

Keywords: Thin Films, Energy Distribution, Laser Postionization, Self-Assembled Monolayer

INVESTIGATIONS INTO MECHANISMS OF MOLECULAR DESORPTION INDUCED BY keV ION BOMBARDMENT OF ORGANIC SURFACES

D.E Riederer, S.W. Rosencrance, R. Chatterjee, T.D. Dunbar, D.L. Allara, and N. Winograd

Department of Chemistry, The Pennsylvania State University,
University Park, PA 16802

Z. Postawa

Institute of Physics, Jagellonian University, ul. Reymonta 4, PL-30059
Krakow 16 Poland

Introduction

An area of fundamental interest in surface analysis is the study of mechanisms by which the collision of keV particles induce molecular desorption. Molecular solids vary widely in their physical and chemical properties and it has become clear that sputtering of these materials cannot be understood via a single mechanism.[1,2,3] This situation is further complicated by ionization processes which may involve fragmentation or cationization. Understanding these events is challenging and has become increasingly important as the use of ion beam induced desorption techniques are applied to organic and biological materials. The present work focuses on the behavior of monolayer films of phenethylmercaptan bound to a gold substrate (Figure 1) during ion bombardment. Detection of the ejected neutral molecules by laser multiphoton ionization (MPI) permits separation of the desorption and ionization events.

Experimental

Self-assembled monolayers (SAMs) [4] were prepared by immersing vapor deposited gold substrates in a 30 millimolar solution of phenethylmercaptan (PEM) [$C_6H_5CH_2CH_2SH$] in ethanol. The gold substrates were kept in solution for at least five days prior to use and rinsed with ethanol before introduction into the UHV analysis chamber. Thiols adsorb to gold by a strong S-Au bond and are stable in air and vacuum. Molecular species desorbed by 8 keV, 1 μs pulses of Ar^+ or H_2^+ were ionized using a 6 ns pulsed beam of 266 nm photons (3 mJ/pulse) located approximately 1 cm above the surface. The density of molecular species in the laser plane was recorded as a function of time by varying the delay between the primary ion beam impact and the laser pulse. Analysis of the ionized particles was achieved by time-of-flight mass spectrometry using a gated detector to select the ion of interest. The distribution of flight times from the surface to the laser was recorded while monitoring m/z 105 [$C_6H_5CH_2CH_2^+$] which was the most abundant

ion in the mass spectrum. No molecular ion was observed during sputtering or during a gas phase MPI experiment in which PEM vapor was introduced into the chamber. A detailed description of the apparatus has been given previously.[5]

Results and Discussion

Time-of-flight distributions for phenethylmercaptan desorbed upon bombardment with Ar^+ and H_2^+ are displayed in Figure 1. The shape of the distributions obtained using both Ar^+ and H_2^+ projectiles are nearly identical in the region between 20 and 200 μs and the most probable time to traverse the distance from the surface to the photon field is 35 μs . The corresponding kinetic energy distribution (flux) for the H_2^+ projectile is represented by the solid points in Figure 2. This curve indicates that the desorbed molecules have thermal translational energies (ca. 0.025eV) and have been fit by a Maxwell-Boltzmann distribution at room temperature. Cooling the sample to 165 K causes a marked shift to lower energy which is again described by a Maxwell-Boltzmann distribution. The dependence of the desorbed molecule kinetic energy on substrate temperature is observed for both projectiles. Note that the time-of-flight axis was transformed to kinetic energy under the assumption that $[\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2]$ (105 amu) was the species desorbed from the surface. It is possible that the entire PEM molecule was desorbed and that photofragmentation to form m/z 105 occurred during the ionization process. Such a scenario would cause a shift toward slightly higher kinetic energies, however, the trends observed as a function of surface temperature would still hold.

A small peak centered at approximately 7 μs is evident in the PEM time-of-flight distribution produced by the Ar^+ projectile (Figure 1). This peak has nearly the same position in time as that of the sputtered gold dimer (Figure 3), indicating that the molecules in the high energy component of the PEM distribution have velocities nearly identical to that of sputtered Au_2 . No gold signal was observed while using H_2^+ as a projectile.

An interesting result is that almost all of the desorbed molecules leave the surface with thermal kinetic energies. This is a striking result when considering that the PEM molecules are bound to the surface through a S-Au bond estimated to have an energy of 2 eV [4], and brings forth a number of questions and mechanistic implications. An obvious conclusion is that the energy imparted to the gold substrate has no effect on the low energy, high intensity portion of the time-of-flight distribution since its shape is independent of projectile mass. An intriguing question is how the primary ion beam initiates a process which breaks a strong S-Au or C-S bond (2-4 eV) and leaves the nascent species physisorbed on the surface to evaporate after attaining thermal equilibrium with the substrate. Bond breakage through ballistic interactions with primary or secondary particles seems unlikely since such a process will inevitably impart energies greater than the bond energy which would result in immediate desorption without time for thermal equilibration. Desorption via a thermal spike can also be ruled out on the basis that breaking a 2 eV surface bond would require temperatures in excess of 15,000 K.

While it is difficult to draw firm mechanistic conclusions at this time, we believe that the low kinetic energies and apparent thermal equilibration are consistent with bond cleavage by a chemical reaction. Highly reactive species, such as H , H^- and H^+ , created by interaction of the primary beam with the organic film

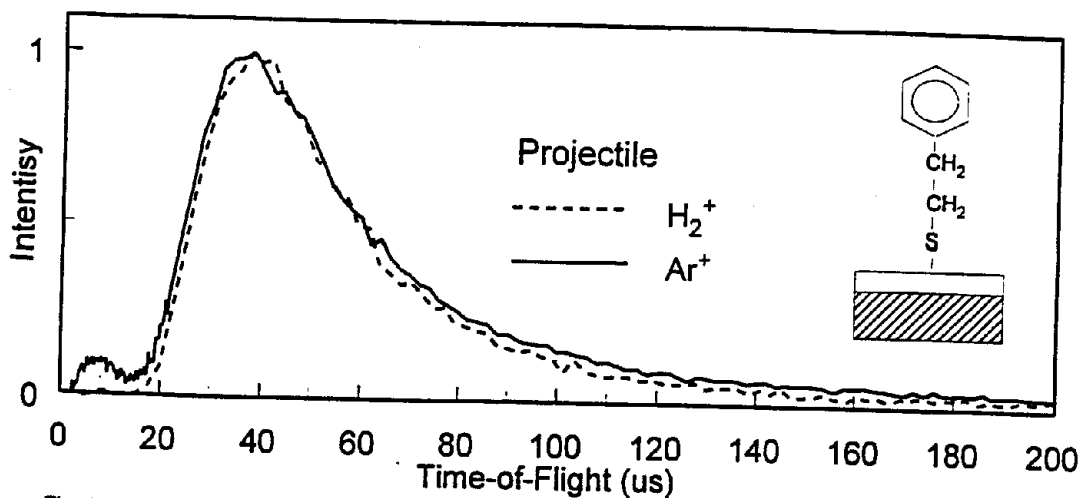


Fig. 1 Time-of-flight distributions of phenethylmercaptan subsequent to impact of H_2^+ and Ar^+ .

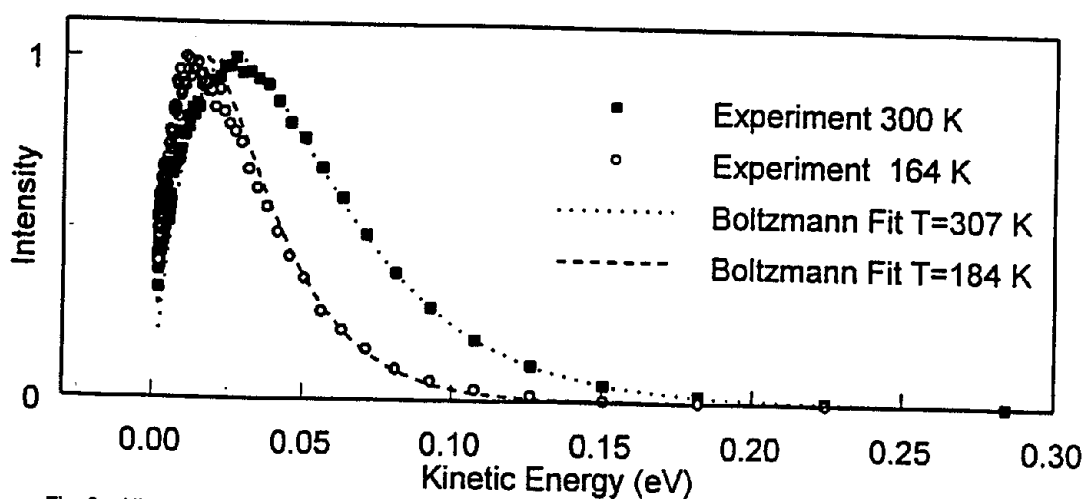


Fig. 2 Kinetic energy distributions of phenethylmercaptan at 300 K and 164 K shown with corresponding Maxwell-Boltzmann fit.

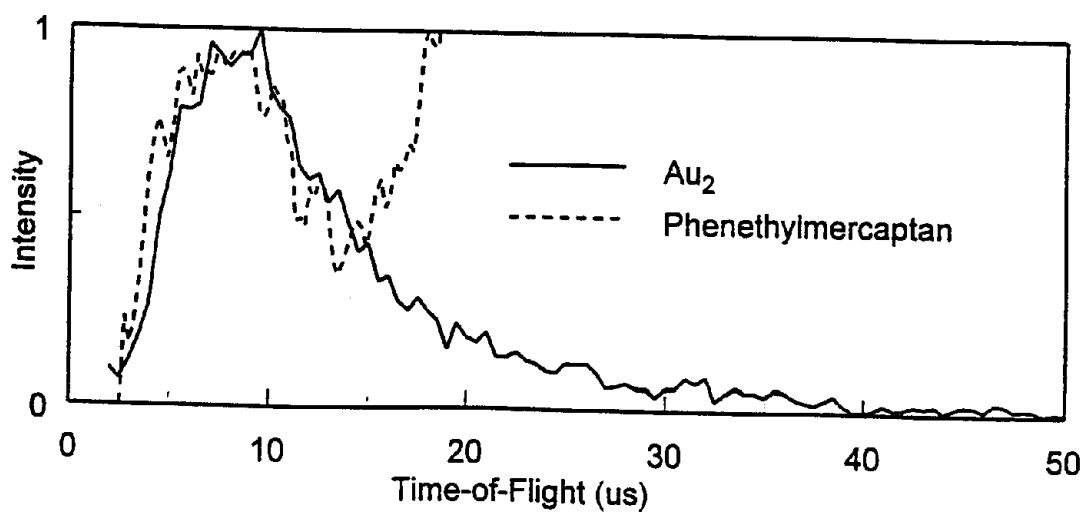
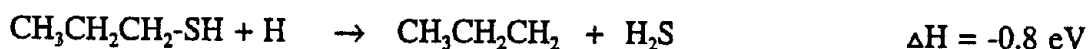
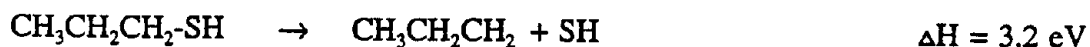


Fig. 3 The time-of-flight distributions for gold dimer shown with the high energy component of PEM.

may react with intact molecules to sever the surface bond. Bond cleavage by reaction will have a significantly lower energy deficit than direct bond scission and thus is more likely to form products with near thermal translational energies. Although thermochemical data for surface bound molecules are not available, estimates can be made using data for gas phase species. For example direct scission of a carbon sulfur bond is more than 3 eV endothermic, while cleavage by reaction with a hydrogen radical is mildly exothermic.[6]



While such a reaction, even if thermoneutral, may possess a reverse activation barrier of a few tenths of an eV, it is likely that a significant portion of this energy may be partitioned into the surface before separation.

Conclusion

The kinetic energy distributions of molecules desorbed from a self-assembled monolayer of phenethylmercaptan on gold have been measured subsequent to 8 keV bombardment with H_2^+ and Ar^+ . For both projectiles, the primary desorption event for neutral molecules appears to be evaporation. Specifically, the desorbed molecules have kinetic energies that can be fit by a Maxwell-Boltzmann distribution corresponding to the macroscopic temperature of the surface. These observations are consistent with surface bond cleavage via an ion beam induced chemical reaction. A small high energy component is present in the distribution of neutral molecules produced by the impact of Ar^+ . These high energy species have the same time-of-flight distribution as Au_2 which indicates that these molecules are sputtered ballistically and may leave the surface with one or more gold atoms attached.

Acknowledgements

The authors gratefully acknowledge the support of the National Science Foundation and the Office of Naval Research.

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