

## 4.0 Chemical Reaction Dynamics at Surfaces

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### 4.1 Lack of Translational Energy Activation of the Dissociative Chemisorption of CO on Ni(111)

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Joint Services Electronics Program (Contract DAAL03-86-K-0002)*

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The activation of the dissociative chemisorption of CO on Ni(111) by translational and vibrational energy is probed. Molecular beam techniques produce CO molecules with high kinetic energies and with some vibrational excitation. Thermal desorption and high resolution electron energy loss spectroscopy detect the product of the chemisorption event. The maximum translational and vibrational energies attainable in these experiments, 45 kcal/mole and 18 kcal/mole, respectively, are observed not to activate the dissociative chemisorption of CO. These experiments are sensitive to dissociation probabilities as small as  $2 \times 10^{-6}$  and  $9 \times 10^{-4}$  at the maximum values of translational and vibrational energy, respectively. It is concluded that translational energies greater than 45 kcal/mole do not contribute to the CO dissociation rate at high pressures. Rather, the potential energy surface of the CO-Ni(111) interaction likely requires vibrational excitation greater than the amount that can be achieved in this experiment for activation of the C $\equiv$ O bond.

### 4.2 Dynamics of the Activated Dissociative Adsorption of CH<sub>4</sub> on Ni(111)

*M.I.T. Energy Laboratory, Synthetic Fuels Center  
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The dynamics of the activated dissociative chemisorption of  $\text{CH}_4$  on Ni(111) are studied by molecular beam techniques coupled with high resolution electron energy loss spectroscopy. The probability of the dissociative chemisorption of  $\text{CH}_4$  increases exponentially with the normal component of the incident molecule's translational energy and with vibrational excitation. The dissociative chemisorption probability of  $\text{CD}_4$  exhibits the same trends with a large kinetic isotope effect. High resolution electron energy loss spectroscopy identifies the nascent products of the dissociative chemisorption event as an adsorbed methyl radical and a hydrogen atom. These results, which have shown that there is a barrier to the dissociative chemisorption, are interpreted in terms of a deformation model for the role of translational and vibrational energy in promoting dissociative chemisorption. The barrier likely arises largely from the energy required to deform the molecule sufficiently to allow a strong attractive interaction between the carbon and the Ni surface atoms. Tunneling is suggested as the final process in the C-H bond cleavage. The presence of this barrier to dissociative chemisorption presents a plausible explanation for the pressure gap in heterogeneous catalysis.

### 4.3 Chemical Reaction Dynamics on Semiconductor Surfaces

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The etching of semiconductor materials in halocarbon plasma environments is a complex chemical process. The purpose of the plasma is the production of radical species that are highly reactive with the semiconductor surface. Since many different species, including neutral dissociation products of the halocarbon to atomic halogens and halocarbon radicals and ions and fragment ions produced by electron bombardment, are produced in the plasma, the chemistry is difficult to probe in this environment. Our program is aimed at systematically probing with molecular beam reactive scattering techniques the role of the neutral radical species in the etching process.

In this experimental arrangement, a beam of reactant atoms is aimed at a semiconductor surface and the volatile product molecules are detected after desorption from the surface by a quadrupole mass spectrometer. Since the molecular beam allows the production of a single reactive neutral species, the chemistry of the reactive species can be studied in a controlled fashion. The product molecule is unperturbed by collisions before detection allowing the reaction probabilities and the nascent product distribution to be determined unambiguously. We are planning to determine the reaction probabilities of F, C1, O and H atoms, common neutral radical species present in plasma environments, with silicon and to determine the identities of their reaction products and the dynamics of the chemical reaction. Test experiments are underway.

## 4.4 Spectroscopic Study of the Adsorption of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> on Gd(0001)

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The adsorption of ethylene and acetylene on a rare earth metal surface, Gd(0001), has been studied primarily by ultraviolet photoemission and Auger electron spectroscopy. Both species adsorb dissociatively on the clean Gd(0001) surface at 165 K. Sticking probabilities for both species are estimated to be in the range 0.18 - 0.42. Carbon-carbon bond scission occurs with unit probability. Carbon-hydrogen bond scission is also observed. Molecular adsorption occurs at 165 K after passivation of the Gd(0001) surface with adsorbed C and CH<sub>x</sub> species. As the substrate temperature is increased above 300 K, these molecularly adsorbed species dissociate rather than desorb. Gadolinium carbide is formed at higher temperatures.

## 4.5 Stabilization of the CO Precursor Molecule to Molecular Chemisorption

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We have recently found that there are two pathways through which CO chemisorbs on Ni(111): a pathway through which the CO molecule is initially adsorbed as a precursor to molecular chemisorption and a pathway through which adsorption into the molecular chemisorption state occurs directly from the gas phase. These conclusions result from initial adsorption probabilities, saturation coverages and CO mobilities measured in an apparatus combining molecular beam techniques with ultrahigh vacuum surface spectroscopies. We are pursuing this work in an attempt to trap the CO precursor molecule and to identify it spectroscopically. We have built a liquid helium cryostat that is capable of cooling the crystal to 8 K. This temperature should be sufficiently low to prevent the precursor from converting into a chemisorbed molecule. We will identify the precursor molecule by high resolution electron energy loss spectroscopy.

### Publications

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