

# Chapter 4. Chemical Reaction Dynamics at Surfaces

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## 4.1 Dynamics of the Reaction of Fluorine with Si(100)

### Sponsor

Joint Services Electronics Program  
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It has long been believed that molecular fluorine,  $F_2$ , would not react with or etch Si. To overcome this problem, scientists used a plasma environment. Because the plasma dissociates the molecular  $F_2$  or other fluorine containing molecules into F atoms, it was believed that these species are responsible for reacting with the Si surface to form the volatile product  $SiF_4$ . While atomic fluorine, F, certainly does react with Si, we have shown that, contrary to popular belief, molecular  $F_2$  also reacts with Si(100) with very close to unity probability ( $\sim 0.95$ ).

With support from the Joint Services Electronics Program, we used our molecular beam-ultrahigh vacuum surface scattering apparatus to direct a well-characterized, monoenergetic beam of  $F_2$  molecules at a Si(100) surface. Not only have we shown that fluorine reacts via the well-known mechanism in which both F atoms of the incident  $F_2$  molecule adhere to the surface (known as dissociative chemisorption), but also that some of the incident  $F_2$  reacts so that only one of the F atoms sticks to the surface while the other atom is scattered from the surface. This latter mechanism is called an abstraction reaction and, while its existence has been predicted theoretically, we were the first group to demonstrate it experimentally.

In essence, the dangling bonds on the Si surface strip off one of the F atoms as the  $F_2$  molecule flies

by it. We were able to observe this mechanism in the angular and time-of-flight distribution measurements only as the direct consequence of the high resolution, the high signal to noise, and the collisionless environment of the detector in our apparatus. This mechanism could not have been observed with any other existing apparatus either custom-built or commercially available. As expected, the surface temperature has no effect on the abstraction process, but the incident energy of the  $F_2$  molecule does determine the branching ratio between F atom abstraction and dissociative chemisorption.

Presently, we are continuing our angular and time-of-flight (energy) distribution measurements of the scattered F and  $F_2$  signal to more accurately quantify this ratio as a function of the kinetic energy of the incident  $F_2$  molecule. These accurate measurements are necessary because the F atom abstraction mechanism has implications for models of the plasma environment during etching reactions. The abstraction of  $F_2$  by the Si surface provides an additional source of F atoms, in addition to the known source of F atoms from the gas phase decomposition of  $F_2$  in the plasma. Therefore, this source of reactive species must now be included in a quantitative model of the plasma etching environment.

### Publications

Ceyer, S.T. "New Mechanisms for Chemistry at Surfaces." *Sci.* 249:133 (1990).

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, 1991. Forthcoming.

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." In preparation.

## 4.2 Dynamics of the Reaction of Fluorine with Fluorinated Si(100)

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While the reaction probability of  $F_2$  with a clean Si(100) surface is near unity, we have shown that the probability for reaction decays to zero as the fluorine coverage increases to one monolayer. That is,  $F_2$  is not unreactive with Si but it is unreactive with a fluorinated surface of Si. This lack of reactivity with the fluorinated Si surface is the source of the misconception that  $F_2$  does not react with Si. The lack of reactivity with the fluorinated surface precludes the build up of a sufficient layer of fluorine to produce the volatile etch product,  $SiF_4$ . However, we have shown that if the kinetic energy of the incident  $F_2$  molecule is increased above a threshold value of 6 kcal/mol ( $\sim 0.25$  eV), the reaction probability of  $F_2$  with a fluorinated Si surface increases linearly with the normal component of kinetic energy. The enhancement in the reaction probability allows enough fluorine to be deposited to form the volatile etch product,  $SiF_4$ . Therefore, we have observed efficient etching of Si(100) at 300K for an incident  $F_2$  normal kinetic energy of 15 kcal/mol (0.5 eV). This energy is two orders of magnitude below the energies used in plasmas. This result establishes that Si can be etched with low energies using molecular beam techniques without the use of plasmas. The low energies afforded by molecular beam techniques prevent the introduction of radiation damage or defects into the Si lattice, which is a typical result of plasma etching.

### Publication

Schulberg, M.T. *The Reaction of Molecular Fluorine with Silicon (100): Adsorption, Desorption, and Scattering Dynamics*. Ph.D. diss., Dept. of Chem., MIT, 1990.

## 4.2.1 New Mechanisms for Surface Processes

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With partial support from the Joint Services Electronics Program (JSEP), we have found that the kinetic energy of an inert gas atom incident on  $CH_4$  physisorbed on Ni(111) activates the dissociative chemisorption of  $CH_4$  just as the translational energy of the  $CH_4$  molecule incident on the surface. This process occurs because the impact of the inert gas atom pounds the molecularly adsorbed  $CH_4$  into the distorted shape of the transition state that leads to dissociation. The products of the dissociative chemisorption event after collision induced activation, identified by high resolution electron energy loss spectroscopy as an adsorbed methyl radical and an adsorbed hydrogen atom, are identical to those observed after translational activation. This observation represents the discovery of a new mechanism for dissociative chemisorption: collision induced dissociation of adsorbates. These results for translational and collision induced activation as well as the translational activation of  $F_2$  on fluorinated Si(100) signal the demise of the long-standing and pervasive notion in surface science that the surface is the all-important and sole source of energy in activating the dissociation of a molecule at or adsorbed on a surface.

With the goal of uncovering the detailed mechanism and dynamics of this new process, the absolute cross section for collision induced dissociation of  $CH_4$  physisorbed on Ni(111) is measured over a wide range of kinetic energies and angles of incidence of a Ne, Ar and Kr atom beam. Unlike the translational activation of  $CH_4$ , which exhibits strict normal energy scaling, the collision induced dissociation cross section displays a complex dependence on the energy of the impinging inert gas atoms characteristic of neither normal nor total energy scaling. A two-step, dynamic model for the mechanism for collision induced dissociation provides excellent agreement with the energy and angular dependence of the cross section for dissociation. The model shows that the origin of the breakdown in normal energy scaling in the inert gas kinetic energy is the range

of impact parameters which contribute to the dissociation cross section. By properly summing over the impact parameter, the model calculations allow the previous translational activation results to be mapped onto the cross sections for collision induced dissociation. In this way, translational activation and collision induced activation are shown to be completely consistent. They are simply different ways to provide the energy to deform the  $\text{CH}_4$  molecule but, once deformed, the mechanism for the dissociation is the same.

In competition with collision induced dissociation, another process, collision induced desorption, occurs. Previously, the desorption of adsorbates by the impact of an inert, neutral species has been predicted, but ours was the first experimental observation of this process. Specifically, the absolute cross section for collision induced desorption of  $\text{CH}_4$  physisorbed on  $\text{Ni}(111)$  is measured as a function of the kinetic energy and incident angle of an Ar beam. The mechanism for desorption is shown to involve a direct and impulsive, bimolecular collision between Ar and  $\text{CH}_4$ . Molecular dynamics simulations show that the complicated energy and incident angle dependence of the desorption cross section are the consequence of the competition between the decrease in the energy transferred in the normal direction and the increase in the collision cross section as the incident angle increases. The results of detailed trajectory calculations also assess the minor roles of multiple and mirror collisions, normal energy accommodation and neighboring molecules.

The impact of the observations of collision induced chemistry and desorption for understanding surface chemistry in a high pressure environment is potentially large because, in a high pressure environment, an adsorbate-covered surface 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 including those that occur in plasma environments, can now be considered complete without an assessment of the importance of collision induced processes as a major reaction step. In fact, there are many unexplained observations in the literature of effects of inert gases on the rates of high pressure, heterogeneous catalytic reactions. It is now important to reinvestigate these reactions in light of the knowledge that these collision induced processes occur. Collision induced chemistry and desorption are additional reasons why surface chemistry at high pressures is often very different from the chemistry in UHV environments.

Knowledge of these microscopic origins for the pressure gap has allowed us to develop a scheme

to bypass the high pressure requirement by simply 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  $\text{CH}_3$  radical for the first time under low pressure, ultrahigh vacuum conditions. More recently, higher resolution and higher sensitivity spectra of  $\text{CH}_3$ ,  $\text{CH}_2\text{D}$  and  $\text{CD}_3$  have confirmed a Fermi resonance between the overtone of the asymmetric deformation and the low frequency or "soft" C-H symmetric stretch. These spectra have also allowed a symmetry analysis to be carried out that establishes that the  $\text{CH}_3$  species is adsorbed with  $\text{C}_{3v}$  symmetry in a threefold hollow site with the hydrogens either eclipsed over or staggered between the surrounding Ni atoms.

Because of our unique ability to produce a  $\text{CH}_3$  species, we have been able to probe its stability. Above 150 K,  $\text{CH}_3$  begins to dissociate to adsorbed CH. An unambiguous identification of the spectrum as that of CH is only possible because of the high resolution ( $32\text{cm}^{-1}$  FWHM) and high sensitivity ( $5 \times 10^6$  counts/sec for the elastically scattered electron beam) of our spectrometer. This assignment is also supported by the spectra measured after the thermal decomposition of the mixed isotope  $\text{CH}_2\text{D}$ . This work rectifies a previous assignment of a spectrum in the literature to a CH species.

Our ability to bypass the high pressure requirement has allowed us to carry out a high pressure reaction at low pressure: the synthesis of  $\text{C}_6\text{H}_6$  from  $\text{CH}_4$ . 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  $\text{CH}_4$  physisorbed on  $\text{Ni}(111)$  at 47 K to a beam of Kr atoms. The collision of the incident Kr with the physisorbed  $\text{CH}_4$  distorts the  $\text{CH}_4$  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  $\text{CH}_3$  dissociates to CH and the CH recombines to form adsorbed  $\text{C}_2\text{H}_2$ . Some of the  $\text{C}_2\text{H}_2$  trimerizes to adsorbed  $\text{C}_6\text{H}_6$  and at 410 K and 425 K, respectively, the atomically adsorbed hydrogen desorbs as  $\text{H}_2$  and some of the chemisorbed  $\text{C}_6\text{H}_6$  desorbs. The gas phase benzene is detected mass spectrometrically in a thermal desorption experiment. These data also provide mechanistic information useful to the possible extrapolation of this synthesis from molecular beam-UHV environments to more practical conditions.

**Publications**

Beckerle, J.D., A.D. Johnson, and S.T. Ceyer. "Collision Induced Desorption of Physisorbed CH<sub>4</sub> from Ni(111): Experiments and Simulations." *J. Chem. Phys.* 93:4047 (1990).

Ceyer, S.T. "New Mechanisms for Chemistry at Surfaces." *Sci.* 249:133 (1990).

Ceyer, S.T. "The Activation and Reactions of CH<sub>4</sub> on Ni(111)." Paper presented at the Gordon

Conference on Organometallic Chemistry, June 1990.

Ceyer, S.T. "Collision Induced Absorption of H into Ni(111)." Paper presented at the American Chemical Society Meeting, Washington, D.C., August 1990.

Ceyer, S.T. "Adsorbate Synthesis with Molecular Beams." Paper presented at the Chemistry at Surfaces Symposium, University of California, Irvine, October 1990.