Development of High-pressure X-ray Photoelectron Spectroscopy (XPS) Unit

Omar Mussa
Environmental Sciences, University of California, Berkeley

Abstract

X-ray Photoelectron Spectroscopy (XPS) is a spectroscopic method that determines elemental composition of surfaces. XPS has traditionally been conducted under ultra high vacuum (UHV) conditions, however most of the important surface processes in the environment take place under non-UHV conditions. Therefore, an XPS unit capable of working under environmental conditions has now been developed. The XPS unit utilizes an electron lens system and differential pumping to extract electrons from a high-pressure cell and transfer them into an electron analyzer. The unit was tested with several sample and background-gas combinations. These combinations included N_2 with gold and H_20 with SiO_2. The spectra successfully created in these experiments show both the unit's functionality, and that high-pressure experiments should generate new understanding of surfaces in the environment. The high-pressure XPS unit will benefit environmental sciences by allowing molecular level understanding of surfaces found in the environment, such as minerals, and their interactions with atmospheric gases.

Introduction

Surface science investigates the chemical composition and properties of surfaces. Environmental surface science focuses on the study of surfaces, such as minerals, found in the environment (LefEvre *et al*. 1999). Recent development of environmental surface science experiments has been rapid. Over the past decade, there has been increasing effort to utilize synchrotron sites for environmental surface science. The synchrotron light source is advantageous to other X-ray sources because of its high resolution (Robinson 1997). X-ray fluorescence and absorption spectroscopy and microscopy are among the techniques used to study a diverse array of topics (Robinson 1997).

Some environmental surface science topics studied include observing environmental effects of latex paints (Sankar *et al*. 1990), performing surface analysis of airborne particles (Lazar *et al*. 1999) and investigating properties of metals after interaction with atmospheric gases (Ismail *et al*. 1996). These environmental studies are conducted under ultra high vacuum (UHV) conditions. UHV conditions are utilized for two reasons. First, the electrons must reach the detector and their mean-free path is short at high pressures. Second, the analyzers are designed to work under UHV conditions.

Electrons have a short mean-free path under atmospheric conditions. The mean free path is the average distance between collisions of randomly moving molecules and other molecules or walls (Resnick, 1992). The mean-free path of electrons in a gas depends on the pressure in the chamber. For example at a pressure of 1 Torr, 100 eV electrons will travel 1 mm. Under vacuum conditions, the mean-free path increases. UHV chambers ($\sim 10^{-9}$ Torr) help maximize the mean-free path so that a high number of electrons will reach the detector/analyzer. As fewer electrons reach the analyzer, the signal/noise ratio decreases making it impossible to analyze the spectrum produced. This constraint makes UHV the standard environment of X-ray Photoelectron Spectroscopy (XPS) experiments (Briggs & Seah 1990).

XPS is a powerful surface analysis technique. Soft x-rays ($\lambda < 3$ nm) are focused onto a sample and the electrons emitted from the sample are sorted by energy (Wagner *et al*. 1979). XPS is used in surface science because it is surface specific and has high sensitivity (Robinson 1997). XPS is surface specific because only electrons from the surface are analyzed. In a solid, electrons have a short mean free path so only electrons originating from the top few atomic layers are detected. XPS has a high sensitivity to the elements present (Wagner *et al.* 1979). XPS can also detect chemical states because each chemical bond causes a change in electrostatic potential as valence electron charge density changes in an atom (Briggs & Seah 1990).

XPS is used to identify the elements on a surface, using the conservation of energy equation: $BE = h\nu - KE$, where BE is the binding energy, $h\nu$ is the energy of the incident photon beam and KE is the kinetic energy of the emitted electrons (Briggs & Seah 1990). Each element has a different binding energy (BE), which is the ionization energy of the atom at a particular shell (Wagner *et al.* 1979). If the energy of the incident photon beam is larger than the BE, electrons are emitted. Since the energy of the incident beam is known and the KE is detected experimentally, the BE can be determined. The KE of the electrons can be identified using an electron analyzer, which scans energies and counts the number of electrons detected.

The UHV environment represents deep space conditions that are not present within Earth's atmosphere. For instance, the equilibrium vapor pressure of water at 10°C is ~10 Torr and thus wet samples cannot be maintained at room temperature using traditional UHV methods (Briggs & Seah 1990). Therefore, a new XPS tool was designed to overcome the UHV constraint on surface science techniques. The benefits of creating such a device include the capability to study liquid substrates and the ability to simulate atmospheric and environmental conditions that exist on Earth.

The "high-pressure" chamber is designed to work at up to 10 Torr of pressure. This is much higher than traditional XPS chamber pressures and allows for investigation of wet samples at temperatures of up to 10 ºC. Differential pumping stages allow the sample to remain at environmental pressures, while maximizing the mean free path of emitted electrons, so they can reach the detector. Additionally, voltages are applied to electrostatic lenses in the unit to accelerate and focus the electrons onto the focal plane of the electron energy analyzer. The detector is a standard hemispherical electron energy analyzer and must remain in vacuum to function.

The high pressure XPS unit is shown in Figure 1. A thin SiN_x membrane (120 nm thickness) separates the high pressure in the sample cell from the vacuum in the main chamber. The beam enters the sample cell through the SiN_x window, which is transparent for

X-rays. The beam strikes the sample surface at a 15° angle. A manipulator allows for the adjustment of the distance between the sample and the first lens. The first lens extracts emitted electrons. The lens is an electrostatic cone shaped nozzle that can be positively charged to accelerate electrons. Due to the small aperture of the nozzle (0.9 mm diameter), the lens also provides for differential pumping. The small aperture prevents a large airflow from filling the next volume in the chamber. The pressure between the sample cell and the volume behind the first nozzle is reduced by approximately a factor of 1000. After an electron passes through the first nozzle there is a second electrostatic nozzle, which also provides for differential pumping (1.5 mm diameter), that the electron passes through. Passing through the second lens, an electron enters a third volume at a lower pressure. On their way to the focal plane of the analyzer, the electrons pass an electrostatic quadrupole, a set of four metal plates that form a cylindrical shape, which helps steer electrons into the focal point of the electron analyzer. The electron analyzer operates at pressures up to 10^{-7} Torr, making the pressure change from the sample cell to the analyzer approximately seven orders of magnitude.

Differential pumping maintains the pressure ratios between the different volumes in the chamber constant. Three high-speed turbo pumps, operating at 56 krpm, are connected to different sections of the chamber. The pressure of the sample cell can be manipulated by changing the flow rate of the gas being pumped into the cell.

This high-pressure XPS unit has been tested in several experiments to provide a proof of principle by generating spectra that identify the composition of a known surface in the presence of a gas. This paper reviews the performance of the device in these tests and the unit's potential for future applications.

Methods

The unit utilizes new and untested methods for obtaining spectra. This makes it necessary to provide a proof of principle in this experiment. Testing the unit employed changing the background pressure of homogenous gases and determining their effect on the spectra. Influences on the electrons' mean-free path, based on the electron yield in the analyzer, were also recorded.

The first test involved a gold sample in the presence of nitrogen gas (N_2). N_2 is the most abundant gas in the atmosphere. Gold has characteristic 4f doublet peaks (BE 86 and BE 84, 4th orbital). This makes gold a good sample to use for reference in our proof of principle experiment (Wagner *et al.* 1979). N_2 is inert (unreactive) and should not alter the surface. This test is designed to show that the unit can perform normal XPS functions (can generate a spectrum), and that it works under high pressure. The sample was tested in UHV and at 1.5 Torr of N_2. A piece of gold foil was placed on the sample holder and N_2 was pumped into the sample cell. Different voltages were applied to the lenses until the signal was maximized. Spectra were then obtained from the analyzer.

The second test involved testing silicon oxide (SiO_2) in a water vapor environment. SiO_2 is abundant in rocks and minerals. A silicon wafer, which immediately oxidizes in air, was placed on the sample holder. Voltages were applied to the electrostatic lenses until the signal was maximized. Water vapor was pumped into the cell and the pressure of the vapor in the cell was increased over time. Spectra were obtained in intervals, at increasing pressures, after the pressure was stabilized at a specific pressure level. SiO_2 and water vapor form XPS peaks that are well separated from each other (~3 eV), which allow distinguishing the surface signal from the gas phase signal.

Results and Discussion

The result of nitrogen gas on gold experiment is shown in Fig.2. One scan was performed in vacuum conditions, and another scan was done at high pressure (1.5 Torr). A spectrum was successfully produced in each scan. The gold doublet peak at BE 84 eV was observed in both scans. Since the signal is weaker at higher pressures due to the shortened mean free path of electrons, the high-pressure scan is multiplied by a factor of 25 for comparison with the vacuum scan (Fig. 2). The spectra show that the high-pressure XPS setup is indeed able to obtain spectra at pressures above 1 Torr, a result that has never been achieved before.

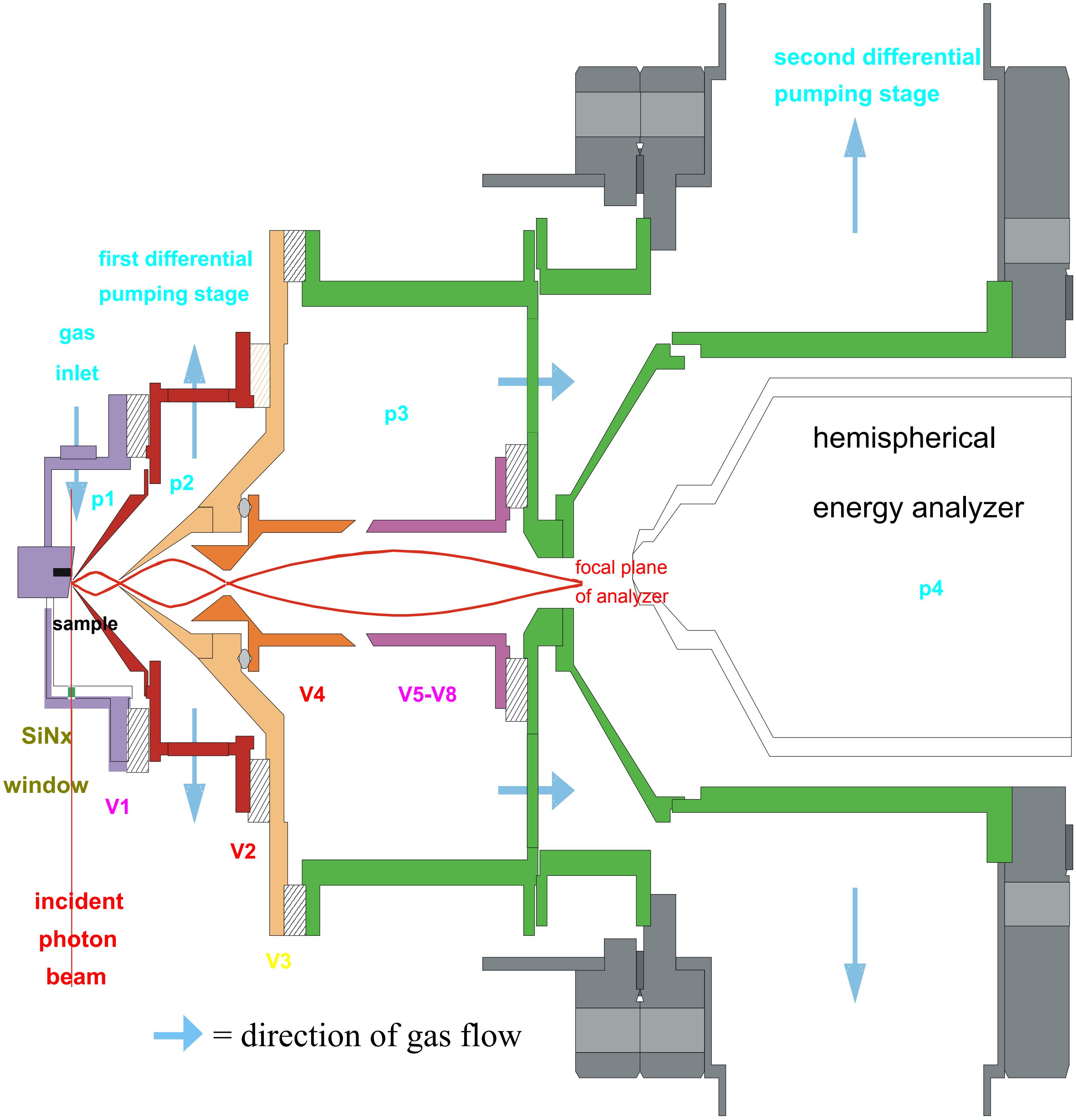
Water vapor on SiO_2 experiments have been performed, results are shown in Fig. 3. In order to increase the influence of the gas phase pressure on the signal from the surface, multiple scans were performed under increasing gas pressure. The signal generated decreased exponentially as the pressure increased (Fig. 4). As the pressure increased, the surface peak decreased due to the reduced mean free path of electrons in gas. Thus, the presence of water vapor in the chamber reduced the SiO_2 signal. Simultaneously, the water vapor peak increased in intensity. This signifies that the water vapor is masking the surface signal. This experiment shows that gas phase oxygen and surface oxygen signal are detected at different BE, which is important for distinguishing the gas phase sample contributions to the spectra.

The unit was successful in obtaining spectra from conducting surfaces. The next goal of the experiments is to scan insulators such as salts and ice. In the future, this unit could help bridge synchrotron physics to numerous environmental sciences.

Environmental Importance

The development of the high-pressure unit will be a significant advancement helping to further *in-situ* environmental surface science. Currently, a few environmental studies utilize XPS techniques such as for the identification of toxic elements of samples extracted from the environment (Brami *et al*. 1999). These (*ex-situ*) experiments generally utilize environmental samples that can be extracted from multiple time frames, such as sedimentary layers, and extrapolate which reactions must have occurred through time (Schreiner *et al.* 1999).

Molecular characterization of surface interactions under environmental conditions can give us a better understanding of the environment. Already, paleoclimatology, chemistry and some ecological fields have been furthered through studying environmental samples under UHV conditions. The experiments that have been used are particularly powerful in studying surfaces extracted from specific environments. With the development of the high-pressure XPS unit, experiments can now model environmental conditions that currently exist, may have existed, or may exist in the future in a simulated environment. For example, the interaction of greenhouse gases, such as carbon monoxide gas (CO) with environmentally relevant surfaces can now be examined. A practical experiment might study a trace metal catalyst found in catalytic converters, such as Rhodium, and determine how the interaction of NO and CO will influence the performance of the catalytic converter.



Lens system design: Gennadi Lebedev, GETOM, Petaluma, CA.

Figure 1- High-pressure XPS Unit: This figure shows the electron lens and differential pumping system. This unit is capable of obtaining spectra at up to 10 Torr of pressure. The pressure ratio of p1:p2:p3:p4 = $1:10^{-3}:10^{-5}:10^{-7}$. The voltages applied to V1-V4 range from 0-5000V. V5-V8 are applied to the quadrupole and range from 0-500V.

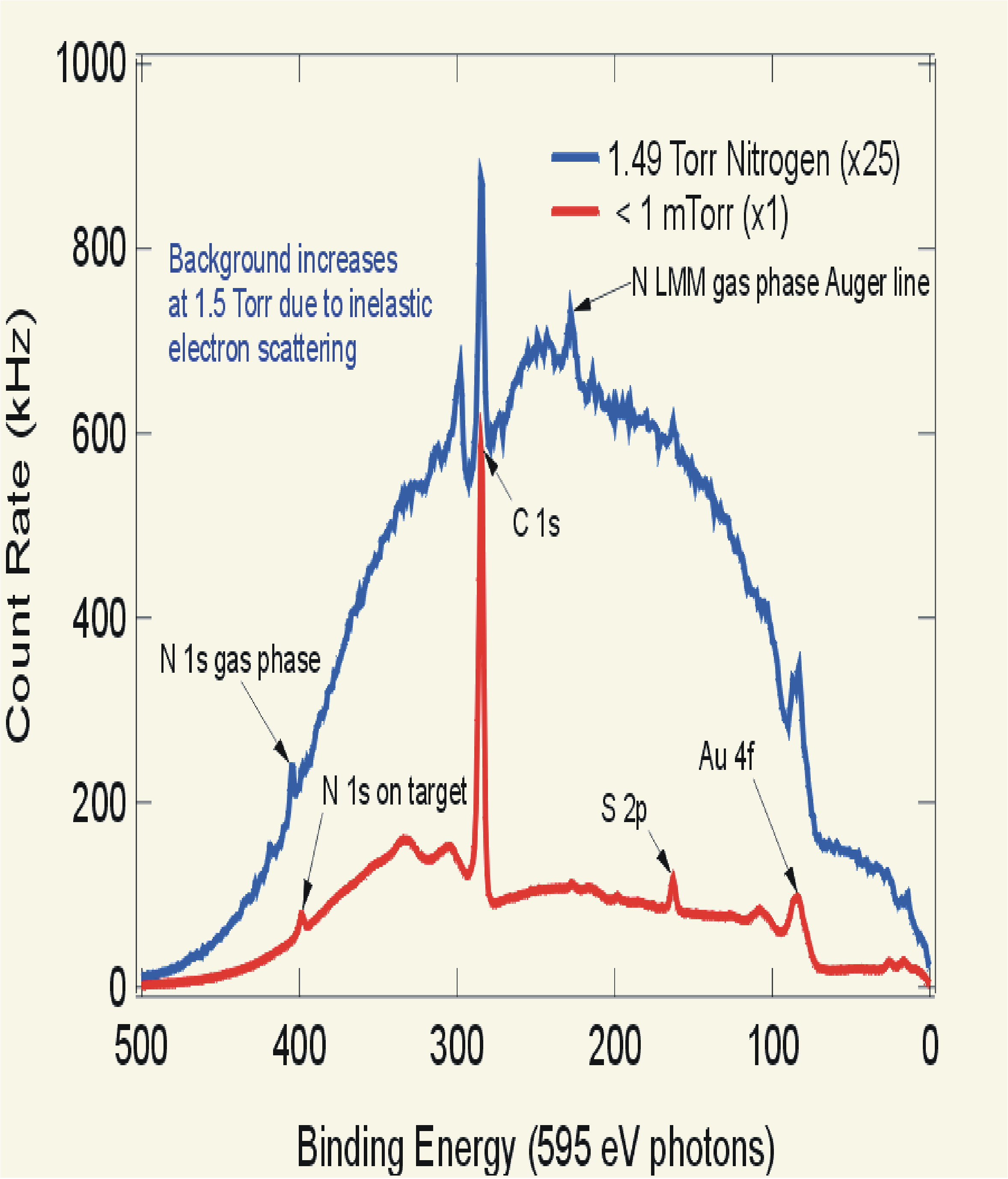
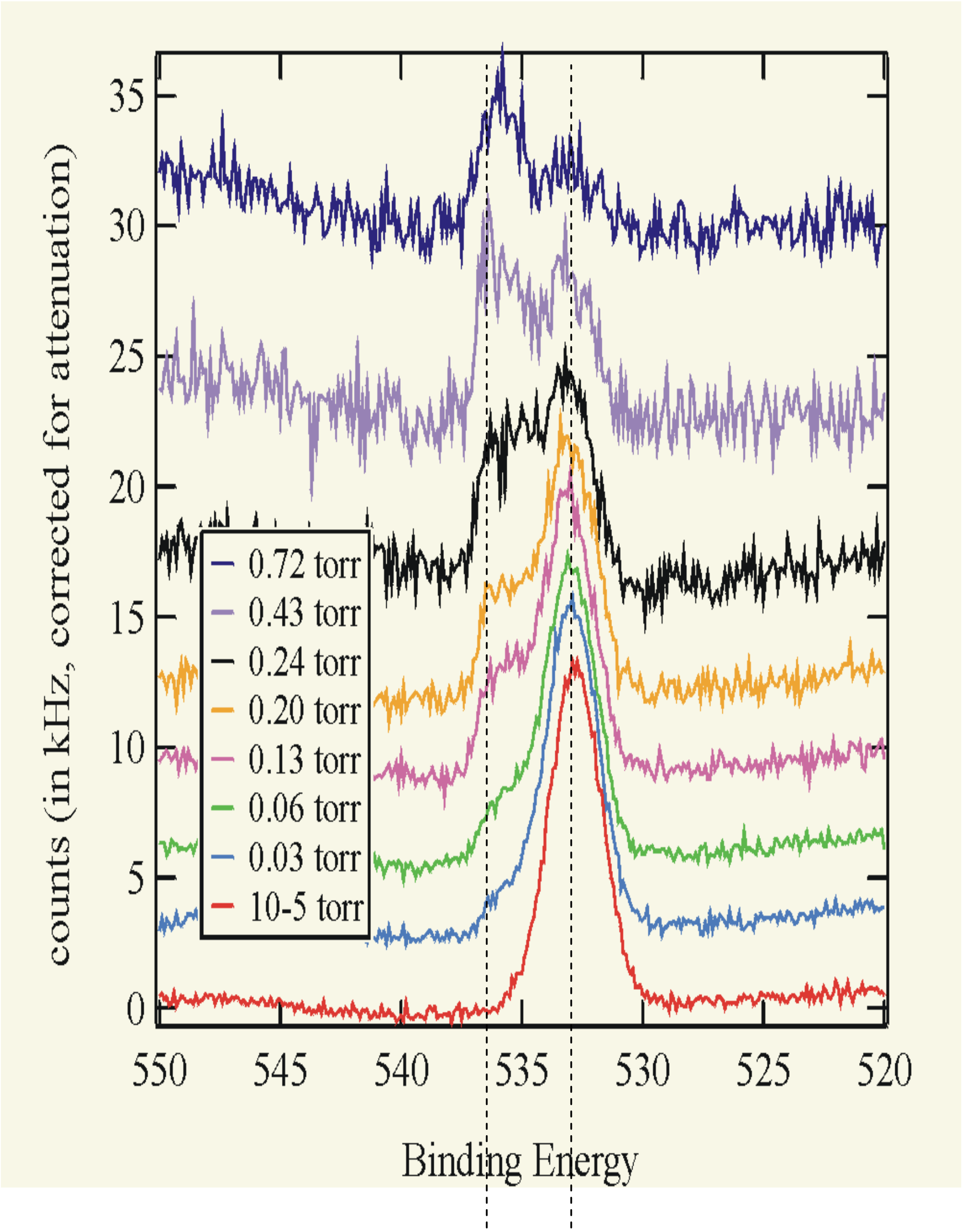


Figure 2- XPS at Torr Pressures: This graph compares the difference between spectra produced in vacuum (bottom) and at high pressure (1.49 Torr N_2). N_2 is inert and does not react with the sample. The gold peak at 84 BE is visible on both spectra showing that the unit is capable of identifying elements using standard XPS procedures. The gold doublet was not resolved due to the broad range of the scan.



Gas phase water peak

Silicon oxide peak

Figure 3 - XPS at Torr Pressures: Changing the water pressure in the chamber influences the spectrum produced. At lower vapor pressures, there is a large silicon oxide (SiO_2) peak. As the water pressure increases, the SiO_2 peak decreases while the water vapor peak increases. This Graph shows that it is possible to differentiate the gas phase water peak from the surface oxygen molecules.

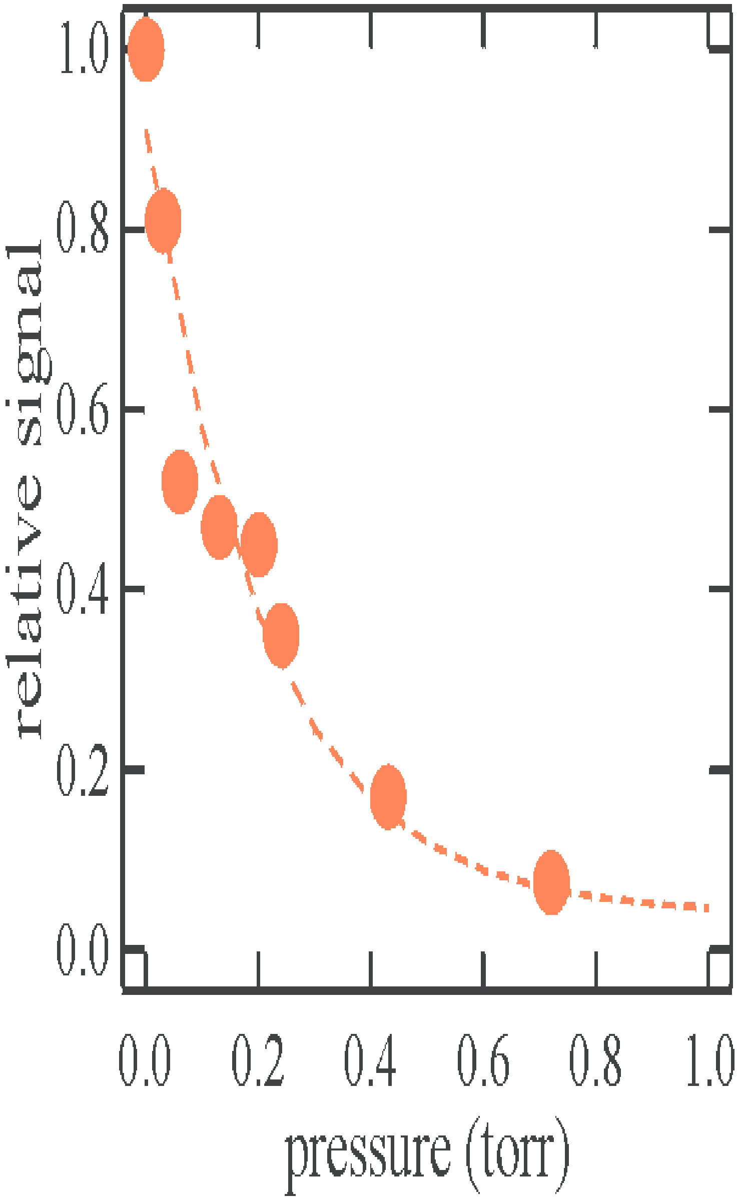


Figure 4 – Signal vs. Pressure: The XPS signal decreases exponentially as the pressure increases. This makes it increasingly difficult to obtain spectra at higher pressures. In order to obtain spectra at higher pressures, differential pumping, electrostatic lenses and large voltage potentials are required to extract electrons into the analyzer.

Acknowledgements

I would like to thank my friends at the ALS: Hendrik Bluhm, Alfred Huan, and Frank Ogletree for their help and patience. I would also like to thank my ALS supervisors Zahid Hussain and Miquel Salmeron. Finally, I would like to thank Tom Dudley for his support and guidance throughout this project.

References

Brami, Y., B. Herut, A. Shemesh, H. Cohen. 1999. Surface chemical characteristics of coal fly ash particles after interaction with seawater under natural deep sea conditions. Environmental Science and Technology 33: 276-281.

Briggs, D. and M.P. Seah. 1990. Practical Surface Analysis, Second edition, Vol. 1. Auger and X-ray Photoelectron Spectroscopy. John Wiley & Sons, Chichester, England.

Holman, Hoi-Ying N., M.C. Martin, G.M. Lamble, W.R.McKinney & J.C. Hunter-Cevera. 1999. Real-time Characterization of Biogeochemical Reduction of CR(VI) on Basalt Surfaces by SR-FTIR Imaging. Geomicrobiology Journal 16: 307-324.

Ismail, Hamdy M., Cadenhead, D.A., & M.I. Zaki. 1999. Surface Reactivity of Iron Oxide Pigmentary Powders toward Atmospheric Components:XPS and Gravimetry of Oxygen and Water Vapor Adsorption. Journal of Colloid and Interface Science 183: 320-328.

Lazar, A., Reilly, P.T.A., Whitten, W.B., & J.M. Ramsey. 1999. Real-time surface analysis of individual airborne environmental particles. Environmental Science and Technology 33: 3993-4001.

LefEvre, G., M. Alnot, J.J. Ehrhardt & J. Bessiere. 1999. Uptake of Iodide by a Mixture of Metallic Copper and Cupric Compounds. Environmental Science and Technology 33: 1732-1737.

Resnick, R., D. Halliday, K.S. Krane. 1992. Physics, Volume 1 Fourth Edition. John Wiley & Sons, INC., New York. 427, 533 pp.

Robinson, Arthur L. 1997. Soft X-ray Spectromicroscopy: Materials Characterization on a Microscale. Advanced Light Source and Department of Energy Publication 786: 9-18.

Sankar, S.S., Schadt, R., Fornes, R.E., & R.D. Gilbert. 1990. Environmental effects on latex paint coatings 2 CP MAS C-13-NMR and XPS investigations of structural changes in the base polymer. Journal of Applied Polymer Science 41: 1251-1260.

Schreiner, M, Woisetschlager, G, Schmitz, I, & M. Wadsak. 1999. Characterisation of surface layers formed under natural environmental conditions on medieval stained glass and ancient copper alloys using SEM, SIMS and atomic force microscopy. Journal of Analytical Atomic Spectrometry 14: 395-403.

Wagner, C.D., W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg. 1979. Handbook of X-ray Photoelectron Spectroscopy. Perkin-Elmer Corporation, Minnesota. 4,5 pp.