

Photoionization of Sputtered Neutrons with a VUV Free-electron Laser

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Introduction

The vacuum ultraviolet (VUV) represents the ultimate frontier in terms of photoionization, and techniques that rely on photoionization for the efficient detection of atoms, clusters, and molecules may work best in the 175- to 50-nm spectral region (photon energies corresponding to 7 to 25 eV). In this wavelength range, half of the elements and the majority of molecules may be ionized in a single-photon process. For molecules, this process has typically led to soft (i.e., low-fragmentation) ionization of the molecule, which is often desirable for quantification and identification purposes. For elements, a single-photon process is useful, since the cross section is usually very high and since saturation of the ionization may be readily achieved, simplifying measurement and standardization for quantitative work [1, 2].

To analyze the composition of materials containing elements with high first-ionization energies (C, N, O, P, Au, Be, B, Si, and many others), a focused ion beam can be used to sputter material from the sample, and this can be followed by single-photon ionization (SPI) with a VUV laser. Because there are few efficient VUV lasers and most of them are not tunable, the free-electron laser (FEL) that is operating at the APS and is tunable in this wavelength range is of great interest for these studies.

Methods and Materials

A state-of-the-art mass spectrometer named SPIRIT (stands for SPI or resonant ionization to threshold) is located at the end station of the low-energy undulator test line (LEUTL) FEL [3]. SPIRIT extracts photoions from relatively large volumes by using a unique push-pull ion optical system [4] that will ultimately allow for unprecedented trace measurements. Installation of SPIRIT was complete in November 2002, and commissioning continues. Experiments with the VUV beam from LEUTL are currently possible only during limited times defined by the non-top-up operation of the APS storage ring, when no training or injector studies are scheduled.

The experiment is initiated by a timing signal from the rf system. A primary ion pulse (or alternatively, a UV laser pulse) is fired at the sample, desorbing some

material from a microscopic part of the surface. After approximately 1 microsecond, the VUV pulse from the FEL arrives and passes through the expanding cloud of neutral atoms and molecules. Particular species are ionized, depending on their ionization energy (IE) and the wavelength of the VUV. Then the ions are extracted with a pulsed electric field and sent through a complex time-and-energy refocusing path to a detector. The time of flight determines the mass of the ion, and counting these ions gives the ultimate measurement of the precise composition of the sample.

Results and Discussion

Two studies are summarized briefly here. In the first, a pure gold target was sputtered with a 15-keV Ar⁺ beam to give predominately neutral atoms and gold clusters (Au₂, Au₃, Au₄, etc.) The VUV was tuned to two different wavelengths (157 and 127 nm) corresponding to energies below and above the IE of Au. The Au cluster species have lower IEs and also have considerable internal energy from the sputtering process, allowing them to be ionized from excited states with lower photon energies. Figure 1 compares the mass spectra from sputtered Au obtained with SPIRIT, showing that below the ionization edge (157 nm), Au₂ and Au₃ are predominant. The relatively small Au signal could be due to fragmentation of these clusters into atomic ions. Above the IE (127 nm), Au predominates, and while there is relatively little change in the Au₂ cluster yield, the Au₃ signal is decreased. The Au signal could be due to efficient ionization of sputtered Au atoms or due to fragmentation of the clusters as a result of accessing dissociative states during the ionization process.

In the second study, guanine (one of the DNA nucleobases) was crystallized in an α -CN-4-hydroxycinnamic acid matrix to form a sample. This sample was also sputtered with a 15-keV Ar⁺ beam. In Fig. 2, the bottom spectrum shows the direct ions from the sputtering pulse. There is a small signal indicating guanine, a guanine and Na⁺ adduct, and a few fragment ions (due to the breaking of chemical bonds in the molecule during either the desorption or ionization process). The top spectrum shows the identical experiment with the addition of the VUV FEL beam

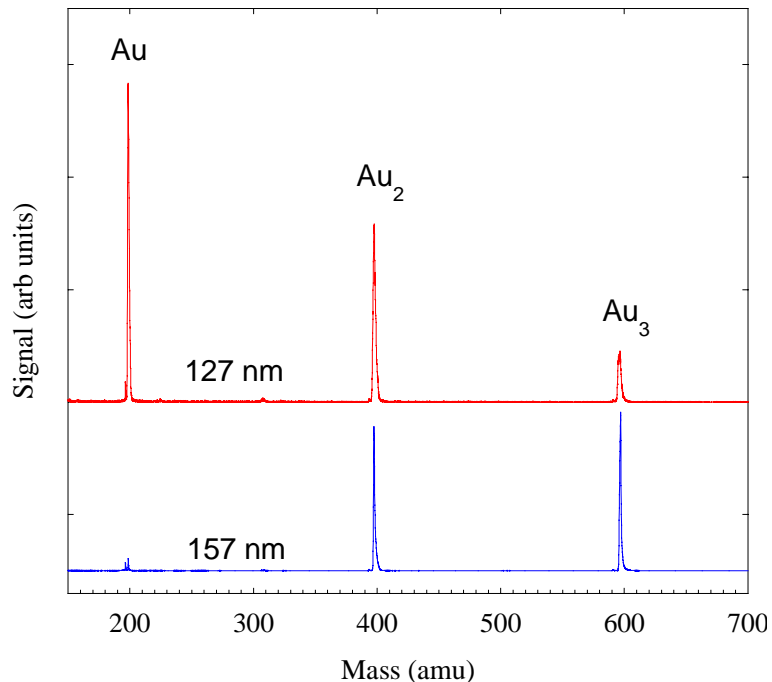


FIG. 1. Mass spectra showing the photoionization of sputtered gold at different VUV wavelengths. At 157 nm (bottom), the photon energy of 7.9 eV is insufficient to single-photon ionize Au atoms, but the clusters have lower IEs and greater internal energy and may be ionized. At 127 nm, there appears to be substantial SPI of Au atoms.

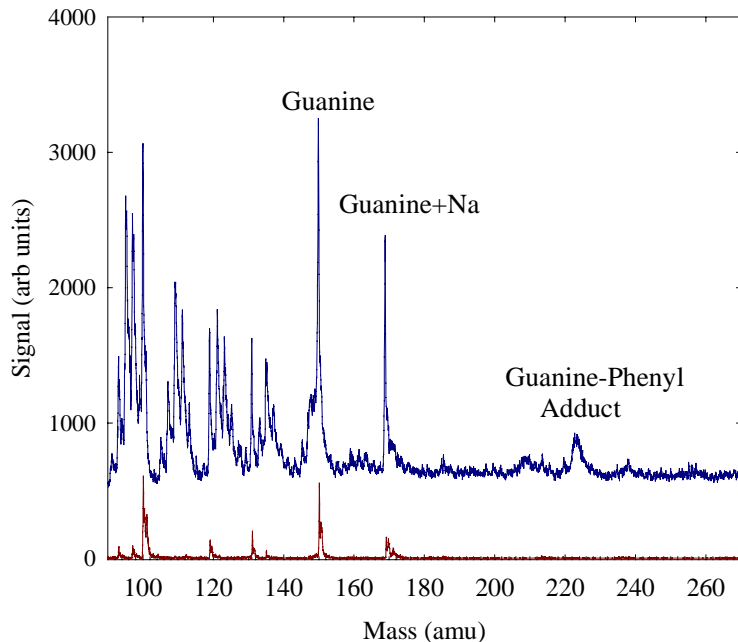


FIG. 2. Mass spectrum showing the secondary ion mass spectrum (SIMS, bottom) and VUV photoionization spectrum (top) for guanine in an acidic matrix. There is substantial gain in sensitivity shown for the photoionization, especially for the guanine-adduct species at the higher mass. This species is similar to carcinogen adducts that initiate some types of cancer. Spectra have been offset for clarity.

tuned to near 160 nm, which is above the IE for guanine. A signal that is at least five times greater exists in the guanine peak, and a much greater number of fragment ions can be observed. Further study is needed to confirm if these fragments are due to the breakup of the photoions or due to the desorption process. More significantly, there is now a substantial peak at a higher mass that is identified as a guanine-phenyl adduct that was not present before. Since gas-phase photochemistry can be clearly ruled out, this represents a significant improvement in the detectability of a molecular species, with important implications in cancer research.

Experiments in a number of different areas of science are continuing, along with improvements in the performance of SPIRIT and the FEL. Beam transport and diagnostic systems are also being improved. The user community has expressed substantial interest in turning the FEL into a full-time user facility, which is referred to as ALFF (Argonne Linear FEL Facility).

Acknowledgments

This work and the use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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