

# Electronic and Geometric Structure of Pu Compounds: A High-Resolution Photoelectron Spectromicroscopy Study

J. Terry<sup>1</sup>, R. K. Schulze<sup>1</sup>, M. Neu<sup>1</sup>, J. D. Farr,<sup>1</sup> K. Heinzelman<sup>2</sup>, and E. Rotenberg<sup>2</sup>

<sup>1</sup>Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

<sup>2</sup>Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, USA

## INTRODUCTION

There is a great need to study the interactions of Pu species with solid surfaces. Knowledge of these fundamental interactions is critical to the understanding of a variety of processes in the areas of environmental and nuclear materials, including sorption reactions of Pu species from solution onto mineral grain surfaces in an environmental setting; interactions of Pu compounds in waste and process streams with contacting surfaces; and surface reactions of Pu at phase boundaries in actinide materials systems. Furthermore, studies of these reactions will allow us to extend the understanding of the chemistry in these strongly f-electron dominated systems. This is critical, as it is one of the unique challenges in chemistry and materials science at our national laboratories, as exemplified by the greater than \$25M annual budget of the nuclear waste programs at Los Alamos National Laboratory.

These experiments described below investigated the oxidation states of plutonium in molecular solids using photoelectron spectroscopy and the interactions of these molecular compounds with well characterized model environmental surfaces. Chemical shifts in photoemission spectra have long been used to identify the oxidation states of atoms in chemical compounds. Very simply, these chemical shifts depend upon the amount of charge transfer between the emitting atom and its ligands. Lower oxidation states have smaller chemical shifts than do higher oxidation states with respect to the neutral atom. Determination of the oxidation state of an actinide can be made by measuring the chemical shift of the photopeaks from an actinide compound and comparing the shifts to appropriate standards. Unfortunately, a detailed tabulation of chemical shifts is presently not available for the actinides. Our first measurements at the Spectromicroscopy Facility at Beam Line 7.0.1 involved the measurement Pu in oxidation states of III, IV, V, and VI. Core Level and Valence Band Photoemission spectra were measured to probe the occupied electronic structure of the f electrons in plutonium. Pu 5d NEXAFS spectra were also collected in order to study the unoccupied 5f electrons of Pu. Core Level photoemission spectra were taken from the constituents of the ligands.

The sorption of actinides on to silica and brucite was also studied using photoelectron spectroscopy. Oxidation states of the adsorbed actinide compounds will be determined by comparison of the observed chemical shifts with those from the standards described above. In the determination of oxidation state, photoelectron spectroscopy has a clear advantage over near edge X-ray absorption fine structures spectroscopy (NEXAFS) measurements performed with hard X-rays. The features assigned to different oxidation states of the same element often overlap in NEXAFS spectra making determination difficult, while the chemical shift information in photoemission spectra is usually easily resolved. This feature of the photoemission spectra will allow us to determine if Pu species adsorb in multiple oxidation states or in a single favored oxidation state.

## RESULTS

Pu 4f core level spectra were collected from various Pu molecular compounds with Pu in oxidation states ranging from III to VI. There were some difficulties with differential charging as these

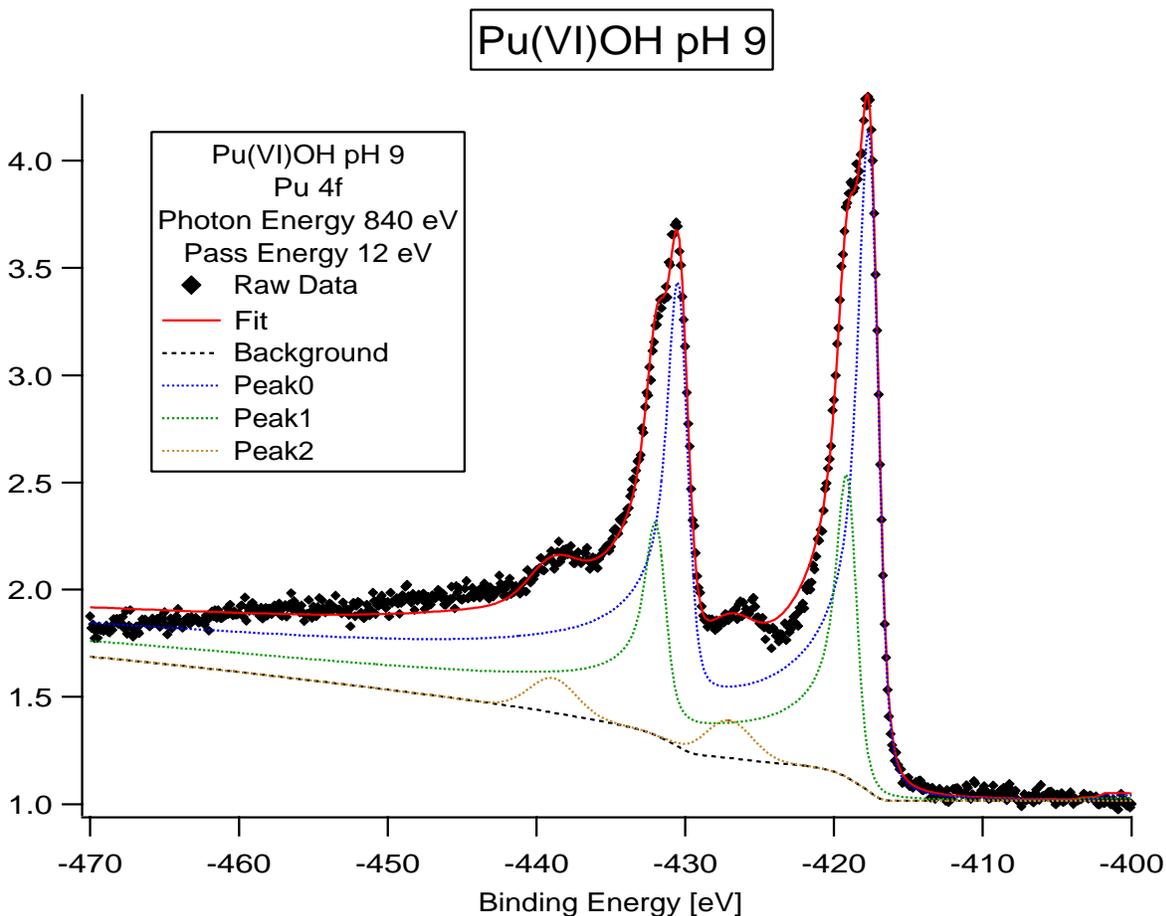


Figure 1: The Pu 4f core level spectrum from plutonium(VI) hydroxide is shown. This spectra was decomposed into 3 spin-orbit split components. The two components at binding energies of 417 and 419 eV indicated that two chemical states of plutonium were present. The third doublet at a binding energy of 428 eV is a satellite state known to occur whenever the plutonium(IV) state is measured.

samples were non-uniform pressed powders. We will only show here spectra (Figure 1) collected from Pu(VI)OH crystallized at a pH of 9. Three components were observed in the spectrum. A satellite structure characteristic of Pu(IV) was observed. The Pu 4f spectra did not change as a function of time and as such did not suffer from beam related damage. This indicates that during shipment some fraction of the samples was converted into Pu(IV).

These spectra were deconvolved using 2 Doniac-Sunjic lineshapes and with a Gaussian component representing the satellite. The average FWHM of the peaks was 1.33 eV. To our knowledge, these are the sharpest core level spectra observed for Pu compounds. These spectral lines were about half the width of peaks typically measured in an XPS system at Los Alamos National Laboratory. These spectra then allow us to estimate the natural linewidth of the Pu 4f core level.

Pu 4f core level spectra were collected from Pu sorbed onto silica, brucite, and MgO from solutions containing Pu(III to VI). This data is not shown here. The data suggests that Pu may sorb into a preferred oxidation state.

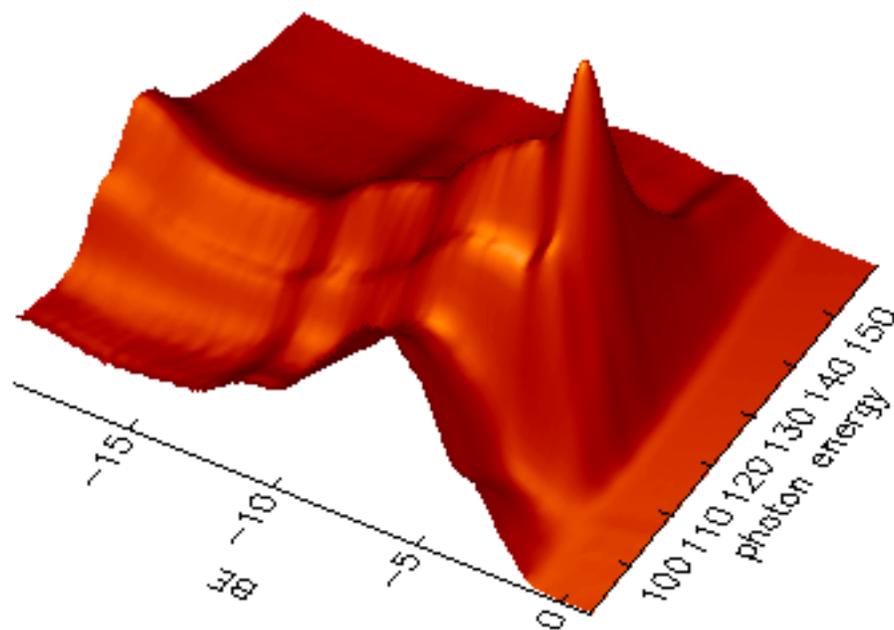


Figure 2: Resonant Photoemission data from Pu(VI) sorbed on SiO<sub>2</sub>.

Resonant photoemission spectra were collected of the 5d-5f resonant transition from the above materials. This transition allowed us to directly measure the 5f density of states in the valence band. Resonant photoemission data from Pu (VI) sorbed on silica is shown in Figure 2.

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Principal Investigator: Jeff Terry, Los Alamos National Laboratory. Email: [jterry@lanl.gov](mailto:jterry@lanl.gov). Telephone: (505) 665-9975.