

4.0 Chemical Reaction Dynamics at Surfaces

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4.1 Methane Dissociative Chemisorption: Origin of the Pressure Gap in Catalysis

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MIT Energy Laboratory, Synthetic Fuels Center*

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Many surface chemical reactions appear to proceed at high pressures but not at low pressures ($< 10^{-5}$ torr), despite favorable thermodynamics. This lack of reactivity at the low pressures where ultrahigh vacuum-surface science techniques are operable is known loosely as the pressure gap and casts doubt on the relevance of UHV surface science to high pressure processes such as heterogeneous catalysis and chemical vapor deposition.

Our group proposed that an origin of the pressure gap in the catalytic reactivity was the presence of a barrier to the dissociative chemisorption of at least one of the reactants. Since it is the translational energy of the incident molecule that is important, in surmounting this barrier and not the surface temperature, the rate of the reaction is limited by the flux of incident molecules with energies above the energy of the barrier. High pressures simply increase the absolute number (not the fraction) of high energy molecules, thereby increasing the reaction rate sufficiently for the products to be detected.

To verify this hypothesis, we used molecular beam techniques coupled with high resolution electron energy loss spectroscopy to probe the effect of translational energy on the dissociative chemisorption of CH_4 on Ni(111). We chose this system because the steam reforming of CH_4 over a Ni catalyst is an example of a reaction which appears to proceed only at high pressures. We showed that there is indeed a barrier to the dissociation of CH_4 and that the normal component of the translational energy and vibrational energy are effective in overcoming it. Rates for CH_4 decomposition under high pressure conditions have been shown to agree very well with rates calculated from our low pressure, dissociation probability measurements as a function of energy. The agreement between the low and high pressure experiments carried out in different laboratories firmly establishes the presence of a barrier along the reaction coordinate as an origin of the pressure gap in heterogeneous catalysis.

Besides providing a link between UHV surface science and high pressure catalysis, our studies of the dynamics of CH₄ dissociation and our ability to identify chemically the product of the dissociative chemisorption event have also provided a detailed microscopic picture of the mechanism of the C-H bond breaking process. A deformation model explains the role of translational and vibrational energy in promoting dissociative chemisorption and suggests that tunneling is the final step in the C-H bond cleavage. In short, the barrier arises largely from the energy required to deform or splatter the methane molecule sufficiently to allow a strong attractive interaction between the carbon and the Ni surface atoms.

4.2 New Mechanisms for Dissociative Chemisorption and Desorption

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If the deformation model discussed above is correct, then the impact of an Ar atom beam on a physisorbed layer of CH₄ should deform the molecule into the configuration for the transition state that leads to dissociation. Execution of this experiment shows indeed that dissociation of CH₄ to adsorbed CH₃ and H fragments does occur under the impact of an Ar atom. This observation represents the discovery of a new mechanism for dissociative chemisorption: collision induced dissociation of adsorbates (or chemistry with a hammer). In competition with collision induced dissociation another process, collision-induced desorption occurs. The desorption of adsorbates by the impact of an inert, neutral species has been predicted previously but this is the first experimental observation of this process.

The impact of the observation of these collision induced processes for understanding the chemistry in a high pressure environment is potentially large because, in a high pressure environment, an adsorbate-covered catalyst is continually bombarded by a large flux of high energy molecules. Therefore, having shown that collision induced processes occur, we believe that no mechanism for surface reactions under high pressure conditions can now be considered complete without an assessment of the importance of collision processes as a major reaction step. Collision induced chemistry and desorption are additional reasons why surface chemistry at high pressures is often very different from the chemistry in UHV environments.

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4.3 Chemical Reaction Dynamics on Semiconductor Surfaces

Joint Services Electronics Program (Contract DAAL-03-86-K-0002)

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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 studying the reaction probability of F atoms, a common neutral radical species present in plasma environments, with silicon to determine the identities of the reaction products and the dynamics of the chemical reaction. We are also probing the chemistry of HF with silicon with the long range goal of studying the effect of the electronic excitation of silicon on the HF reactivity.

4.4 Spectroscopic Study of the Adsorption of C₂H₄ and C₂H₂ on Oxidized Gd(0001)

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

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The adsorption of ethylene and acetylene on a rare earth oxide surface has been studied primarily by ultraviolet photoemission and Auger electron spectroscopy. The Gd oxide surface is produced by exposure of the clean Gd(0001) surface at 300 K to O₂. The adsorption probability for ethylene is at least a factor of 3 and probably a factor of 100 lower than that for acetylene on the oxidized surface at 165 K. The surface species formed upon low-temperature acetylene adsorption is identified as molecular C₂H₂. The molecularly adsorbed C₂H₂ decomposes below a substrate temperature of 350 K, leaving carbon on the surface. These results are compared with those of a previous study of C₂H₂ and C₂H₄ adsorption on the metallic Gd(0001) surface. The possible catalytic significance of the selectivity of the oxidized Gd surface toward acetylene adsorption is immense.

4.5 Synthesis and Chemistry of New Kinds of Adsorbates

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MIT Energy Laboratory, Synthetic Fuels Center*

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Having established this link between high pressure catalysis and UHV surface science, we now know how to bypass the high pressure requirement simply by raising the energy of the incident molecule or collisionally inducing dissociation. We have used the former trick to synthesize and identify spectroscopically, by high resolution electron energy loss spectroscopy, an adsorbed CH_3 radical for the first time in low pressure, ultrahigh vacuum conditions. Because of our unique ability to produce CH_3 species, we have been able to probe its stability and chemistry. From these studies, a complete picture of the relative stabilities of C_xH_n species on Ni has emerged.

4.6 Definition of the CO Precursor Molecule to Molecular Chemisorption

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Two years ago we showed that a precursor molecule to molecule chemisorption exists. We presented two models for the precursor molecule. To distinguish between these models, we have designed, constructed and assembled a liquid He cryostat that enables us to cool a Ni(111) crystal to 8 K. We observed that we could not stabilize the CO precursor molecule at 8 K. This implies that the precursor molecule to molecular chemisorption is a dynamical hindered rotor rather than a stable single configuration of the CO molecule. These results enable us to complete our picture of the precursor molecule to chemisorption.

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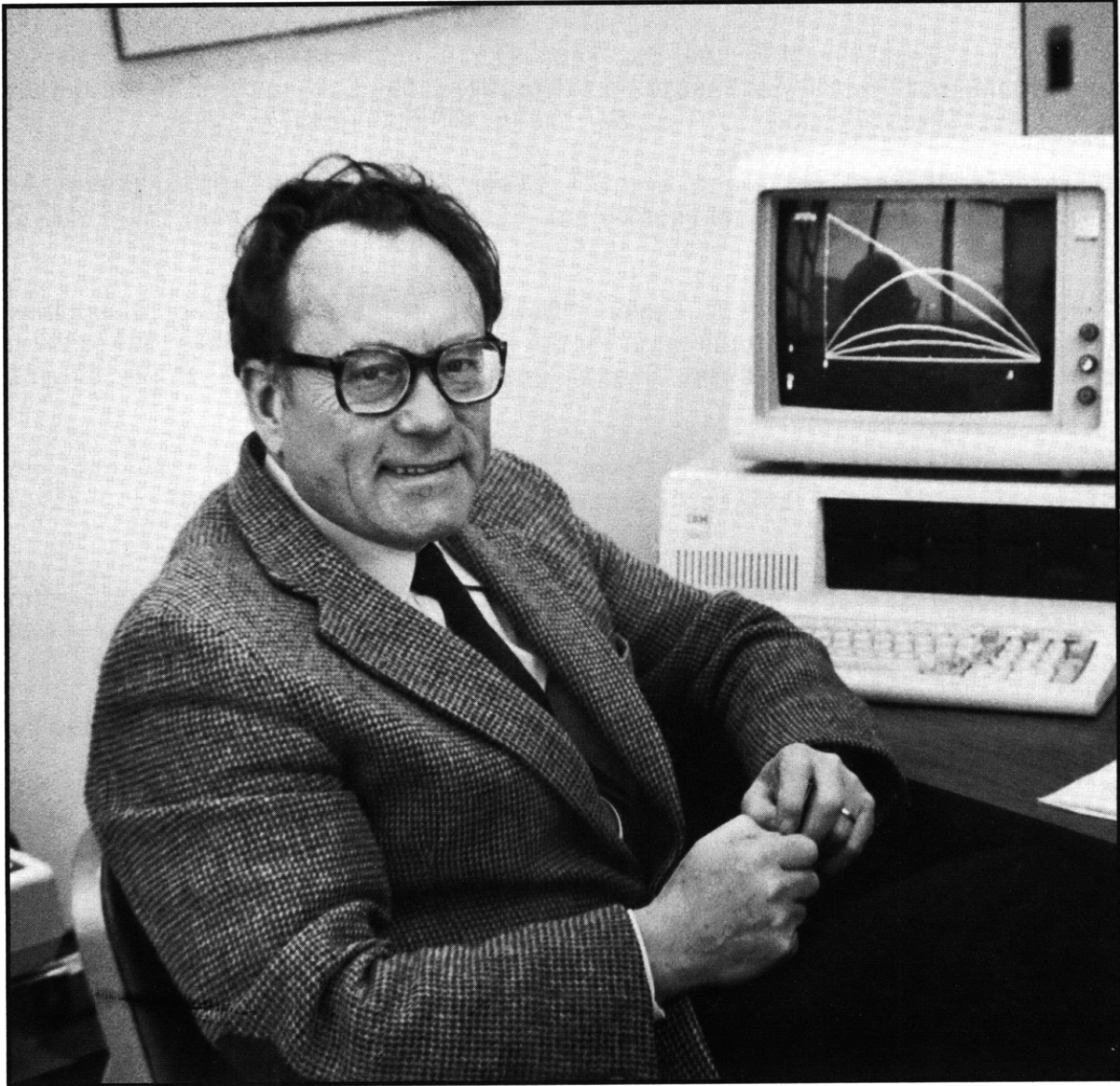
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