq. (A1) would lead to the same bending frequency that appears in Eq. (II.15) and hence the same rate expression, Eq. (II.20). However, this expression ignores the dependence of the internal vibration on x_i and y_i . The correct potential energy is

$$V = \frac{1}{2} \mu (\Omega_r^2 + \bar{\omega}_i^2) (x_i^2 + y_i^2) + \frac{1}{2} \mu \bar{\omega}_i^2 z_i^2. \quad (\text{A2})$$

Thus, the system can only be described in terms of two independent frustrated rotations if we assign to them a frequency Ω_{eff} which is given by

$$\Omega_{\text{eff}}^2 = \Omega_r^2 + \bar{\omega}_i^2. \quad (\text{A3})$$

Therefore, a choice of Cartesian coordinates leads to a coupling between the bending and stretching modes. This coupling is avoided by choosing the coordinate system described in the text.

¹(a) S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941), p. 347; (b) S. Benson, *Thermochemical Kinetics*, 2nd ed. (Wiley-Interscience, New York, 1976), p. 79; (c) P. Pechukas, *Annu. Rev. Phys. Chem.* **32**, 159 (1981).

²B. J. Garrison and S. A. Adelman, *J. Chem. Phys.* **67**, 2379 (1977).

³H. Pfnür, P. Feulner, H. A. Engelhardt, and D. Manzel, *Chem. Phys. Lett.* **59**, 481 (1978).

⁴(a) K. J. Laidler, in *Catalysis*, edited by P. H. Emmett (Reinhold, New York, 1954), Vol. 1, Chap. 5; (b) D. O. Hayward and B. M. W. Trapnell, *Chemisorption* (Butterworths, London, 1964), p. 150; (c) F. C. Tompkins, *Chemisorption of Gases on Metals* (Academic, London, 1978), p. 66.

⁵C. R. Helms and R. J. Madix, *Surf. Sci.* **52**, 677 (1975).

⁶(a) A. Redondo, Y. Zeiri, and W. A. Goddard III, *Phys. Rev. Lett.* **49**, 1847 (1982); (b) Y. Zeiri, A. Redondo, and W. A. Goddard III, *Surf. Sci.* (in press); (c) A. Redondo, Y. Zeiri, and W. A. Goddard III (submitted).

⁷J. Horiuti, *Bull. Chem. Soc. Jpn.* **13**, 210 (1938).

⁸(a) G. Wolken, *J. Chem. Phys.* **58**, 3047 (1973); (b) G. Wolken, *ibid.* **59**, 1159 (1973); (c) L. M. Hubbard and W. H. Miller, *ibid.* **78**, 1801 (1983).

⁹*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun, Natl. Bur. Stand., AMS 55 (U. S. GPO, Washington, D.C., 1964), p. 374.

¹⁰I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1965), p. 480.

¹¹(a) The participation of rotational modes in the desorption process has been previously suggested in J. L. Falconer and R. J. Madix, *Surf. Sci.* **48**, 393 (1975); see also (b) J. M. Bowman and J. L. Gossage, *Chem. Phys. Lett.* **96**, 481 (1983); D. O. Hayward and B. M. W. Trapnell, *Chemisorption* (Butterworths, London, 1964), p. 153.

¹²(a) R. R. Cavanagh and D. S. King, *Phys. Rev. Lett.* **47**, 1829 (1981); (b) R. R. Cavanagh and D. S. King, *J. Vac. Sci. Technol. A* **1**, 1267 (1983).

¹³(a) G. B. Fisher and G. E. Mitchell, *J. Electron Spectrosc.* **29**, 253 (1983); (b) T. E. Madey, J. E. Houston, C. W. Seabury, and T. N. Rhodin, *J. Vac. Sci. Technol.* **18**, 476 (1981); (c) C. W. Seabury, T. N. Rhodin, R. J. Purtell, and R. P. Merrill, *Surf. Sci.* **93**, 117 (1980); (d) F. P. Netzer and T. E. Madey, *ibid.* **119**, 422 (1982).

¹⁴J. J. Low and W. A. Goddard III (to be published).

¹⁵The nitrogen and hydrogen atoms were described *ab initio* using the Dunning valence double- ζ contraction [T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer (Plenum, New York, 1977), Vol. 3, p. 1] of the Huzinaga [S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965)] N-atom basis plus one set of d polarization functions (exponent of 0.8). The hydrogens were described in terms of a double- ζ contraction of Huzinaga's 4-Gaussian basis scaled by a factor of 1.2. The Ni modified effective potential and basis were those used by Upton and Goddard [T. H. Upton and W. A. Goddard III, *CRC Crit. Rev. Solid State Mat. Sci.* **10**, 261 (1981)].

¹⁶P. A. Redhead, *Vacuum* **12**, 203 (1962).