

Chemical Potential of Adsorbed Molecules from a Quantum Statistical Formulation[†]

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When classical mechanics is used to treat an adsorption system involving a homogeneous surface, it is assumed that all adsorbed molecules have the same adsorption energy. In a quantum mechanical description of a homogeneous surface, the energy at an adsorption site could be any one of a discrete set of values and, at any time, a particular value would exist randomly at different adsorption sites. If the adsorbed molecules are allowed to have internal structure, to interact, and to change the substrate, then their energy spectrum becomes more complex. We report the result of approximating the adsorption of antisymmetric, diatomic molecules on a homogeneous substrate as quantum mechanical, double (two point masses) harmonic oscillators in a potential that changes with the amount of adsorption. The expression for the chemical potential is obtained from the canonical partition function and is examined by applying it to obtain the equilibrium adsorption isotherm for CO adsorbing on Ni(111). The expression for the chemical potential contains the unknown, coverage dependent, potential energy that results from both adsorbate–adsorbate and adsorbate–substrate interactions. In addition, four of the six characteristic frequencies of the harmonic oscillators are assumed not to be known. A procedure for obtaining this information from measured equilibrium isotherms allows independent sets of isotherm measurements to be quantitatively compared. Equilibrium properties, including the heat of adsorption and the adsorption-induced change in the surface tension, are predicted. As well, an approximate calculation of the minimum energy of bound molecules is made.

Introduction

When classical mechanics is used to describe molecules adsorbed on a solid surface, two types of heterogeneities are often discussed. If the surface is described as patchwise heterogeneous, areas of the surface that have the “same” adsorption energy are lumped together. Each patch is then treated as if it were a *homogeneous* surface. The second type of heterogeneity discussed is the random approximation. In this case, the adsorption sites of the same energy are assumed to be randomly distributed over the surface. An essential element in both of these descriptions of a heterogeneous surface is the definition of a *homogeneous* surface. Classically, it has been taken to be a surface for which all adsorption sites may be approximated as having the same energy.¹

The quantum mechanical description stands in contrast to these descriptions of molecules adsorbed on a surface. In this description, a surface is said to be homogeneous if the solid substrate is homogeneous. An ideal single crystal surface would be ideally homogeneous in the quantum mechanical sense. However, once molecules are adsorbed on a homogeneous surface, the energy at a site could be any one of a discrete spectrum of energies and, at any instant in time, a particular value of the energy would be randomly distributed over the bonding sites of the surface. The number of adsorption sites having a particular energy would be related to the temperature. The energy spectrum for the surface becomes progressively more complex (and realistic) as (1) the internal structure of the molecule is taken into account, (2) the substrate is allowed to have more than one type of bonding site, e.g.,

bridge or linear bonding, and (3) the adsorbed molecules are allowed to interact and to change the substrate. In early attempts² to use the quantum mechanical description of adsorption, these complexities were either not taken into account or only considered in a limited way. Thus, if one observes an energy distribution associated with a surface, it may be due (as others have pointed out) to physical heterogeneity of the surface or it may be due to the fact that molecules may be in a variety of excited states, even when they are adsorbed on a homogeneous surface with one type of bonding. In order to distinguish between the two causes of an energy distribution, one must have additional information about the character of the surface. In the case considered here, a single crystal surface, CO–Ni(111), is used which has been shown spectroscopically to exhibit (predominantly) one type of bonding.³

To explore the possibility of adopting a quantum mechanical description of a surface (i.e., a surface upon which molecules adsorbed on the same type of bonding sites may occupy one of many different energy states), we introduce a method that can take each of these complexities into account approximately. Thus, we consider the adsorption of a diatomic molecule on a homogeneous surface having one type of bonding site and approximate the adsorbed molecule as an antisymmetric, double harmonic oscillator. In order to account for interactions between adsorbed molecules and changes in the substrate due to adsorption, we allow the potential energy of the adsorbed molecules to vary with coverage. After using this approximation to obtain the expression for the partition function, the expression for the chemical potential is derived. This allows the expression for the adsorption isotherm to be obtained. The isotherm relation is then evaluated by applying it to the CO–Ni(111) system. Isotherms for this system have been measured by two different techniques, but in two different temperature and

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(1) Cerofolini, G. F.; Re, N. *Riv. Nuovo Cimento* **1993**, 16 (7), 1.

(2) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Dover Publications Inc.: New York, 1986; p 124.

(3) Surnev, L.; Xu, Z.; Yates, J. T., Jr. *Surf. Sci.* **1988**, 201, 14.

pressure ranges.^{4,5} Also, one measurement technique was used to determine the isotherms when the Ni(111) surface was prepared by two different techniques.⁵

The new isotherm expression allows all of these sets of empirical isotherms to be compared quantitatively, even though they were measured in different temperature and pressure ranges. It is found for CO–Ni(111) that if the Ni(111) surface were prepared with similar techniques in different laboratories, then the isotherms were quantitatively the same. However, if different techniques were used to prepare nominally Ni(111), then the differently prepared samples of Ni(111) had different isotherms.

Once the isotherms have been examined and it has been established that the surface being examined is a repeatable, well-defined surface, the properties in the chemical potential expression for the adsorbed molecules may be tabulated for this surface. The expression for the chemical potential of the adsorbed molecules may then be used to predict equilibrium phenomena such as the coverage dependence of the heat of adsorption⁶ and the adsorption-induced change in surface tension. The chemical potential of adsorbed molecules also plays a fundamental role in adsorption kinetics.^{7–9} The CO–Ni(111) surface was selected to examine the model proposed herein. However, the method and equations may be generalized to other simple molecular adsorption systems including atomic adsorption⁶ and systems with multiple binding sites.¹⁰

System Description

Following refs 6 and 9, we consider an isolated system consisting of three phases: a solid phase, a gas phase, and an interphase. Diatomic gas molecules are partitioned between the gas phase and an adsorbed layer. The treatment will be limited to localized, sub-monolayer, nondissociative adsorption on a surface with a single type of bonding.

If F^s , F^g , and F^i are the Helmholtz functions of the solid, gas phase, and interphase respectively, then the Helmholtz function for the system may be written

$$F = F^s + F^g + F^i \quad (1)$$

The statistical mechanics treatment of an ideal diatomic gas phase is well-known. The treatments of the solid phase and interphase will be discussed in some detail here.

The adsorption of molecules onto the solid may affect the solid phase. The change in the solid substrate due to the adsorption can be accounted for in two ways. The first is to include the effect of substrate changes in the potential seen by the adsorbed molecules which will affect the Helmholtz function of the interphase. The second way is to allow changes in the thermodynamic properties of the solid as a result of adsorption which will effect the Helmholtz function of the solid.

Although the gas phase and the interphase have intensive thermodynamic properties that have single values over their respective extents, this is not necessarily true for the solid. The effect of the adsorption on the solid atoms will depend on the displacement of individual solid atoms from the surface giving rise to a Helmholtz function

for the solid that depends on displacement. For this reason, gradients may develop in the intensive properties of the solid. Thus, the total Helmholtz function for this phase must be written as an integral over the solid volume, V^s . Following the treatment of systems exposed to an external field,^{11,12} one finds:

$$F^s = \int_{V^s} f^s dV^s \quad (2)$$

where f^s is the Helmholtz function of the solid per unit volume and may be written

$$f^s = u^s + \varphi - Ts^s \quad (3)$$

where u^s and s^s are the internal energy and entropy of the solid, respectively, each per unit volume, T is the temperature, and φ is the potential energy of a unit volume of solid arising from the field generated by the adsorbed molecules. The potential energy is assumed to be a function of the number of adsorbed molecules, N^p , and the distance of the solid volume element from the surface, z .

$$\varphi = \varphi(N^p, z) \quad (4)$$

Equations 2, 3, and 4 imply that the Helmholtz function for the solid has the following functional dependence

$$F^s = F^s(T, V^s, N^s, N^p) \quad (5)$$

The interphase will be modeled by a mathematical surface placed at a location such that there is no adsorption of solid atoms in the interphase.¹³ The definition of the dividing surface will determine the limits of integration in eq 2. This definition of the extent of the three phases will allow each of the phases to be treated as a homogeneous simple system,^{13,14} a point that will be important for the heat of adsorption derivation. With this definition, the Helmholtz function of the interphase may be written

$$F^i = \gamma A + \mu^\sigma N^\sigma \quad (6)$$

where γ is the gas–solid surface tension, A is the surface area, and μ^σ is the chemical potential of the adsorbed molecules. If γ_0 is the surface tension when no molecules are adsorbed, then the Helmholtz function in this limit, F_0^i , reduces to

$$F_0^i = \gamma_0 A \quad (7)$$

The general expression for the Helmholtz function may then be divided into a portion that depends on coverage, F^p , and a portion that is coverage independent, F_0^i :

$$F^i = F_0^i(T, A) + F^p(T, A, N^p) \quad (8)$$

After comparing eq 6 with eqs 7 and 8, one finds that the coverage dependent term of the Helmholtz function may be written

$$F^p = (\gamma - \gamma_0)A + \mu^\sigma N^\sigma \quad (9)$$

Also, F^p may be written in terms of the partition function,

(4) Christmann, K.; Schober, O.; Ertl, G. *J. Chem. Phys.* **1974**, *60* (12), 4719.

(5) Gijzen, O. L. J.; van Zandvoort, M. M. J.; Labohm, F.; Vlieg, J. A.; Jongert, G. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 771.

(6) Ward, C. A.; Elmoselhi, M. B. *Surf. Sci.* **1988**, *203*, 463.

(7) Ward, C. A.; Findlay, R. D. *J. Chem. Phys.* **1982**, *76* (11), 5615.

(8) Ward, C. A.; Elmoselhi, M. *Surf. Sci.* **1986**, *176*, 457.

(9) Elliott, J. A. W.; Ward, C. A. In *Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces*; Rudziński, W., Steele, W. A., Zgrablich, G., Eds.; Elsevier: Amsterdam, 1996.

(10) Garcia, J. A.; Elliott, J. A. W.; Ward, C. A. To be submitted for publication, 1996.

(11) Münster, A. *Classical Thermodynamics*; Wiley Interscience: London, 1970.

(12) Elliott, J. A. W.; Ward, C. A.; Yee, D. *J. Fluid Mech.* **1996**, *319*, 1.

(13) Gibbs, J. W. *The Scientific Papers of J. Willard Gibbs*; Dover Publications Inc.: New York, 1961; Vol. 1.

(14) Callen, H. B. *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed.; John Wiley & Sons: New York, 1985.

Q^s , of the adsorbed molecules

$$F^s = -kT \ln Q^s \quad (10)$$

where k is Boltzmann's constant. The required partition function will be constructed from the quantum mechanical model under investigation so that eqs 8, 9, and 10 may be used to find expressions for both the chemical potential of the adsorbed molecules and the adsorption-induced change in surface tension.

An Expression for the Chemical Potential of Adsorbed Diatomic Molecules

Since, in the model system, there are no solid atoms located in the interphase, the chemical potential of the adsorbed molecules can be formulated using only properties of the adsorbed molecules. As in refs 6 and 9, the adsorbed diatomic molecules will be modeled as quantum mechanical, double harmonic oscillators with six independent degrees of freedom. Thus, an adsorbed molecule may be in any one of a discrete spectrum of energy levels. We assume that the Hamiltonians of each degree of freedom may be separated and that molecular interactions affect only the potential energy. The possible molecular energy levels may then be written in terms of the six characteristic vibration frequencies

$$\epsilon_{ijklmn} = E_0' + \left(i + \frac{1}{2}\right)\hbar\omega_1 + \left(j + \frac{1}{2}\right)\hbar\omega_2 + \dots + \left(n + \frac{1}{2}\right)\hbar\omega_6 \quad (11)$$

$$i, j, k, l, m, n = 0, 1, 2, \dots$$

where \hbar is Planck's constant divided by 2π and E_0' is the potential energy of an adsorbed molecule. The potential energy results from interactions. Hence, E_0' will be allowed to be a function of coverage since changing the number of adsorbed molecules will, in general, affect both the adsorbate-adsorbate interactions and interactions of the adsorbed molecule with the surface atoms of the substrate. It is in this way that interactions are being accounted for in this model.

It is assumed that at most one molecule may be adsorbed on a particular site, so that there is a configurational degeneracy appearing in the partition function arising from the number of ways of distributing N^s adsorbed molecules over AM adsorption sites where M is the number of adsorption sites per unit area. Using this degeneracy and the energy levels in eq 11, the canonical partition function may be written⁶

$$Q^s = \frac{AM!}{N^s!(AM - N^s)!} (q_1 q_2 \dots q_6)^{N^s} \quad (12)$$

where

$$q_i = \frac{\exp\left(-\frac{\epsilon_{0i}}{kT}\right)}{1 - \exp\left(-\frac{\hbar\omega_i}{kT}\right)} \quad (13)$$

and

$$\epsilon_{0i}' = E_0' + \frac{\omega_i}{6} + \frac{\hbar\omega_i}{2} \quad (14)$$

Note that although eqs 12 through 14 appear to represent the familiar Langmuir partition function, they contain additional coverage dependence, since E_0' is a function of coverage. Thermodynamic properties found by differentiating the partition function may be quite different from those found from the Langmuir model as a result of this additional functional dependence.

The chemical potential of the adsorbed molecules may now be found from

$$\mu^s = \left(\frac{\partial F^s}{\partial N^s}\right)_{T,A} \quad (15)$$

Substituting eqs 8, 10, and 12 into eq 15 yields

$$\mu^s(T, N^s) = kT \ln \left[\frac{N^s}{(AM - N^s) \psi \exp\left(\frac{b - \beta'}{kT}\right)} \right] \quad (16)$$

where

$$\psi(T) \equiv \prod_{j=1}^2 \frac{\exp\left(\frac{\hbar\omega_j}{2kT}\right)}{\exp\left(\frac{\hbar\omega_j}{kT}\right) - 1} \quad (17)$$

$$b(T) \equiv kT \ln \left[\prod_{i=3}^6 \frac{\exp\left(\frac{\hbar\omega_i}{2kT}\right)}{\exp\left(\frac{\hbar\omega_i}{kT}\right) - 1} \right] \quad (18)$$

and

$$\beta'(N^s) \equiv \frac{d(E_0' N^s)}{dN^s} \quad (19)$$

Note that the vibration frequencies have been divided into those that have experimentally resolved¹⁵ ($\omega_j, j = 1, 2$) and those that are unknown ($\omega_i, i = 3-6$).

In the chemical potential expression given in eq 16, only the functions $b(T)$ and $\beta'(N^s)$ are unknown. These functions will be obtained from measured equilibrium isotherms. An expression for equilibrium adsorption isotherms may be found by equating the chemical potential of the adsorbed phase with that of the gas phase.

Using the Born-Oppenheimer approximation, the chemical potential of an ideal diatomic gas can be found from the partition function¹⁶ to be

$$\mu^g = kT \ln(P\phi) \quad (20)$$

where P is the pressure in the gas phase and ϕ is given by

$$\phi \equiv \frac{\left[1 - \exp\left(-\frac{\hbar\omega_g}{kT}\right)\right] \exp\left(-\frac{D_0}{kT}\right) \hbar^5 (2\pi)^{3/2}}{(kT)^{7/2} 2m_1 m_2 r_e^2 (m_1 + m_2)^{1/2}} \quad (21)$$

where ω_g is the characteristic vibration frequency of a gas molecule, D_0 is its dissociation energy, m_1 and m_2 are the masses of the two component atoms, and r_e is their separation distance. The gas phase properties are known¹⁶ and are given in Table 1.

(15) Erley, W.; Wagner, H.; Ibach, H. *Surf. Sci.* **1979**, *80*, 612.

(16) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Dover Publications Inc.: New York, 1986; p 147.

Table 1. Gas Phase Properties of Carbon Monoxide¹⁶

$\omega_g(\text{rad/s})$	$r_e(\text{nm})$	$D_0(\text{J/molecule})$
4.017×10^{14}	11.28	1.464×10^{-18}

The coverage, θ , is defined as the number of adsorbed molecules per surface substrate atom

$$\theta \equiv N^s/AM_0 \quad (22)$$

where M_0 is the number of surface substrate atoms per unit area. Equating eqs 16 and 20 and converting to a coverage formulation, one gets as the isotherm relation

$$P_e(T, \theta_e) = \frac{\theta_e}{(\theta_M - \theta_e)\psi\phi \exp\left(\frac{b - \beta'}{kT}\right)} \quad (23)$$

where the subscript e has been used to denote equilibrium values and where

$$\theta_M \equiv M/M_0 \quad (24)$$

Since ψ and ϕ are tabulated functions of temperature and known adsorbed phase and gas phase properties, the only unknown in eq 23 is the difference $b - \beta'$, which may be found by comparing eq 23 with measured equilibrium isotherms. Solving eq 23 for the unknown

$$b(T) - \beta'(\theta_e) = kT \ln \left[\frac{\theta_e}{(\theta_M - \theta_e)\psi\phi P_e} \right] \quad (25)$$

The right-hand side of eq 25 may be evaluated at each point on a measured isotherm and the left-hand side has been separated into a function of temperature only and a function of coverage only. We then note that by subtracting a single value from each of the calculated points, $b - \beta'$, from one isotherm, the values for that isotherm should be made to lie directly on top of those of another isotherm as indicated by eq 25.

The procedure⁹ for obtaining $b - \beta'$ from empirical isotherms may now be stated. One isotherm is selected as a reference. (In the case to be presented here, the reference isotherm chosen was at $T = 370$ K.) The reference isotherm is arbitrarily assigned a value of b . (In the case to be presented, $b = 0$.) This choice of an arbitrary reference means that b will only be determined to within an additive constant. The value of $b - \beta'$, however, will be uniquely determined from the isotherms. Once this reference is assigned, values of $b - \beta'$ are calculated for each measured point on the reference isotherm from the right-hand side of eq 25. These reference values will be denoted ξ^{ref} . If the j th value of $b - \beta'$ on the i th isotherm is denoted ξ_j^i , then the value of $b(T)$ for the i th isotherm can then be found from

$$b(T) = \frac{\sum_{j=1}^{n^i} (\xi_j^i - \xi_j^{\text{ref}})}{\eta^i} \quad (26)$$

where η^i is the number of coverage values selected on the i th isotherm at which to compare the values of ξ with those of the reference isotherm.

Since measured isotherms do not usually each span the same coverage range, not all of the measured points will necessarily be comparable with the reference isotherm. In cases where an isotherm does not have a sufficient number of points in common with the reference isotherm, the isotherm must first be referred to an intermediate isotherm and the intermediate value of b used to get the

desired value. If, for each of a series of isotherms, measurements are made at the same coverage values,⁴ then the above method is straightforward. If, however, the coverage values used are not the same from isotherm to isotherm,⁵ then interpolation of the isotherms must be performed first in order to use this technique.

For each isotherm, one value of b is obtained from eq 26. This single value of b is then subtracted from each of the several calculated values of ξ for that isotherm to yield several values of β' . When this is repeated for all of the measured isotherms, the β' values may be represented by a single function of coverage and the b values by a single function of temperature.

The above procedure has been used to examine isotherms for CO adsorbing on Ni(111) that were reported by Christmann *et al.*⁴ and by Gijzeman *et al.*⁵ The isotherms of Christmann *et al.* are those which were used in ref 9. However, the interpretation of these isotherms has been improved slightly for the results reported here. The number of adsorption sites per substrate surface atom, θ_M , has been increased to 0.57. The reason for this is that the number of sites corresponds to the maximum number of adsorbed molecules that can be put on the surface geometrically and not to the equilibrium coverage at a specific pressure. Christmann *et al.* report a maximum observed coverage of 0.53, but this is for low pressures (below 10^{-8} Torr). Froitzheim and Köhler¹⁷ interpret the LEED pattern observed by Erley *et al.*¹⁸ at room temperature and a pressure of 10^{-2} Torr as corresponding to a coverage of 0.57. (This same coverage can also be achieved¹⁹ at temperatures below 220–240 K.) Also, the coverage scale of the Christmann *et al.* isotherms has been reinterpreted from the work function measurements using a work function versus coverage measurement made more recently by Surnev *et al.*³ In ref 9 a linear relationship between coverage and work function was assumed. According to Surnev *et al.*, a linear relationship is not valid over the entire coverage range.

In order to examine the isotherms measured by Gijzeman *et al.*, the factor relating the ellipsometric signal to coverage must be determined. Gijzeman *et al.* attempted to obtain the proportionality factor by leaving it as an adjustable parameter in their fitting procedure. They found a factor that varied from 0.69 to 0.8. However, this determination is dependent on the isotherm equation with which they fit the measurements. The isotherm measurement taken at the lowest temperature (389 K on the annealed surface) falls within the range measured by Christmann *et al.* From the functions $\beta'(\theta)$ and $b(T)$ inferred from the Christmann isotherms, an isotherm at 389 K can be predicted. By comparing the isotherm measured by Gijzeman *et al.* at 389 K to the predicted isotherm, one may determine a factor relating the ellipsometric signal to coverage. The value that we inferred was 0.77, which is within the range proposed by Gijzeman *et al.* For the work reported herein, a constant proportionality of 0.77 was used for both the annealed and reduced surfaces. Once a coverage scale has been determined, the isotherms of Gijzeman *et al.* may be examined and compared with those of Christmann *et al.*

The functions obtained from the three sets of isotherms are shown in Figures 1 and 2. Christmann *et al.* made measurements on a surface that had been annealed. Gijzeman *et al.* report CO isotherms from two different Ni(111) surfaces, one that has been annealed and one that has been reduced with CO after being initially oxidized. As can be seen in Figures 1 and 2, the two sets

(17) Froitzheim, H.; Köhler, U. *Surf. Sci.* **1987**, *188*, 70.

(18) Erley, W.; Besocke, K.; Wagner, H. *J. Chem. Phys.* **1977**, *66*(12), 5269.

(19) Netzer, F. P.; Maday, T. E. *J. Chem. Phys.* **1982**, *76*(1), 710.

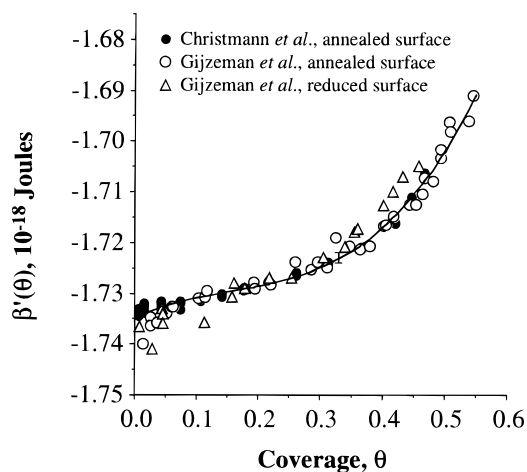


Figure 1. $\beta'(\theta)$ found from the isotherm measurements of refs 4 and 5. The Gijzeman *et al.* measurements were interpreted using a proportionality factor of 0.77. The error bar represents the standard error in the results for the annealed surfaces of both Christmann *et al.* and Gijzeman *et al.*

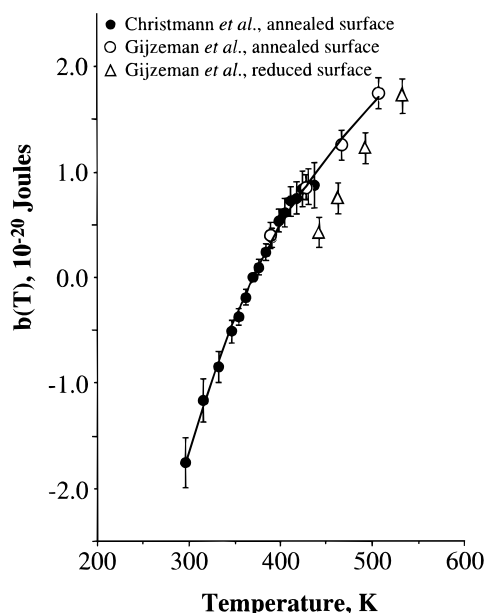


Figure 2. $b(T)$ found from the isotherm measurements of refs 4 and 5. The Gijzeman *et al.* measurements were interpreted using a proportionality factor of 0.77. The error bar represents the propagated error in determining the b values from the isotherms.

of isotherms measured on the annealed surfaces are in very good agreement, while the isotherms measured on the reduced surface are seen (particularly in Figure 2) to be different. Third-order polynomial fits of the combined Christmann *et al.* and the annealed Gijzeman *et al.* measurements are shown in both figures. The parameters relating to the adsorbed molecules and appearing in eq 16 are given in Table 2 along with the coefficients obtained from the polynomial fits. The parameters have been separated into those obtained from the literature and those obtained in the present study.

One way to assess²⁰ how well a polynomial represents a data set is to calculate the coefficient of multiple determination, R^2 . For the data from the annealed surfaces, R^2 values of 0.986 and 0.977 were found for the measurements of Christmann *et al.* and Gijzeman *et al.*, respectively, indicating that this data is well represented by the polynomial. For the data measured by Gijzeman

et al. on the reduced surface, the value of R^2 was 0.889. Third-order polynomial fits were chosen as the lowest order fit for which increasing the order of the fit produced a negligible (0.1%) increase in R^2 .

A statistical error was assigned to β' based on the standard deviation of the Christmann *et al.* and Gijzeman *et al.* (annealed) data from the polynomial fit. An error bar representing this error of $\pm 1.3 \times 10^{-21}$ J is shown in Figure 1. Note that this error represents only the statistical error in the data and could be smaller than the systematic, experimental error. The values of b are obtained by comparing values of β' for different isotherms, and hence the error in the b values can be found by assigning the standard error in β' to each of the points in Figure 1 and propagating this error through the calculation of each value of b . Error bars representing the propagated error are shown in Figure 2. The results from the reduced surface lie outside this error. Thus, using the procedure presented here, one can see that the results obtained from the annealed surface of Christmann *et al.* agree with those obtained from the annealed surface of Gijzeman *et al.* but that the results obtained from the reduced surface of Gijzeman *et al.* are quantitatively different. For the rest of the results reported herein, unless otherwise stated, the measurements from the reduced surface were not used.

The two sets of measurements (from the annealed surface of Christmann *et al.* and from the annealed surface of Gijzeman *et al.*) were made in different temperature and pressure ranges. Without the method for separating the coverage and temperature dependence (which was a direct result of the double harmonic oscillator model) the measurements could not easily be compared. If both sets of isotherms are used, the function $b(T)$ can be determined over a larger temperature range. The temperature range includes 300 K, which means that no extrapolation needs to be performed in order to examine room temperature measurements such as the calorimetric heat of adsorption. Also, the function $\beta'(\theta)$ has been determined over the entire coverage range. Thus the chemical potential of the adsorbed molecules (based on the quantum mechanical, harmonic oscillator model) is now known and may be examined by predicting independent, experimental results that were not used in determining the expression for the chemical potential of CO adsorbed on Ni(111).

As an initial check of the consistency of the isotherm relation, the parameters listed in Tables 1 and 2 may be used to calculate the isotherms which may be compared to the original measurements. In Figure 3, the isotherms measured by Christmann *et al.* are shown along with those calculated from the tabulated parameters. In Figure 4, the isotherms measured by Gijzeman *et al.* (for the annealed surface) are compared with the calculated isotherms. In both instances the measured and redrawn isotherms are in agreement.

The chemical potential equation and the method for examining equilibrium adsorption isotherms may be generalized to systems with more than one type of bonding site¹⁰ or to other systems of well-defined molecules. For example, Ward and Elmoselhi⁶ derived a similar equation for the chemical potential of hydrogen atomically adsorbed on nickel.

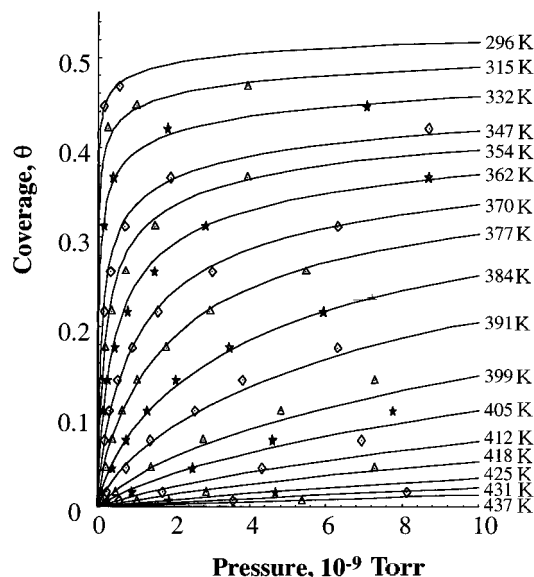
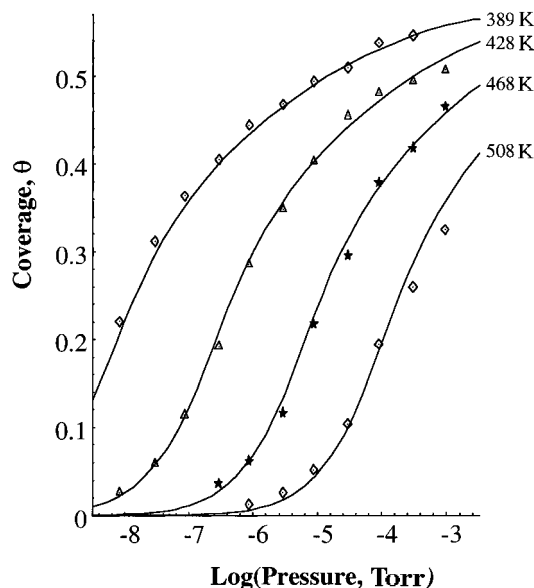
Heat of Adsorption

The double harmonic oscillator model has previously been used to predict the coverage dependence of the heat of adsorption.⁶ Although the equations developed here are similar to those in the previous work, the improved isotherm relation should lead to a more accurate prediction of the heat of adsorption at 300 K. The improved accuracy will allow us to propose a method whereby the adsorption-

(20) Devore, J. L. *Probability and Statistics for Engineering and the Sciences*; Wadsworth: Belmont, CA, 1982.

Table 2. Properties of Carbon Monoxide Adsorbed on Ni(111)

property	value	source
M_0 (atoms/m ²)	1.86×10^{19}	geometry
M (sites/m ²)	$0.57M_0$	Froitzheim and Kohler ¹⁷
ω_1 (rad/s)	7.73×10^{13}	electron energy loss spectroscopy ¹⁵
ω_2 (rad/s)	3.50×10^{14}	electron energy loss spectroscopy ¹⁵
$b_0 - c_0$ (J/molecule)	1.4921×10^{-18}	present work, obtained by fitting the measured data of Christmann <i>et al.</i> ⁴ and Gijzeman <i>et al.</i> ⁵
b_1 (J/molecule K)	1.3627×10^{-21}	
b_2 (J/molecule K ²)	-2.5408×10^{-24}	
b_3 (J/molecule K ³)	1.7016×10^{-27}	
c_1 (J/molecule)	5.6821×10^{-20}	
c_2 (J/molecule)	-2.2721×10^{-19}	
c_3 (J/molecule)	4.8990×10^{-19}	

**Figure 3.** Comparison of measured and recalculated isotherms. The data points represent the values measured by Christmann *et al.*⁴ The solid lines are calculated from the properties listed in Tables 1 and 2.**Figure 4.** Comparison of measured and recalculated isotherms. The data points represent the values measured by Gijzeman *et al.*⁵ The solid lines are calculated from the properties listed in Tables 1 and 2.

induced enthalpy change of the solid may be inferred from calorimetric heat of adsorption measurements and the coverage dependence of the heat of adsorption predicted.

The system being considered consists of three phases: a nonvolatile solid phase, a gas phase, and an interphase consisting of adsorbed gas molecules. The system is

surrounded by a reservoir that maintains the temperature and pressure of the system constant. As the adsorption occurs, we consider two states differing by the adsorption of ΔN^s molecules, where ΔN^s is small compared to N^s . For each of these two states we assume that equilibrium exists within each phase but that equilibrium does not necessarily exist between phases. If the operator Δ is used to indicate the difference in a property between these two states, then the quasi-static heating of the reservoir (after a change from one state to the other) would be ΔQ . The heat of adsorption would then be defined

$$q_A = \left(\frac{\Delta Q}{\Delta N^s} \right)_{T,P,A} \quad (27)$$

where the subscripts indicate that the pressure, temperature, and surface area are the same for the initial and final equilibrium states. From the first law statement for the system and the reservoir

$$\Delta Q = -\Delta U^g - \Delta U^s - \Delta U^i - P\Delta V^g - P\Delta V^s \quad (28)$$

where U is internal energy, V is volume, and the superscripts refer to the three phases. Hence the heat of adsorption may be written

$$q_A = -\frac{\Delta H^g}{\Delta N^s} - \frac{\Delta U^s}{\Delta N^s} - \frac{\Delta H^i}{\Delta N^s} \quad (29)$$

where H^g is the enthalpy of the gas phase and the last term represents the enthalpy change of the solid per molecule adsorbed.

The sum of the first two terms in eq 29 is equal to the isosteric heat of adsorption.^{6,21} It is the last term in eq 29 that is neglected when the isosteric heat is compared with calorimetric measurements (i.e., the solid is assumed to be inert). Although Ward and Elmoselhi⁶ intended to take into account a change in the solid by treating it as a non-homogeneous system, their assumptions amount to neglecting the last term, and thus what they derived was an expression for the isosteric heat of adsorption. We adopt a different approach here.

From the partition function for the gas phase molecules,¹⁶ the change in the enthalpy of the gas phase may be written

$$\Delta H^g = \Delta N^s \left[-\frac{7}{2} kT - \frac{\hbar\omega^g}{\exp\left(\frac{\hbar\omega^g}{kT}\right) - 1} + D_0 \right] \quad (30)$$

where the gas phase properties are those defined after eq 21. Similarly, the internal energy of the adsorbed

(21) Clark, A. *The Theory of Adsorption and Catalysis*; Academic: New York, 1970; p 9.

molecules can be found from their partition function by noting

$$U^s = F^s + T \left(\frac{\partial F^s}{\partial T} \right)_{A, N^s} \quad (31)$$

Combining eq 10 with eqs 12 through 14, and substituting in eq 31, the internal energy of the adsorbed molecules may be found

$$U^s = N^s \left[E_0' + \sum_{i=1}^6 \frac{\hbar\omega_i}{2} + \sum_{i=1}^6 \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{kT}\right) - 1} \right] \quad (32)$$

Using the above equation, the change in the internal energy of the adsorbed molecules as the result of ΔN^s molecules adsorbing may be written

$$\Delta U^s = \Delta N^s \left[E_0' + N^s \frac{dE_0'}{dN^s} + \sum_{i=1}^6 \frac{\hbar\omega_i}{2} + \sum_{i=1}^6 \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{kT}\right) - 1} \right] \quad (33)$$

where a Taylor expansion of $E_0'(N^s + \Delta N^s)$ has been made about N^s and terms up to first order retained.

After substituting eqs 30 and 33 into eq 29, making use of eqs 18 and 19, and simplifying, the equation for the heat of adsorption may be written

$$q_A = \frac{7}{2} kT + \frac{\hbar\omega_g}{\exp\left(\frac{\hbar\omega_g}{kT}\right) - 1} - D_0 - \frac{\hbar\omega_1}{2} - \frac{\hbar\omega_1}{2} - \frac{\hbar\omega_1}{\exp\left(\frac{\hbar\omega_1}{kT}\right) - 1} - \frac{\hbar\omega_2}{\exp\left(\frac{\hbar\omega_2}{kT}\right) - 1} + b - \beta' - T \frac{db}{dT} - \frac{\Delta H^s}{\Delta N^s} \quad (34)$$

The last term in eq 34 is the change in the enthalpy of the solid per molecule adsorbed. If the solid were assumed to be inert (as is often done^{21,22}), this term would be set equal to zero. The sum of the other terms would be the isosteric heat of adsorption. The isosteric heat can be readily calculated from the properties listed in Tables 1 and 2. The value of the isosteric heat obtained at different coverages by this procedure is shown in Figure 5, where the calorimetric measurements reported by Stuckless *et al.*²³ are also shown. The error on the prediction of the isosteric terms is shown as a single error bar because it is not coverage dependent. The error in this prediction arises from the statistical error in β' and the propagated error in b . Although this results in a small error in $b - \beta'$, the error in $T db/dT$ is appreciable. Note that although the coverage dependence of the predicted isosteric heat appears to be in agreement with the measurements, the isosteric heat is below the calorimetric measurements.

There is reason to doubt the validity of assuming the solid to be inert during the adsorption process. The measured calorimetric heats are much in excess of 20 kJ/mol. This indicates that there is strong bonding in the

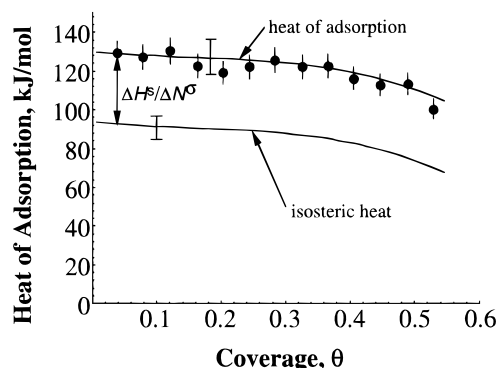


Figure 5. Predicted heat of adsorption compared with calorimetric measurements from ref 23. The prediction for the heat of adsorption is based on the sum of the isosteric prediction and an adsorption induced solid enthalpy change of -36 kJ/mol. The error bars on the measurements represent an error of $\pm 5\%$. The error bar on the isosteric heat arises from the error in the slope of $b(T)$. The error bar on the predicted heat of adsorption results from a combination of these two errors.

adsorption process, or in other words, both the gas molecules and the solid atoms undergo substantial electronic change.²⁴ This would give rise to field effects and a nonuniform composition in the solid near the surface. As indicated in eqs 2, 3, and 4, these field effects could change the thermodynamic properties of the solid. At small coverages ($N^s \rightarrow 0$) an adsorbed molecule would interact only with the solid, and the value of $\Delta H^s/\Delta N^s$ would be independent of coverage. As the coverage increases (yet is still sub-monolayer), the adsorbed molecules experience lateral interactions. The primary effect of these interactions would be within the adsorbed layer, so that lateral interactions would be expected to have a small effect on the value of $\Delta H^s/\Delta N^s$. Thus, for the circumstance that we consider, the value of $\Delta H^s/\Delta N^s$ is assumed to be independent of coverage. This would mean that the coverage dependence of the heat of adsorption would have to be predicted by the other terms in eq 34. Note that, of those terms, only β' may contain coverage dependence. The function β' is related to the potential energy of the adsorbed molecule. Had the heat of adsorption been formulated from the Langmuir model (i.e., the coverage dependence of the potential energy neglected), there would be no predicted coverage dependence of the heat, a result that is in contradiction with the measurements.

The hypothesis that $\Delta H^s/\Delta N^s$ is independent of coverage has been examined, and the results are summarized in Figure 5. The term $\Delta H^s/\Delta N^s$ has been assigned the value -36 ± 9 kJ/mol which brings the heat of adsorption into agreement at small coverages with the measurements reported by Stuckless *et al.* Then, the remaining terms in the heat of adsorption (including the coverage dependent β') were predicted using eq 34 and the values of the properties listed in Tables 1 and 2. The error of ± 9 kJ/mol in this prediction would then be a combination of the error in the terms calculated from the tabulated properties and the experimental error in the measured calorimetric heat at the lowest coverage which was used to find $\Delta H^s/\Delta N^s$. As indicated, the error is not coverage dependent. As may be seen in Figure 5, the predicted coverage dependence of the heat of adsorption is in close agreement with the measurements.

There is one additional important point to be made about the adsorption-induced enthalpy change of the solid. Recall that the dividing surface was placed at a position such

(22) Christmann, K. *Introduction to Surface Physical Chemistry*; Springer-Verlag: New York, 1991; p 13.

(23) Stuckless, J. T.; Al-Sarraf, N.; Wartnaby, C.; King, D. A. *J. Chem. Phys.* **1993**, *99* (3), 2202.

(24) Lupis, C. H. P. *Chemical Thermodynamics of Materials*; Elsevier Science Publishing Co.: New York, 1983; p 429.

that there are not solid atoms present in the interphase. This means that, by definition, none of the changes occurring in the solid have been included in the internal energy change of the adsorbed molecules. In a common treatment of the heat of adsorption,^{21,22} changes in only two phases (a gas phase and a condensed phase) are included. In the previous treatment, the condensed phase contains both adsorbed molecules and solid atoms and the solid atoms are assumed to be inert.^{21,22} Herein we have treated the full three-phase problem (including gas, adsorbed, and solid phases), which is especially important in the case of electronic bonding (chemisorption) where changes in the solid may be significant and cannot be neglected.

Other causes for the discrepancy between the predicted isosteric heat and the measured calorimetric values cannot be ruled out. For example, we have shown that the preparation of the nickel surface has an effect on the measured isotherms. The calorimetric measurements were performed on very thin films, whereas the isotherms being used to determine the properties in Table 2 were obtained from measurements made on thicker single crystals. There is no way to know at this time whether the thickness of the Ni(111) sample has an effect on the isotherms.

Change in Gas–Solid Interfacial Tension Resulting from Adsorption

Although it has not been measured independently, another important property of the CO–Ni(111) interface that can be calculated from the chemical potential is the adsorption-induced change in surface tension. Under conditions of constant temperature and constant surface strain, the Gibbs adsorption equation can be written²⁵

$$d\gamma = -\frac{N^\sigma}{A} d\mu^\sigma \quad (35)$$

Equation 35 may be written in terms of coverage as

$$d\gamma = -M_0\theta \frac{\partial \mu^\sigma}{\partial \theta} d\theta \quad (36)$$

In order to determine the change of surface tension from the vacuum value, γ_0 , as a function of coverage, one may make use of eq 16 and integrate eq 36 to get

$$\gamma - \gamma_0 = M_0 \left(\int_0^\theta \beta'(\Theta) d\Theta - \theta\beta' \right) - kTM \ln \left(\frac{\theta_M}{\theta_M - \theta} \right) \quad (37)$$

Using the definition of β' in eq 19 and the assumption that the potential energy remains bounded as the coverage approaches zero, one gets

$$E_0' = \frac{1}{\theta} \int_0^\theta \beta'(\Theta) d\Theta \quad (38)$$

which may be used to write eq 37 in the following equivalent form

$$\gamma - \gamma_0 = M_0\theta(E_0' - \beta') - kTM \ln \left(\frac{\theta_M}{\theta_M - \theta} \right) \quad (39)$$

The change in surface tension as a result of adsorption, $\gamma - \gamma_0$, was calculated from eq 37 using the values of surface

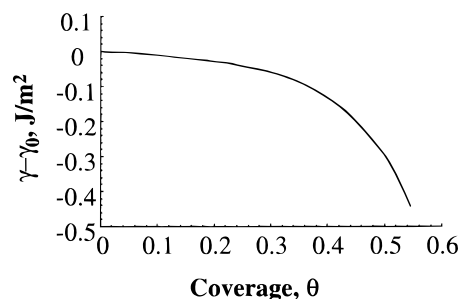


Figure 6. Predicted change in surface tension from the “clean” value as a result of adsorption.

properties listed in Table 2. The result is shown in Figure 6. It is difficult to experimentally measure solid surface tensions especially while accurately obtaining coverage information. However, Bauer *et al.*²⁶ reported a similar decrease in the surface tension of copper as a result of oxygen adsorption.

In order to use the Gibbs adsorption equation to predict the coverage dependence of the change in surface tension with adsorption, the coverage dependence of the chemical potential of the adsorbed molecules must be known. If, for instance, it were assumed that E_0' was not a function of coverage, then the first term in eqs 37 and 39 would not appear.²⁵ Such an assumption is made when the Langmuir approximation is adopted. The Langmuir approximation only gives rise to the last term in eqs 37 and 39. The last term represents only about 30% of the total surface tension change.

In addition to the Langmuir term not accounting for the total change in surface tension, Zangwill²⁵ points out that if one uses the Langmuir equation it is difficult to extract the weak dependence of surface tension on the binding energy. However, with the present chemical potential equation, leading to the full equation for the adsorption-induced change in surface tension, eq 39, the potential energy of the adsorbed molecules, E_0' , appears explicitly.

Minimum Energy of Adsorbed Molecules

There are two energetic quantities which are of interest. The first is the potential energy of a bound CO molecule, E_0' , and its dependence on coverage. Since β' was only determined from the isotherms to within an additive constant, eq 38 can only be used to determine the coverage dependence of the potential energy, but not its value. Thus we shall calculate the change in the potential energy of a bound molecule from its zero coverage value, which can be determined by assuming β' can be represented by a polynomial (the coefficients, c_i , of which are given in Table 2). From eq 38

$$E_0'(\theta) - E_0'(0) = \frac{c_1\theta}{2} + \frac{c_2\theta^2}{3} + \frac{c_3\theta^3}{4} \quad (40)$$

In Figure 7, the change in the potential energy of a bound CO molecule is shown for both the annealed surface (from the measurements of Christmann *et al.* and Gijzeman *et al.*) and the reduced surface (from the measurements of Gijzeman *et al.*).

The second energetic quantity that is of interest is the minimum or ground state energy of a bound CO molecule

(25) Zangwill, A. *Physics at Surfaces*; Cambridge University Press: Cambridge, 1988.

(26) Bauer, C. E.; Speiser, R.; Hirth, J. P. *Met. Trans. A* **1976**, 7A, 75.

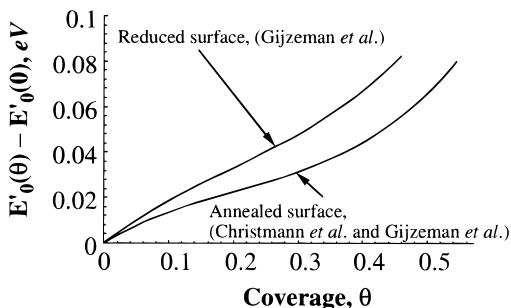


Figure 7. Change in the potential energy of a bound CO molecule with coverage.

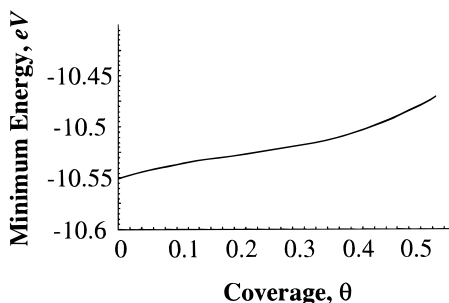


Figure 8. Estimated minimum energy for a bound CO molecule on an annealed Ni(111) surface.

which may be written

$$E_{\min} = E'_0 + \sum_{i=1}^6 \frac{\hbar\omega_i}{2} \quad (41)$$

Neither E'_0 nor all of the vibration frequencies are known. However, after substituting eq 18 into eq 41, performing some algebraic manipulation, and making use of eq 38, the above equation may be written in terms of $b - \beta'$, which is known.

$$E_{\min} = \frac{1}{\theta} \int_0^\theta \beta'(\Theta) d\Theta - b(T) + \frac{\hbar\omega_1}{2} + \frac{\hbar\omega_2}{2} - kT \sum_{i=3}^6 \ln \left[1 - \exp \left(-\frac{\hbar\omega_i}{kT} \right) \right] \quad (42)$$

The last term in the above equation will be small. Ha and Sibener²⁷ have measured two of the vibrational frequencies that may not be obtained from EELS. They are a frustrated rotation, ω_4 , and a frustrated translation, ω_6 . It is assumed that these two are the smallest frequencies and will therefore give the largest contribution to the last term in eq 42. An estimated minimum energy may thus be written

$$\tilde{E}_{\min} = \frac{1}{\theta} \int_0^\theta \beta'(\Theta) d\Theta - b(T) + \frac{\hbar\omega_1}{2} + \frac{\hbar\omega_2}{2} - kT \ln \left[1 - \exp \left(-\frac{\hbar\omega_4}{kT} \right) \right] - kT \ln \left[1 - \exp \left(-\frac{\hbar\omega_6}{kT} \right) \right] \quad (43)$$

The minimum energy calculated from the above equation using the parameters in Table 2 is shown in Figure 8. The last two terms in eq 43 represent 0.3% of the minimum energy. The two terms that have been neglected (i.e., those that represent the contribution of the frequencies ω_3 and ω_5) will be smaller than this.

There are, as yet, no calculations estimating the value of the unmeasured vibration frequencies for CO adsorbed

on Ni(111). However, Ha and Sibener have made a comparison of their four measured vibrational frequencies for CO–Ni(111) with cluster calculations made by Richardson and Bradshaw²⁸ for CO bridge bonded on Ni(100). It is clear from this comparison that the frequencies calculated for CO–Ni(100) will be correlated with but not identical to the required frequencies of CO on Ni(111). As an estimate for the size of the neglected terms for CO–Ni(111) we may use the cluster calculations for CO–Ni(100). This yields the result that the neglected terms are approximately 0.03% of the minimum energy, which is indeed negligible since other parameters that enter into the minimum energy may not be known this well.

Although the error arising from the neglected terms and errors in β' and the measured frequencies is small, it may become important if two minimum energies which are close in value are subtracted to examine, for instance, the difference in minimum energy for CO molecules bound to the (100) and (111) plane of nickel.

Conclusions

For a surface with adsorbed molecules that have a distribution in energy, there are two possible explanations. There may be a physical heterogeneity associated with the surface or the surface may be homogeneous with the energy distribution corresponding to the possible energy levels found from a quantum mechanical treatment of the adsorbed molecules. In the quantum mechanical description, the adsorbed molecules occupying a given energy level would be distributed randomly over the surface. Here we treat the CO–Ni(111) surface, which is known to exhibit predominantly one type of bonding. Adsorbed molecules have been treated as quantum mechanical, double harmonic oscillators in order to formulate an expression for the chemical potential.⁶ Adsorbate–adsorbate and adsorbate–substrate interactions have been included through the potential energy of an adsorbed molecule which was allowed to vary with coverage. Isotherm measurements were then used to accurately obtain the values of the parameters appearing in the chemical potential expression over an extended range of temperatures and coverages.

An improved procedure, presented in ref 9, for determining the parameters appearing in the isotherm relation, has been outlined above. Since all measured isotherms are translated into two functions (one of coverage and one of temperature), the parameters are obtained with more accuracy than when individual isotherms are fit separately. The improved accuracy is due to the large number of data points contributing to each of the two fits, while an individual isotherm may have relatively few data points. In fact, in this procedure isotherms with only one or two points have been included. This is important because isotherms measured near the limit of a measurement technique often have very few points. For example, if measurements are being made in a specific pressure range, then as the temperature decreases, only high coverages can be examined. For this same reason, individual isotherms may span only a limited coverage range. With the new procedure, one function of coverage is obtained for all isotherms so that the information is known (for all measured temperatures) over the entire coverage range spanned by the set of isotherms.

Using this procedure for separating the coverage and temperature dependence, different sets of isotherm measurements have been quantitatively compared even though the measurements were made in different temperature and pressure ranges. Measurements made by Christmann *et al.*⁴ and Gijzeman *et al.*⁵ for CO adsorbing

(27) Ha, J. S.; Sibener, S. J. *Surf. Sci.* **1991**, 256, 281.

(28) Richardson, N. V.; Bradshaw, A. M. *Surf. Sci.* **1979**, 88, 255.

on annealed Ni(111) surfaces are seen to be in very good agreement. Conversely, measurements made by Gijzeman *et al.* for a surface that had been reduced with carbon monoxide after initially being oxidized were shown to be different. This is important because such differently prepared surfaces are often treated as equivalent.⁵ This method provides a technique for establishing whether or not surfaces prepared in different laboratories, by the same or different techniques, have the same adsorption properties. Gijzeman *et al.* used the quasi-chemical isotherm to fit their CO–Ni(111) data. The isotherm presented herein fits the data at least as well as the quasi-chemical isotherm. However, the quasi-chemical isotherm does not lead to a distinction between isotherms measured on an annealed surface and those measured on a reduced surface, whereas this distinction is clearly shown with the current isotherm.

Once isotherms have been used to provide the missing parameters, all of the parameters appearing in the chemical potential expression may be tabulated for a given repeatable surface and used to predict several important properties of the adsorption system under investigation. The first of these is the isosteric heat of adsorption. Previously, when the isosteric heat of adsorption was obtained from the isotherm measurements of Christmann *et al.*, either polynomial fits had to be extrapolated into the temperature range of the measurements (300 K)⁶ or the temperature dependence of the isosteric heat was not considered (i.e., Christmann's measurements at higher temperatures were used to predict the isosteric heat at 300 K).²³

Even when the isosteric heat is calculated accurately as it is here, it does not agree with calorimetric measurements made by Stuckless *et al.*,²³ although the coverage dependence is similar. It is proposed that the difference between the measured calorimetric heats and the predicted isosteric heat of adsorption is due to the adsorption-induced enthalpy change of the solid. This term can be

identified from the calorimetric measurements at low coverages and then the approach developed herein may be used to predict the heat of adsorption at higher coverages. As indicated in Figure 5, when this approach was adopted, very close agreement was found between the theory and the experimental values reported by Stuckless *et al.* Note that the inclusion of interactions in the model (through the coverage dependent potential energy) is directly responsible for the coverage dependence that has been predicted in the heat of adsorption. If the equation for the heat of adsorption were derived without including the coverage dependence of the potential energy (i.e., the Langmuir model adopted), there would be no coverage dependence in the equation found for the heat of adsorption.

The second system property that may be predicted from the chemical potential expression is the change in surface tension in the CO–Ni(111) system as a result of adsorption. Allowing the potential energy of a bound carbon monoxide molecule to be a function of coverage produces explicit dependence of the change of surface tension on the potential energy. A large reduction in surface tension with adsorption is predicted.

Finally, the potential energy of the bound molecules may be examined. The change in this potential energy with coverage has been calculated. As well, the minimum or ground state energy of adsorbed CO molecules has been estimated, and the error in this estimation shown to be small.

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