

# The current status of tribological surface science

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Use of the ultrahigh vacuum methods of surface science allows the preparation and study of highly characterized solid–solid interfaces for tribological investigations. One of the limiting factors in the progress of our understanding of tribology has been the inability to generate solid–solid interfaces with well-defined, reproducible, atomic scale structures and compositions. The preparation of single crystalline surfaces of metals and the characterization of adsorbed molecules on these surfaces has been one of the major accomplishments of the field of ultrahigh vacuum surface science. Combining surface science instrumentation with an ultrahigh vacuum tribometer has made it possible to bring to the study of tribology the same quality of experimental measurement as is available for many other surface phenomena. One phenomenon that has been explored in great detail is the effect of the coverage of adsorbed species on friction between metal surfaces. Other measurements have included the study of friction anisotropy; the effect on the friction between two single crystal surfaces of their relative crystallographic orientations across the sliding interface. Finally, recent results have correlated the friction between adsorbate covered surfaces with the desorption energy of the adsorbed molecules. These results and measurements anticipated for the future offer the opportunity to address truly fundamental questions in tribology and complement many of the other new tools recently developed for the study of tribological phenomena.

**KEY WORDS:** ultrahigh vacuum; tribology; single crystals; friction anisotropy; adsorbed layers; alcohols

## 1. The evolution of tribological surface science

Tribology is inherently a problem in the study of interfaces between solid surfaces in relative motion. Of primary interest are the mechanical properties of such interfaces including friction, adhesion, and wear. Historically, the development of this field has been hindered by the poor ability to reproduce the measurements of interfacial mechanical properties from system to system and from laboratory to laboratory. One probable cause is the fact that interfacial mechanical properties are very sensitive to the atomic scale characteristics of the surfaces from which interfaces are formed. These characteristics include both the structure and the composition of surfaces. Without the proper tools for reproducible preparation of surfaces and for surface characterization at the atomic scale there will always be limitations to the reproducibility of measurements of interfacial mechanical properties. In recent years the situation has been improved by the development of devices such as the surface forces apparatus (SFA) and the atomic force microscope (AFM) and by the development of methods such as molecular dynamics and the use of quartz crystal microbalances (QCM) for measurement and simulation of friction [1–4]. These all probe different fundamental aspects of the tribological interface and are particularly well suited for certain classes of materials. For example, the SFA uses what are arguably the most highly reproducible and well-defined solid–solid interfaces ever prepared, those of mica against mica. The fundamental contributions of these new methods to tribology is that they allow the measurement of mechanical properties with unprecedented sensitivity using interfaces of unprecedented reproducibility.

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The field of surface science evolved in the 1960's as a consequence of the development of technology that readily allowed the production of ultrahigh vacuum (UHV) environments in which surfaces could be kept perfectly clean for periods of days. Over the course of the past four decades numerous techniques have been developed for the preparation and characterization of perfectly clean surfaces [5–7]. Many of these were single crystalline materials such as metals whose surface structure could then be determined at the atomic scale. In addition, many techniques were developed for the preparation and characterization of adsorbed molecular and atomic species on such surfaces. Historically, a great deal of the effort in this field was devoted to the study of problems in catalytic surface chemistry and in semiconductor surface science. In recent years, however, there has been interest in the application of UHV surface science methods to tribology. These efforts can be divided into two categories: the use of surface science methods for the study of lubricant surface chemistry and the coupling of UHV methods with vacuum tribometers for study of surface mechanical properties. Surface science brings both reproducible preparation of surfaces and a host of surface analytical tools to tribology and creates an opportunity to apply these tools to a wide variety of important materials and lubricants.

Historically, the first application of surface science techniques to tribology were those of the group of Buckley at the NASA Lewis Research Center [8]. This effort began in the late 1960's and was spurred by NASA's need to understand tribological phenomena in vacuum environments. In many respects this work was "ahead of its time" in that it was performed in an era when much of the technology of vacuum surface science was still in its infancy and many of the techniques for surface analysis that are routinely avail-

able today did not exist. Nonetheless, that work produced many intriguing results that have motivated current efforts in the field. For example, it was observed that even at very low exposures to oxygen or hydrogen the friction between W surfaces was reduced [9]. The exposure of W surfaces to straight chain alkanes of varying chain length produced surfaces whose frictional properties depended upon the alkane chain length. Over the past ten years there have been a small number of groups around the world developing tribometers that are compatible with UHV surface analysis instrumentation [10–15]. It should be noted that these are attempts to couple measurements of macroscopic interfacial friction with surface analysis and are distinct from the efforts of a number of groups worldwide using AFMs in surface analysis chambers.

The tribology program that is the focus of this paper is based on an instrument that has been developed over the past decade at Carnegie Mellon University [10,16]. The unique feature of this device is that both surfaces used for a friction measurement are single crystalline and both are prepared and characterized to the state-of-the-art of modern surface science. The initial work performed with this device focused on the study of the effects of adsorbed layers of atoms and molecules on the friction between pairs of Ni(100) surfaces and between pairs of Cu(111) surfaces [10,16–18]. Figure 1 shows a result which typifies the observations of that work. The static friction coefficient was measured be-

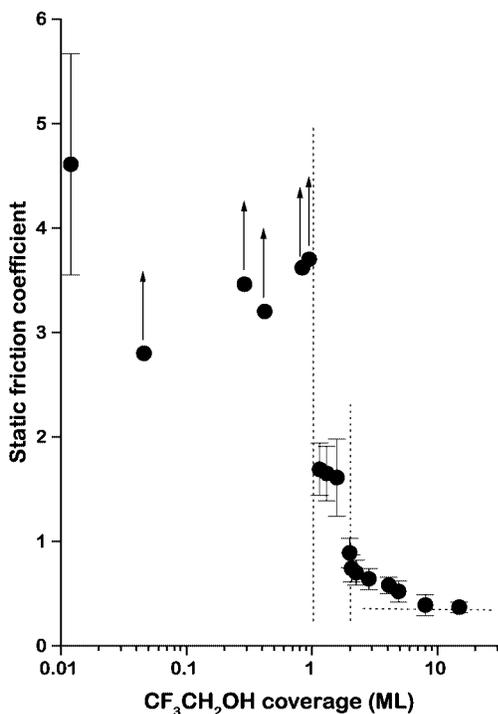


Figure 1. Static friction coefficient versus  $\text{CF}_3\text{CH}_2\text{OH}$  coverage on Cu(111) surfaces. Each data point and error bar represents an average and standard deviation of the friction coefficients from ten measurements. The data points with vertical arrows at coverages less than 1 ML are also averages of ten measurements but represent lower limits of the static friction coefficients. Load  $\approx 40$  mN, sliding velocity = 1, 2, or 3  $\mu\text{m/s}$ , temperature = 120 K.

tween two sliding Cu(111) surfaces modified by adsorbed layers of 2,2,2-trifluoroethanol ( $\text{CF}_3\text{CH}_2\text{OH}$ ) [16]. One of the strengths of our experimental method is the ability to control the coverages of adsorbed species on otherwise perfectly clean single crystal surfaces. In the experiment illustrated in figure 1 the coverage of  $\text{CF}_3\text{CH}_2\text{OH}$  ranges from 0 to 14 monolayers (ML) on each Cu(111) surface. We observe that at  $\text{CF}_3\text{CH}_2\text{OH}$  coverages  $< 1$  ML the friction coefficient between the surfaces is very high,  $\mu_s > 4$ . This is true for all atomic and molecular adsorbates studied to date [17,18]. It is only when the adsorbate coverages on both surfaces reach 1 ML that the friction begins to decrease. Ultimately, the friction coefficient falls to a limiting value of  $\mu_s \approx 0.3$ – $0.4$ . This data gives a good example of the types of information that can be gleaned from a UHV surface science investigation of friction and provides a good illustration of the quality of data that can be obtained from such an instrument. The remainder of this paper describes the UHV tribometer in its current state of evolution and some of the results obtained most recently which illustrate the breadth of the phenomena that can be studied with this instrument. The final section of the paper attempts to predict the course of the near future and the types of problem that will be addressed.

## 2. Instrumentation for UHV tribological surface science

The UHV tribometer used for the research program described in this report is based on a custom designed, cylindrical, stainless steel bell jar. The tribometer is housed on the upper of two levels which is shown schematically in figure 2. A detailed schematic of the tribometer itself is shown in figure 3 and will be described below. The apparatus contains

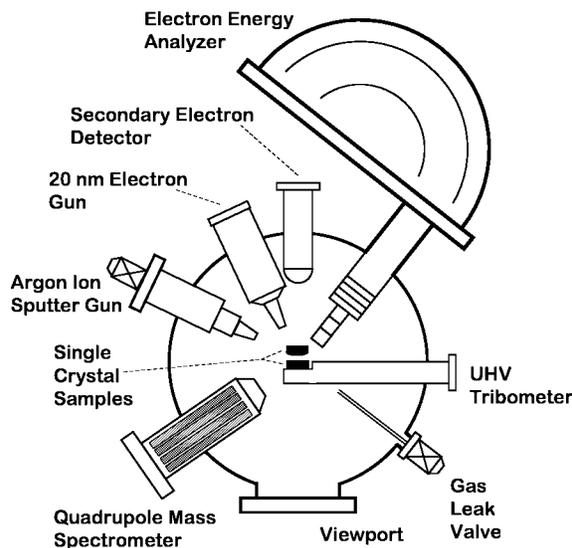


Figure 2. Schematic of a cross section through the cylindrical UHV chamber housing the UHV tribometer. The black objects at the center represent the single crystal samples; one attached to the tribometer and the other to a manipulator that allows it free motion in the chamber. On a lower level of the chamber is a low energy electron diffraction (LEED) optics.

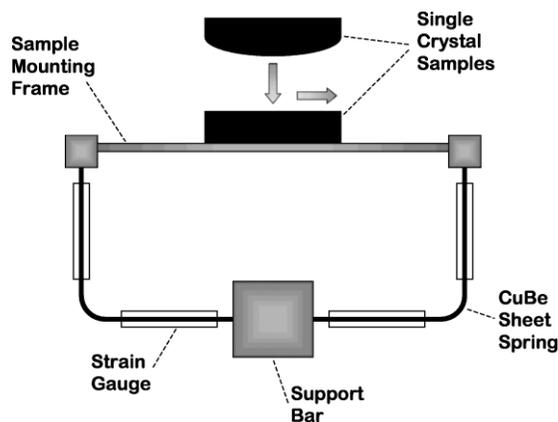


Figure 3. Expanded schematic of the UHV tribometer. There are a total of eight strain gauges, to on either side of each of the four arms of the CuBe sheet springs. The support bar is mounted on a liquid nitrogen reservoir for sample cooling. There is also a filament (not shown) for electron beam heating of the sample on the tribometer. The curved sample is mounted on the manipulator and can also be heated and cooled.

two single crystal samples that are positioned at the focal point of much of the surface analysis instrumentation in the UHV chamber. The upper sample in both figures is mounted to an UHV manipulator that allows free motion within the chamber. The other sample is fixed to the tribometer which measures the shear and normal forces between the two surfaces when they are in contact. Both surfaces can be cooled to  $T < 120$  K and heated to  $T > 1000$  K. Cleaning of the sample surface uses the  $\text{Ar}^+$  sputter gun and annealing treatments. Once cleaned both surfaces can be analyzed using scanning Auger microscopy (SAM) and scanning electron microscopy (SEM). In addition the surface of the sample that is free to move on the manipulator can be analyzed using low energy electron diffraction (LEED) to determine that it is ordered and single crystalline. The clean surfaces of the two samples can be modified by the adsorption of species that are introduced into the vacuum as vapor through standard leak valves. The mass spectrometer is used to analyze the species in the gas phase and can also be used to measure the desorption kinetics of species on the surface of the manipulator sample. In total this system allows the preparation of two single crystal surfaces to the state-of-the-art allowed by modern surface science prior to their being brought into contact for friction measurements.

The UHV tribometer has been designed and built in-house [10]. The schematic in figure 3 shows a cross section through the tribometer. To give a rough idea of the dimensions the samples are  $\sim 1$  cm diameter by  $\sim 2$  mm thick disks (shown in cross section). Again the upper sample is free to move on a manipulator while the lower one is fixed to the tribometer. As shown the sample on the manipulator is polished to have a surface with some curvature ( $\sim 10$ – $20$  cm radius) so that the two surfaces do not come into contact at the edges. The tribometer sample is spot-welded to a sample mounting frame which, in turn, is connected to a vertical support bar by two CuBe sheet springs bent into elbows. There are eight strain gauges bonded to the sides of the CuBe

sheet springs that are used to transduce the forces applied to the surface of the tribometer sample by the manipulator sample. Roughly speaking, a normal force between the two surfaces induces strain in the lower (horizontal) sheet springs while a shear force between the two surfaces (friction during sliding) induces strain in the side sheet springs. Both sets of four strain gauges are connected in Wheatstone bridges in such a way that the responses due to the normal and the shear forces are decoupled from one another. During sliding under an applied normal load both the normal and shear forces can be measured simultaneously in order to determine the coefficient of friction.

The measurement of a friction coefficient between two surfaces in the UHV apparatus requires several steps. First, the surface normals have to be aligned with sufficient accuracy that they do not come into contact at the edges. Then the direction of sliding of the curved surface on the manipulator has to be aligned such that it moves parallel to the flat surface on the tribometer. Once aligned the two surfaces are prepared by cleaning and then modification by adsorption of species (if desired). At that point the sample on the manipulator is brought into contact with the sample on the tribometer to apply the desired normal load and then sheared at a constant velocity in order to generate a friction force that can be transduced by the strain gauges of the tribometer. The real contact occurs at a small point that is  $\sim 2$ – $5$   $\mu\text{m}$  in diameter depending upon the load [16]. In order to obtain good statistics for the experiment, ten to twelve measurements are performed under any given set of conditions. Between each pair of measurements the manipulator surface is moved and rotated slightly in order to be sure that contact is occurring at different points across the surfaces. Typically, the coefficients of friction can then be measured with standard deviations on the order of 15–20%. The range of conditions that can be used for sliding are:  $F_N = 5$ – $250$  mN,  $v_{\text{shear}} = 1$ – $200$   $\mu\text{m/s}$ ,  $T = 120$ – $800$  K.

### 3. Recent progress in UHV tribometry

The two sections below give short descriptions of two results obtained quite recently that illustrate the types of phenomena that can be observed using the UHV tribometer.

#### 3.1. Friction anisotropy between Ni(100) surfaces

The friction between two single crystalline surfaces in sliding contact might be expected to depend upon the relative orientations of their lattices. For example, in the case to be described, two Ni(100) surfaces have been brought into contact with different rotational orientations about their aligned  $\langle 100 \rangle$  axes. One of the best examples of the anisotropy of interfacial mechanical properties is a set of measurements of the friction and adhesion between mica surfaces [19–21]. These have been made with the SFA and a device similar to the SFA. The adhesion and the friction between the two mica surfaces are highest when they are crystallographically

aligned. The cause of the high friction and adhesion is that the two surface lattices are aligned and commensurate with one another. As a result the potential energy surface that describes displacement of one piece of mica with respect to the other is highly corrugated and a large force is needed to induce sliding. When the two surfaces are misaligned they are incommensurate and the inter-surface potential is smooth with respect to displacement of one piece of mica over the other. As a result sliding can occur in the limit of zero applied force. These ideas apply perfectly well to mica–mica contacts which are in elastic contact and are not plastically deformed. In the case of metal–metal interfaces under macroscopic loads there is plastic deformation and it is not clear that surface lattice commensurability plays an important role in determining friction.

Friction anisotropy between pairs of Ni(100) surface has been measured using the UHV tribometer [22]. In this experiment the sample on the tribometer was fixed while the sample surface on the manipulator was rotated about its normal between friction measurements. The sliding direction on the tribometer sample was fixed to lie along its  $\langle 110 \rangle$  direction. As a result the sliding direction across the surface of the manipulator sample varied as it was rotated. The friction coefficients as a function of the misorientation angle between the two clean Ni(100) surfaces are plotted as (■) in figure 4. The data points with arrows over them represent lower limits on the friction which was too high to measure. It is clear that at all angles the friction is high but that it has a minimum at a misorientation angle of  $45^\circ$ . The static friction coefficient was also measured between two Ni(100) surfaces modified by the adsorption of both sulfur and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). The sulfur layer is at a coverage of 0.5 ML and forms a  $c(2 \times 2)$  layer that passivates the surface. The ethanol is adsorbed molecularly on the sulfur layer at a coverage of 2 ML. The friction coefficients between pairs of these surfaces are plotted as (○) in figure 4. The  $\text{CH}_3\text{CH}_2\text{OH}$  clearly lubricates the surface in the sense that it lowers the friction coefficient but the anisotropy leading to the minimum at  $45^\circ$  still remains. The primary difference between the two surfaces used for the experiments illustrated in figure 4 is that while the Ni(100) surfaces have long range order and can come into commensurate contact at  $0^\circ$  (or  $90^\circ$ ), the surfaces modified by the presence of  $\text{CH}_3\text{CH}_2\text{OH}$  do not exhibit any long range order and thus should be in incommensurate contact at all misorientation angles. The fact that both types of interfaces exhibit the same friction anisotropy suggests that the friction anisotropy between metal surfaces is not due to surface lattice commensurability. Instead it may arise from anisotropy of the bulk mechanical properties which, of course, would be independent of the nature of the surfaces. The origin of this friction anisotropy has yet to be determined.

It should be noted that friction anisotropy is actually a phenomenon with two degrees of freedom since one can vary either the relative orientations of the crystal lattices or the direction of shearing with respect to the crystal lattices. We have chosen to fix the shearing direction with

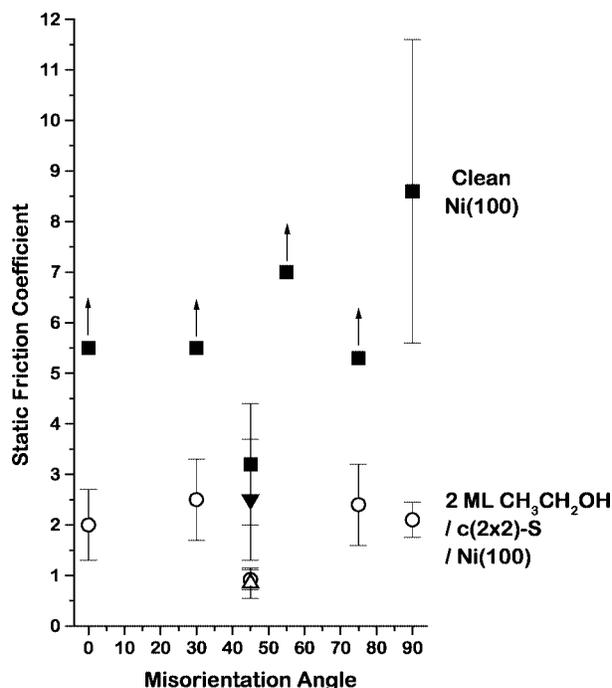


Figure 4. Plot of the static coefficient of friction between Ni(100) surfaces as a function of the rotational misorientation angle between them. At  $0^\circ$  (or  $90^\circ$ ) the two (100) lattices are aligned with one another and sliding occurs along the  $\langle 110 \rangle$  direction of both. Once misaligned the sliding direction remains along the  $\langle 110 \rangle$  of the fixed crystal. The friction coefficients were measured between two clean Ni(100) surfaces (■) and two Ni(100) surfaces modified by 0.5 monolayer of sulfur in a  $c(2 \times 2)$  array and 2 ML of  $\text{CH}_3\text{CH}_2\text{OH}$  (○). Note the minimum in the friction at  $45^\circ$ . The points denoted (▼) and (△) were obtained at a misorientation of  $135^\circ$  which is crystallographically equivalent to  $45^\circ$  misorientation and reveals the same minimum in the friction. Sliding conditions were:  $F_N \approx 20$  or  $40$  mN,  $v_{\text{shear}} = 20 \mu\text{m/s}$ ,  $t_c \approx 6\text{--}10$  s,  $T \approx 300$  K.

respect to one surface lattice and rotate the crystal lattices with respect to one another. This experiment could reveal the possible effects of surface lattice commensurability. Rotating the shearing direction while maintaining the relative surface lattice orientations is an equally interesting experiment, although much more difficult in our current apparatus.

### 3.2. Adsorbate layering effects on friction

Studying the chemistry and properties of molecules buried at the interfaces between solids is one of the greatest challenges to surface and interface science. Because they are sandwiched between dense media they are not accessible to study by the usual tools of surface science which are based on ion and electron spectroscopies. Nonetheless, this is of critical importance in the field of tribology since lubrication is due to thin molecular films at such interfaces.

One of the most dramatic experimental observations of the properties of molecules at interfaces has shown that layering occurs when molecules confined between mica surfaces are squeezed into thin films that are a few molecular diameters in thickness. This has been observed by using the SFA to measure the force needed to squeeze two mica sur-

faces together as a function of separation distance [20,23–26]. Once the two surfaces come to within a few molecular diameters of one another, the force–separation curve goes through pronounced oscillations as successive layers of molecules are squeezed from the interface. Such layering effects ought to influence the tribological properties of interfaces that confine very thin molecular films.

Recent work using the UHV tribometer has provided some evidence of molecular layering between metal surfaces in contact [27]. The interface that has been studied is that formed between two Ni(100) surfaces passivated with 0.5 ML of sulfur and then modified by the adsorption of  $\text{CH}_3\text{CH}_2\text{OH}$  at varying coverages. The 0.5 ML of sulfur forms a well ordered  $c(2 \times 2)$  array on the Ni(100) surface and is present only to passivate the surface and prevent the decomposition of the adsorbed  $\text{CH}_3\text{CH}_2\text{OH}$ . Measurements of the thermally programmed desorption of  $\text{CH}_3\text{CH}_2\text{OH}$  as a function of increasing coverage on this surface reveal a complicated set of desorption features. There are four distinct desorption features with characteristic desorption peak temperatures that are filled in order from highest temperature to lowest temperature as the coverage is increased. These desorption curves have been used to estimate the desorption energy ( $\Delta E_{\text{des}}$ ) which is plotted as a function of coverage in figure 5 ( $\square$ ). This plot reveals the discontinuous changes in the  $\Delta E_{\text{des}}$  of  $\text{CH}_3\text{CH}_2\text{OH}$  as the coverage is increased. At the lowest coverage is the  $\Delta E_{\text{des}}$  of the monolayer and at the highest coverage is the  $\Delta E_{\text{des}}$  of the thick multilayer. The steps at intermediate coverages are suggestive of the formation of some type of layered structure. It should be noted that this is not proof of the formation of discrete layers and the steps in the  $\Delta E_{\text{des}}$  do not occur at coverage increments that are simple integer multiples of the monolayer coverage. Nonetheless, the data indicates that there are discontinuous changes in the properties of the  $\text{CH}_3\text{CH}_2\text{OH}$  films as a function of coverage.

The static friction coefficient between the  $c(2 \times 2)$ -S/Ni(100) surfaces has also been measured in the presence of varying coverages of  $\text{CH}_3\text{CH}_2\text{OH}$ . These friction coefficients are plotted in figure 5 as ( $\bullet$ ). Although they are not shown, the error bars are similar to those in figure 4 with the 2 ML of  $\text{CH}_3\text{CH}_2\text{OH}$ . The interesting feature of the friction coefficients is that they appear to go through discontinuous changes with coverage in much the same way and at the same coverages as the discontinuities in the  $\Delta E_{\text{des}}$ . Clearly the frictional properties of the interface are sensitive to the properties of the  $\text{CH}_3\text{CH}_2\text{OH}$  films adsorbed on the surfaces forming the interface. This is quite remarkable given that these interfaces are between metal surfaces and are probably in plastic contact rather than the elastic contact of mica–mica interfaces in the SFA. What is equally interesting to note is that a close inspection of the data in figure 1 for the friction of Cu(111) interfaces separated by layers of  $\text{CF}_3\text{CH}_2\text{OH}$  also reveals what appear to be discontinuities in the friction versus coverage curve on increasing the coverage past 1 ML and then past 2 ML. Although it is tempting to

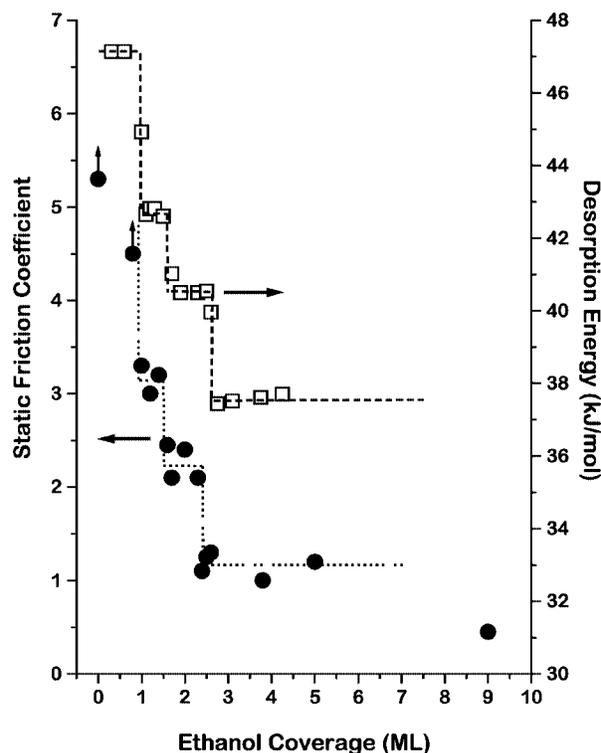


Figure 5. Plots of the static friction coefficients ( $\bullet$ ) and the desorption energies ( $\square$ ) for  $\text{CH}_3\text{CH}_2\text{OH}$  adsorbed at varying coverages on  $c(2 \times 2)$ -S/Ni(100). The desorption energies were obtained from thermally programmed desorption spectra and appear to have discontinuities as a function of increasing coverage. The static friction coefficients also appear to have discontinuities occurring at the same coverages. These are suggestive of layering of the adsorbate that is influencing the frictional properties of interfaces between the surfaces. The conditions for the friction measurements were:  $F_N \approx 40$  mN,  $v_{\text{shear}} = 20$   $\mu\text{m/s}$ ,  $T \approx 120$  K.

suggest that this is a consequence of adsorbate layering at these interfaces the origin of the effect is not yet clear.

#### 4. The future of UHV tribometry

The future of UHV surface science applications to tribology will certainly include efforts to identify and isolate the characteristics of interfaces that influence their tribological properties. In some sense the existing work using the SFA to study friction at mica–mica interfaces serves as a guide to phenomena that might be observed at the interfaces between metal surfaces in sliding contact. Measurements of friction anisotropy will continue between surfaces that are in plastic and elastic contact in order to understand the relative importance of surface lattice commensurability and bulk lattice plasticity in determining interfacial friction. Another avenue of opportunity will be the study of the effects of adsorbate characteristics on friction between metal surfaces.

In addition to allowing the study of friction itself, UHV tribometry measurements offer an opportunity to study important aspects of lubricant surface chemistry. In much the same way as has been done in the past for understanding catalytic surface chemistry one can observe and probe the reaction mechanisms that lead to lubricant degrada-

tion [5,6]. In other cases such as vapor phase lubrication it is possible to determine the mechanisms by which complex lubricant-surface reactions lead to the formation of lubricating films [28,29]. Another problem which can be addressed by the methods of UHV surface science is the effect of friction on lubricant surface chemistry. One can hope to determine whether there are reactions that are induced by the frictional forces between surfaces that would not occur otherwise.

Careful measurements of friction under controlled, characterized, and reproducible conditions will play an important role in the continued development of our understanding of tribology whether or not they are done under UHV conditions. The methods of UHV surface science are merely one of the ways in which these conditions can be realized. One of the advantages that UHV methods offer is that they are amenable to use with an extremely wide variety of materials from metals to ceramics. The ultimate goal, of course, is to generate measurements of sufficiently high quality and under sufficiently well understood conditions that they can be compared with theories or simulations that might ultimately allow prediction of the tribological properties of interfaces.

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