

## 4. Chemical Reaction Dynamics at Surfaces

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## 4.1 Dynamics of Molecular Chemisorption

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We have confirmed the presence of a precursor state to the molecular chemisorption of CO on Ni(111) for CO molecules with incident energies of less than 4 kcal mol<sup>-1</sup>. We have also identified for the first time a barrier to adsorption into the molecular chemisorption state directly from the gas phase. This was accomplished by measuring the intensity profiles (by Auger electron spectroscopy) of equivalent amounts of CO deposited on a Ni(111) surface by a well-collimated, supersonic molecular beam for a range of incident translational energies. Between incident translational energies of 4 to 7 kcal mol<sup>-1</sup>, the beam spot intensity profile as well as the initial sticking coefficient undergo a dramatic change. Below 4 kcal mol<sup>-1</sup>, the beam spot intensity profile is very broad and low in intensity. Above 7 kcal mol<sup>-1</sup>, the intensity at the center of the beam spot is 2 to 3 times higher and consequently the intensity profile is narrower and sharper than that resulting from deposition of CO with incident translational energies below 4 kcal mol<sup>-1</sup>. Therefore, the broad, diffuse beam profile results from CO which is initially trapped in a highly mobile and weakly bound precursor state. As the incident translational energy is increased, a new adsorption pathway directly into the tightly bound and relatively immobile chemisorbed state becomes accessible resulting in a beam spot intensity profile similar to that of the incident beam. There are, of course, electron beam effects due to the Auger probe. However, the Auger measurements are made (60 sec after dosing) when all the molecules are in the tightly-bound chemisorption state thus precluding any effects of Auger sensitivity on the adsorption state of the molecule. In addition, all measurements of the profiles resulting from deposition at different incident energies were made under identical conditions of electron beam exposure.

At saturation coverages, the intensity at the center of the beam spot profile is the same for all incident energies but, again, the beam spot profile is broader for the lower incident energies. The result of the increased width is that the effective saturation coverages for the lower incident energies are 80% larger than those for the higher incident energies for the same exposure since adsorption through the more mobile state effectively allows the molecules to sample a larger number of adsorption sites than those available in the surface area directly exposed to the beam.

The initial adsorption state that is populated at low energies is interpreted as a precursor state to molecular chemisorption while the state accessible only at high incident energies is interpreted as the molecular chemisorption state. These results indicate that there is a barrier to adsorption into the molecular chemisorption state directly from the gas phase and that this barrier of a height between 4 and 7 kcal mol<sup>-1</sup> is the dominant feature of the interaction potential that forces the population of the precursor state.

## **4.2 Dynamics of Dissociative Adsorption**

*National Science Foundation (Grant DMR81-19292)*

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An investigation into the dynamics of the dissociative chemisorption process on transition metal surfaces is underway. As in our study of the dynamics of molecular chemisorption, the collision energy of the incident adsorbate is employed as a probe of the dominant features of the molecule–surface potential energy surface. High resolution electron energy loss spectroscopy and photon detection are employed as sensitive detectors of the result of the dissociative adsorption event. The effect of translational energy and, where appropriate, internal energy on the extent of dissociative chemisorption are studied for molecule–metal systems that are believed to dissociate via a precursor state, a direct, and activated and an electronic mechanism or are believed not to dissociate. The emphasis of these studies is on establishing a correlation between the nature of the potential energy surface for the molecule–surface interaction and the dynamics of dissociative adsorption.

## **4.3 Chemical Reaction Dynamics by Molecular–Beam Surface Reactive Scattering**

*Sylvia T. Ceyer, Marianne McGonigal, David J. Gladstone, Michelle Schulberg*

With this experimental arrangement, which is under construction, the angular, energy and mass distributions of scattered or product molecules are measured. These distributions are related to the detailed dynamics of the gas–surface collision or in the case of a surface chemical reaction to the dynamics of the last step of the reaction. For example, the concertedness of the last bond

formation step and the desorption step, dominant features of the potential energy surface such as the presence and orientation of an exit channel barrier, the configuration of the transition state for desorption and the partitioning of the exothermicity of a surface reaction to translational energy of the product molecule are revealed by these measurements. Of particular interest are the corrosion reactions of F with silicon surfaces and the reactions of  $O(^3P, ^1D)$  with  $C_2H_4$  on a Ag surface.

#### 4.4 Spectroscopic Studies of Small Molecule Adsorption on Rare Earth Single Crystal Metal and Metal Oxide Surfaces

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Rare earth metals are believed to be extremely reactive with most molecules, resulting in the immediate dissociation of the molecule and subsequent formation of the stable rare-earth compound. This rapid reactivity renders the metallic rare earth metals useless as catalysts. The goal of our investigation into the adsorption of small molecules on rare earth surfaces is to temper the reactivity of the surface by lowering the temperature and or by oxidation so as to stabilize important reaction intermediates. We have chosen to study the adsorption of oxygen and ethylene on a clean gadolinium (111) single crystal.

The adsorption of  $O_2$  on Gd(111) precedes rapidly to oxide formation at 90 K. There is no stable chemisorbed phase as evidenced by the immediate shift to higher binding energy of the Gd 4f level and the lack of any shift of the O 1s level in the XPS as a function of the surface temperature. The oxygen adsorbed at 90 K cannot be thermally desorbed which is further evidence for immediate sesquioxide formation. However, the UPS data show that the adsorption of ethylene at 90 K on the clean surface results in an ethylidene species, similar to the intermediate observed on platinum and nickel. Adsorption of ethylene at room temperature leads to immediate formation of the carbide of Gd. Curiously, the adsorption of ethylene on the oxidized surface of Gd leads to the same intermediate. We will confirm the structure of the intermediate by a vibrational spectroscopy, high resolution electron energy loss spectroscopy.

##### Publications

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