

^{a)}Department of Physics and Astronomy and Laboratory for Surface Science and Technology, University of Maine at Orono, Orono, ME 04469.

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Summary Abstract: A theoretical study of the effect of lateral interactions on molecular adsorption and desorption^{a)}

E. S. Hood,^{b)} B. H. Toby, and W. H. Weinberg

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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The effect of lateral interactions between coadsorbed molecules on adsorbate island growth and the kinetics of adsorption and desorption have been studied within the constraints of a lattice gas model incorporating a combination of deterministic rate equations with a stochastic formulation. The adsorption and desorption of molecular nitrogen on Ru(001) has been investigated in detail. Recent experiments performed at 77 K reveal an unusual functional dependence of the probability of adsorption which displays a maximum at a coverage of approximately 0.2 monolayer.^{1,2} EEL spectra indicate chemisorption of molecular nitrogen occurs only at atop sites with the molecular axis oriented perpendicular to the surface plane.² Saturation coverage is achieved at approximately 0.5 monolayer.^{1,2} Thermal desorption spectra suggest the presence of two distinct chemisorption states at coverages greater than 0.25 monolayer. Quantitative agreement between calculated and experimental thermal desorption spectra as well as the coverage-dependent probability of adsorption is obtained.

Molecular adsorption from a mobile precursor state is examined by Monte Carlo simulation.^{3,4} Molecules are sequentially placed on randomly chosen surface sites to simulate trapping from the gas phase into a physically adsorbed precursor state. Each precursor state molecule migrates over the surface from atop to atop sites until desorption or chemisorption occurs. Lateral interactions between a precursor state molecule and previously chemisorbed molecules are assumed to be both pairwise additive and limited in range to nearest- and next nearest-neighbor adsorbates. The binding energy of the intrinsic precursor state (a molecule physically adsorbed over an unoccupied lattice site) is given by the binding energy of an isolated precursor to the metal surface plus the sum of attractive interaction energies between next nearest neighbors minus the sum of repulsive interaction energies between nearest neighbors. We assume the binding energy of the extrinsic precursor state (a molecule physically adsorbed over a site occupied by a chemisorbed species) to be independent of local environment.^{5,6} The extrinsic precursor binding energy is fixed at a constant value, 85% of the isolated intrinsic precursor binding energy.⁶ The activation barrier to precursor migration is given by the energy at the intersection

point between harmonic potentials whose equilibrium positions are located at adjacent lattice sites. The relative depth of these neighboring potentials is determined by the sum of lateral interactions specific to each site. The probability for chemisorption is determined by the initial (zero coverage) adsorption probability, which is a function of the precursor state binding energy. All probabilities are normalized such that their sum is unity. Thus the relative probabilities for desorption from the precursor state, migration to adjacent sites, or nondissociative chemisorption are functions of the local molecular environment.

The adsorption simulation is performed at a surface temperature of 77 K on a lattice composed of 10 000 ruthenium atoms. Maps displaying the locations of the chemisorbed nitrogen molecules are constructed which detail the growth of adsorbate lattice structure as a function of coverage. Due to the hexagonal geometry of the Ru(001) surface and the existence of attractive, next nearest-neighbor interactions between chemisorbed molecules, the thermodynamically favored overlayer structure, as indicated by a well-developed LEED pattern at 95 K,⁷ possesses $(\sqrt{3} \times \sqrt{3})R 30^\circ$ symmetry. However, three different, energetically equivalent phases can exist on the hexagonal surface, distinguishable one from another only by rotations of 120° . Distinct adsorbate domains can be observed on a surface where two or more of these phases coexist. The process of adsorbate overlayer formation begins with the chemisorption of isolated molecules which act as seed sites for island growth. As adsorption proceeds, the growth of isolated domains continues up to a fractional coverage of approximately 0.25, when "crowding" between neighboring islands begins. Adjacent domains of the same phase coalesce to form larger islands, while adjacent domains of differing phase develop grain boundaries. Molecules adsorbed along these grain boundaries experience nearest-neighbor repulsions not encountered by molecules adsorbed within the islands proper. Saturation coverage occurs at approximately 0.55 monolayer due to the establishment of a steady-state balance between the rate of adsorption from the precursor states and the rate of desorption from the chemisorption states.

Thermal desorption spectra are computed from adsorbate

maps using a combination of deterministic rate equations⁸ with a Monte Carlo formalism. Even though a single binding geometry is assumed, chemisorbed molecules populate a number [49 for nitrogen adsorbed on Ru(001)] of distinct binding states, each possessing a characteristic activation barrier to desorption which is dictated by the number and magnitude of lateral interactions between the chemisorbed molecules. The rate of desorption from each chemisorption state is computed using a modified first-order Polanyi-Wigner equation with a coverage dependent, preexponential term.^{8,9} This system of coupled differential equations is solved numerically by the method of finite differences.¹⁰ The change in the population of each chemisorption state is computed over a finite temperature interval ($\Delta T = 0.5$ K) using the second-order Euler-Cauchy method.¹¹ The appropriate number of molecules is selected at random from each chemisorption state and removed from the adsorbate lattice map. This process is repeated until all chemisorbed molecules have been removed from the surface and a thermal desorption spectrum has been constructed.

Numerical values for the energy parameters characterizing the system of nitrogen on Ru(001) are obtained by minimizing the differences between the calculated and experimental coverage-dependent probability of adsorption and thermal desorption spectra over adsorbate coverages ranging between 0.05 and 0.55 monolayer. In the absence of lateral interactions between coadsorbates, we compute binding energies of 1.6 and 6.4 kcal/mol for the intrinsic precursor state and the chemisorption state, respectively. We find an activation barrier to precursor migration of approximately 0.3 kcal/mol. Although the precursor-chemisorption state and chemisorption-chemisorption state lateral interaction energies are treated as separately variable parameters, ad-

sorption and desorption simulations yield identical values for both, presumably due to the weak binding energy of chemisorbed nitrogen on this surface. We compute an attractive next nearest-neighbor interaction energy of 0.45 kcal/mol and a repulsive nearest-neighbor interaction energy of 0.25 kcal/mol.

Examination of the maps displaying the locations of chemisorbed molecules reveals an adsorption mechanism dominated by kinetic trapping, resulting in the formation of numerous, small island domains. During the thermal desorption simulation,¹² the effect of annealing (thermal relaxation) is clearly visible through the formation of fewer, but larger, island domains. Complete details delineating clearly the extreme value of this type of simulation will be forthcoming.¹²

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^{b)}Bantrell Postdoctoral Fellow.

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Summary Abstract: A theoretical study of the order-disorder transitions for hydrogen on Pd(111)^{a)}

S. M. Foiles and M. S. Daw

Theoretical Division, Sandia National Laboratories, Livermore, California 94550

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The recently developed embedded atom method (EAM)¹⁻³ has been used to study the order-disorder behavior of H on Pd(111) and the results are compared with the experiments in the preceding paper of this conference.^{3,4} The EAM provides an approximate method for calculating the total energy of an arbitrary arrangement of atoms based on the use of the electron density. The requisite functions have been determined semiempirically by fitting *bulk* material properties such as the lattice constant, elastic constants, sublimation energy, vacancy migration energy, and hydrogen heat of solution.² These functions are applied here without change. Note that there is no fit to any surface properties in these calculations.

Three important points should be made about the EAM. First, because the EAM treats both adsorbate and substrate atoms within the same formalism, the method is used to compute the geometry of *both* substrate and adsorbate atoms. Second, adsorbate-adsorbate interactions arise naturally from the theory, including those interactions mediated by the substrate. Third, the EAM *does not* resort to pair or trio approximations. Rather, the EAM embodies a many-atom interaction that is very general.

For H/Pd(111), the experimental work^{4,5} has shown two ordered structures, suggested to be a primitive and centered $\sqrt{3}$ at $\theta = 1/3$ and $2/3$, respectively (the latter forms a graphitic net of hydrogen). Applying the EAM leads to the fol-