

## Chapter 4. Chemical Reaction Dynamics at Surfaces

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### 4.1 Chemical Reaction Dynamics on Semiconductor Surfaces

#### Sponsor

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#### Project Staff

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The etching of semiconductor materials in halocarbon plasma environments is a complex chemical process. The plasma is used to produce species that are highly reactive with the semiconductor surface. Because many different reactive species, including radicals, ions, and highly excited neutral molecules are produced in a plasma, the mechanism of the etching reaction is difficult to probe. Our program is aimed at using molecular beam reactive scattering techniques to systematically examine the role of each of these species in the etching process.

The initial goal of this project was to measure the barrier to  $F_2$  dissociative chemisorption on Si(100). Contrary to popular belief, we found essentially no barrier to the dissociation of  $F_2$  on the unfluorinated surface. The dissociative chemisorption of  $F_2$  on Si(100) proceeds with unit probability for translational energies of the incident  $F_2$  molecules as low as 0.5 kcal/mol. However, there is a substantial barrier to dissociation above fluorine coverages of 0.5 monolayer. Higher

fluorine coverages sufficient to produce the etch product  $SiF_4$  require a higher translational energy of the  $F_2$  molecule. We have observed efficient etching of Si(100) at 300 K for an incident kinetic energy of  $F_2$  of 15 kcal/mol. The angular and translational energy distributions of the  $SiF_4$  — as measured in our newly constructed scattering apparatus consisting of two beams incident on a surface and a rotatable, triply differentially pumped quadrupole mass spectrometer — indicate that the last step of the reaction is the thermal desorption of the product  $SiF_4$  molecule.

We have established that silicon can be etched without the use of molecules incident with energies of hundreds of electron volts, such as those present in plasma etching environments. Molecular beam techniques utilize molecules with energies only slightly higher than thermal ( $<1$  eV), and therefore do not introduce radiation damage or defects into the Si lattice, which is a typical result of plasma etching. We are continuing our work on this system to understand the lack of  $F_2$  energy dependence on the formation of a second reaction product,  $SiF_2$ .

We have also recently observed a new kind of mechanism for dissociative chemisorption. In the limit of zero fluorine coverage, we observed that the Si surface strips one of the fluorine atoms from the incident  $F_2$  molecule, leaving the other fluorine atom to scatter into the gas phase. Although this stripping reaction is analogous to the well-known stripping reactions in gas phase chemical reaction dynamics, this is the first observation of its kind from a surface.

## **Publications**

Ceyer, S.T., D.J. Gladstone, M. McGonigal and M.T. Schulberg, "Molecular Beams: Probes of the Dynamics of Reactions on Surfaces." in *Physical Methods of Chemistry*. 2nd ed. Eds. B.W. Rossiter, J.F. Hamilton and R.C. Baetzold. New York: Wiley, 1990. In press.

Gladstone, D.J., M.T. Schulberg, K.B. Laughlin, M. McGonigal and S.T. Ceyer. "Design of a Power Supply for Resistive Heating of Semiconductor Crystals."

Gladstone, D.J. *Reaction Dynamics of Fluorine with Silicon (100): Design of a Molecular Beam Surface Reactive Scattering Chamber*. Ph.D. diss. Department of Chemistry, MIT, 1989.

Laughlin, K.B., D.J. Gladstone, M. McGonigal and S.T. Ceyer. "Dynamics of the Reaction of F<sub>2</sub> with Si(100)." Paper presented at the Dynamics of Gas-Surface Interactions, Gordon Conference, August, 1989.

McGonigal, M., M.T. Schulberg, D.J. Gladstone, K.B. Laughlin, S.T. Ceyer. "Reactions of F<sub>2</sub> with Si(100)." Paper presented at Materials Research Society, Boston, December, 1989.

McGonigal, M. *Reactive Chemisorption of Molecular Fluorine on Si(100)*. Ph.D. diss. Department of Chemistry, MIT, 1989.

Schulberg, M.T., M. McGonigal, D.J. Gladstone, K.B. Laughlin, S.T. Ceyer. "The Etching of Si(100) with a Molecular Beam of F<sub>2</sub>." Paper presented at the American Vacuum Society, Boston, October, 1989.

## **4.2 Collision Induced Dissociative Chemisorption of CH<sub>4</sub> on Ni(111) by Inert Gas Atoms: The Mechanism for Chemistry with a Hammer**

### **Sponsors**

MIT Energy Laboratory - Synthetic Fuels Center  
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### **Project Staff**

Professor Sylvia T. Ceyer, John D. Beckerle, Andrew D. Johnson, Qingyun Yang

We observed that the dissociation of CH<sub>4</sub> physisorbed on Ni(111) at 46 K is induced by the impact of incident inert gas atoms. We studied the dynamics and mechanism of this new process — collision induced dissociative chemisorption — using molecular beam techniques coupled with ultrahigh vacuum electron spectroscopies. The absolute cross section for collision induced dissociation is measured over a wide range of kinetic energies (28–109 kcal/mol) and incident angles of Ne, Ar and Kr atom beams. The cross section displays a complex dependence on the energy of the impinging inert gas atom, characteristic of neither total nor normal energy scaling. Quantitative reproduction of the complex dependence of the cross section on the Ar and Ne incident energy by a two-step, dynamical model establishes the mechanism for collision induced dissociation.

Collision induced dissociation occurs by the impulsive transfer of kinetic energy upon collision of Ar or Ne with CH<sub>4</sub>, followed by the translationally activated dissociative chemisorption of the CH<sub>4</sub> upon its subsequent collision with the Ni surface. The dependence of the probability of activated dissociation on the resultant CH<sub>4</sub> normal energy, derived from the fit of the model to the experimental cross section, is in excellent agreement with the results of a previous study of the translationally activated dissociative chemisorption of CH<sub>4</sub> on Ni(111). We have shown that collision induced activation and translational activation are consistent

mechanisms for providing energy to CH<sub>4</sub>, surmounting the barrier to dissociative chemisorption.

### **Publications**

Beckerle, J.D., A.D. Johnson, Q.Y. Yang and S.T. Ceyer. "Collision Induced Dissociative Chemisorption of CH<sub>4</sub> on Ni(111) by Inert Gas Atoms: The Mechanism for Chemistry with a Hammer." *J. Chem. Phys.* 91: 5756 (1989).

Ceyer, S.T. "Translational and Collision Induced Activation of CH<sub>4</sub> on Ni(111): Phenomena Connecting UHV Surface Science to High Pressure Heterogeneous Catalysis." *Langmuir* 6:82 (1990).

Ceyer, S.T. "The Mechanism for CH<sub>4</sub> Dissociation and the Synthesis of C<sub>6</sub>H<sub>6</sub> from CH<sub>4</sub> on Ni(111)." Paper presented at the Pacificchem '89 Conference, American Chemical Society, Honolulu, Hawaii, December, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the National Symposium on Frontiers of Science, National Academy of Science, Irvine, CA March, 1989.

Ceyer, S.T. "Dynamics of Activated Dissociative Chemisorption and Collision Induced Desorption of CH<sub>4</sub> on Ni(111)." Paper presented at the Debye Symposium, American Chemical Society Meeting, Dallas, April, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the Ninth International Summer Institute in Surface Science, University of Wisconsin at Milwaukee, August, 1989.

Ceyer, S.T. "Dynamics of Collision Induced Dissociation and Desorption of CH<sub>4</sub> on Ni(111)." American Institute Chem. Eng. Meeting, San Francisco, November, 1989.

## **4.3 Collision Induced Desorption**

### **Sponsors**

MIT Energy Laboratory - Synthetic Fuels Center  
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Contract 19014-AC5

### **Project Staff**

Professor Sylvia T. Ceyer, John D. Beckerle, Andrew D. Johnson, Qingyun Yang

The desorption of CH<sub>4</sub> physisorbed on Ni(111) is observed to be induced by collision with Ar atoms incident with energies less than 2 eV. The absolute cross section for collision induced desorption is measured as a function of the kinetic energy and incident angle of the Ar beam. The mechanism for desorption is shown to involve a direct and impulsive, bimolecular collision between Ar and CH<sub>4</sub>. Molecular dynamics simulations show that the energy and incident angle dependence of the desorption cross section are the consequence of two competing dynamical effects.

### **Publications**

Beckerle, J.D., A.D. Johnson and S.T. Ceyer, "Observation and Mechanism of Collision Induced Desorption: CH<sub>4</sub> on Ni(111)," *Phys. Rev. Lett.* 62: 685 (1989).

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the National Symposium on Frontiers of Science, National Academy of Science, Irvine, CA, March, 1989.

Ceyer, S.T. "Dynamics of Activated Dissociative Chemisorption and Collision Induced Desorption of CH<sub>4</sub> on Ni(111)." Paper presented at the Debye Symposium, American Chemical Society Meeting, Dallas, April, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the Ninth International Summer Institute in Surface Science, Uni-

versity of Wisconsin at Milwaukee, August, 1989.

Ceyer, S.T. "Dynamics of Collision Induced Dissociation and Desorption of CH<sub>4</sub> on Ni(111)." American Institute Chem. Eng. Meeting, San Francisco, November, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at Workshop on Dynamics of Surface Reactions, Copenhagen, Denmark, May, 1989.

## 4.4 Synthesis of Benzene from Methane

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MIT Energy Laboratory - Synthetic Fuels Center  
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### Project Staff

Professor Sylvia T. Ceyer, Dr. Kevin Maynard, Andrew D. Johnson, Qingyun Yang

With the knowledge gained from our studies of methane activation about the microscopic origins for the pressure gap, we have been able to develop a scheme for bypassing the high pressure requirement. This scheme involves raising the energy of the incident molecule or collisionally inducing dissociation. In this way, we have been able to perform a high pressure reaction at low pressure: the synthesis of C<sub>6</sub>H<sub>6</sub> from CH<sub>4</sub>. In addition, because this reaction is carried out at low pressure, we have been able to identify the adsorbed intermediates by high resolution electron energy loss spectroscopy and to determine the mechanism of this reaction.

The synthesis is effected by exposing a monolayer of CH<sub>4</sub> physisorbed on Ni(111) at 47 K to a beam of Kr atoms. The collision of the incident Kr with the physisorbed CH<sub>4</sub> distorts the CH<sub>4</sub> from its tetrahedral configuration, thereby lowering the barrier to dissociation into an adsorbed methyl radical and an adsorbed hydrogen atom. As the surface temperature is raised to 230 K, all the

adsorbed CH<sub>3</sub> dissociates to CH and the CH recombines to form adsorbed C<sub>2</sub>H<sub>2</sub>. Some of the C<sub>2</sub>H<sub>2</sub> trimerizes to adsorbed C<sub>6</sub>H<sub>6</sub> and at 410 K and 425 K, respectively, the atomically adsorbed hydrogen desorbs as H<sub>2</sub> and some of the chemisorbed C<sub>6</sub>H<sub>6</sub> desorbs. The gas phase benzene is detected mass spectrometrically in a thermal desorption experiment. Although the maximum thermal desorption yield for benzene is 1.5 percent at a crystal heating rate of 17 K/S, the gas phase hydrocarbon selectivity of this synthesis for benzene production is 100 percent. This is the first observation of a reaction of CH<sub>4</sub> to form a gas phase, higher hydrocarbon over a metallic catalyst at the low pressures commensurate with a UHV environment.

### Publications

Ceyer, S.T. "Bridging the Gap Between Surface Science and High Pressure Processes." Langmuir Award Lecture presented at the American Chemical Society, Miami, Florida, September, 1989.

Maynard, K.J., Q.Y. Yang, A.D. Johnson and S.T. Ceyer, "The Synthesis of C<sub>6</sub>H<sub>6</sub> from CH<sub>4</sub>." Paper presented at the American Vacuum Society, Boston, October, 1989.

Yang, Q.Y., A.D. Johnson, K.J. Maynard and S.T. Ceyer. "Synthesis of Benzene from Methane over a Ni(111) Catalyst." *J. Am. Chem. Soc.* 111: 8748 (1989).

## 4.5 The Structure and Chemistry of CH<sub>3</sub> and CH Radicals and Isotopic Variants Adsorbed on Ni(111)

### Sponsors

MIT Energy Laboratory - Synthetic Fuels Center  
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### Project Staff

Professor Sylvia T. Ceyer, Qingyun Yang, Andrew D. Johnson, Dr. Kevin Maynard

We present a detailed analysis of the vibrational spectra of  $\text{CH}_3$ ,  $\text{CH}_2\text{D}$  and  $\text{CD}_3$  adsorbed on Ni(111) and of the products of its reactions. Molecular beam techniques effect the synthesis of adsorbed methyl radicals from  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$  or  $\text{CD}_4$ . Because we can measure these spectra at both higher resolution ( $30\text{ cm}^{-1}$ ) and higher sensitivity ( $5 \times 10^6$  counts/sec), we have been able to observe both new features and also to carry out a symmetry analysis. The  $\text{CH}_3$  radical is shown to be adsorbed with  $\text{C}_{3v}$  symmetry on a threefold hollow site. The symmetric C-H stretch mode of  $\text{CH}_3$  and the overtone of the asymmetric deformation mode are shown to be in Fermi resonance. At temperatures above 150 K,  $\text{CH}_3$  dissociates to form adsorbed CH.

Confirmation for the assignment of the spectrum to a CH species is found in the spectrum measured after thermal decomposition of  $\text{CH}_2\text{D}$ . This species decomposes to a mixture of adsorbed CH and CD. The frequencies of the C-H and C-D stretch modes are identical to the frequencies of these species produced from the decomposition of  $\text{CH}_3$  and  $\text{CD}_3$ . The adsorption site of the CH species is determined to be a threefold hollow site and the geometry of the  $\text{Ni}_3\text{-C-H}$  is determined to be pyramidal. At temperatures above 230 K, carbon-carbon bond formation between the CH species is observed to yield  $\text{C}_2\text{H}_2$ . Low coverages of  $\text{C}_2\text{H}_2$  are shown conclusively to dissociate to  $\text{C}_2\text{H}$  and  $\text{C}_2$  species at 400 K in contrast to a literature report of  $\text{C}_2\text{H}_2$  dissociation to adsorbed CH. At temperatures above 380 K, high coverages of  $\text{C}_2\text{H}_2$  result in trimerization to adsorbed benzene. The relative stabilities of the  $\text{C}_1$  species on Ni(111) are determined to be  $\text{CH}_2 < \text{CH}_3 < \text{CH}$ .

### Publications

Yang, Q.Y. *The Chemistry of  $\text{CH}_4$  on Ni(111)*. Ph.D. diss. Dept. of Chemistry, MIT, 1989.

## 4.6 High Resolution Electron Energy Loss Spectroscopy of H on Ni(111)

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MIT Energy Laboratory - Synthetic Fuels Center  
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### Project Staff

Professor Sylvia T. Ceyer, Qingyun Yang, Andrew D. Johnson, Dr. Kevin Maynard

A high resolution electron energy loss spectrum of half of a monolayer of H(D) adsorbed on Ni(111) has been measured with sufficient intensity and resolution to allow seven vibrational loss features to be observed:  $\nu_{\text{asy}} = 745, 790\text{ cm}^{-1}$ ;  $\nu_{\text{sym}} = 1085, 1105\text{ cm}^{-1}$ ;  $2\nu_{\text{asy}} = 1260, 1400\text{ cm}^{-1}$ ;  $2\nu_{\text{sym}} = 2180\text{ cm}^{-1}$ . The assignments of the fundamentals are based on the measured anharmonicity and angular distributions of the vibrational loss features.

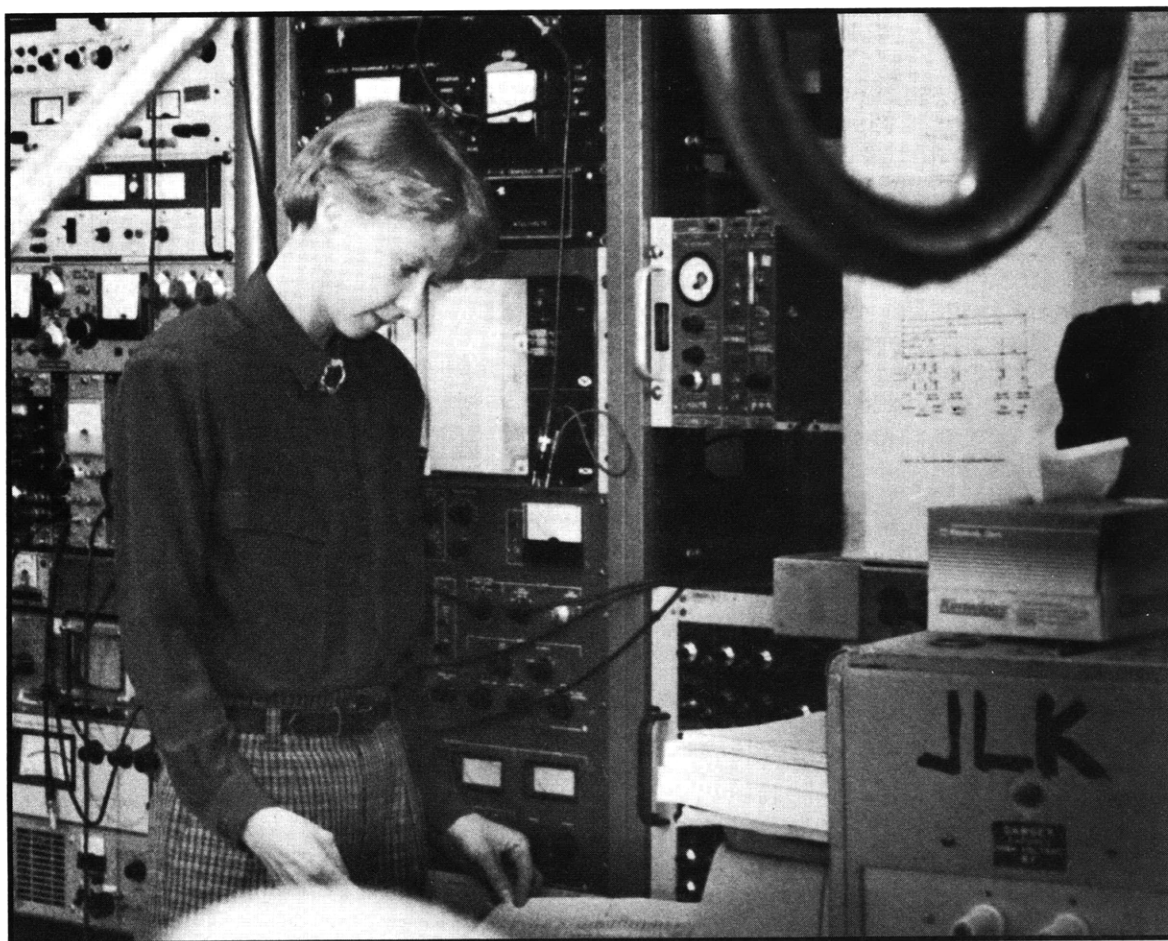
The splitting of the  $\nu_{\text{asy}}$  and  $\nu_{\text{sym}}$  modes is explained by the local potential difference of H adsorbed on the fcc and hcp threefold sites. The absence of dispersion of these modes, as evidenced by measurements of the spectra at  $\Sigma$  of the Brillouin zone, indicate that dynamical coupling between the hydrogen atoms on neighboring sites is not operative to within the resolution of this experiment.

The splitting of the overtone of the asymmetric Ni-H stretch mode is due to a transition of each of the two different hydrogen atoms to the second vibrationally excited state. The observation of two distinct vibrational frequencies corresponding to the hydrogen atoms adsorbed on two threefold sites, whose structures differ only in the presence of a Ni atom in the second layer, confirms the previously proposed structure for the  $(2 \times 2)2\text{H}$  overlayer. Since this is the first observation of any experimentally determined distinction in the physical properties of hcp and fcc threefold sites on any metal surface, these results provide a critical test of theory.

***Publications***

Yang, Q.Y., A.D. Johnson and S.T. Ceyer, "High Resolution Electron Energy Loss Spectroscopy of H on Ni(111)." Paper presented at American Vacuum Society, Boston, October, 1989.

Yang, Q.Y. *The Chemistry of CH<sub>4</sub> on Ni(111)*. Ph.D. diss. Dept. of Chemistry, MIT, 1989.



*Professor Sylvia T. Ceyer with the molecular beam surface scattering apparatus.*