Applied Surface Science
Room 209 B W - Session AS-TuA

Theory and Data

Moderators: Steve Consiglio, Tokyo Electron, **Jeffrey Terry**, Illinois Institute of Technology

2:15pm **AS-TuA-1 Distinguishing the XPS of Surface and Bulk Atoms*, Paul S. Bagus,*** University of North Texas*; Connie J. Nelin,* Consultant **INVITED**

Shifts in XPS binding energies (BEs), which reflect changes in the BE of an element in different environments within a given sample, have been extensively studied through both experimental measurements and theoretical approaches. These shifts are expected to provide insights into the physical and chemical properties of a system. To better understand the relationship between BE shifts and the properties of the ionized atom, we examine the mechanisms responsible for surface core level shifts (SCLSs). These shifts represent the differences between the BEs of surface atoms and bulk atoms. We will discuss the key mechanisms relevant to metals and ionic compounds (such as oxides), focusing on their similarities and differences. In particular, we will identify and distinguish the contributions of atomic charge and environmental factors - especially coordination and atomic distances - to the SCLS. One of the primary objectives is to establish the expected magnitudes of these shifts. The presented SCLS values are derived from ab initio wavefunctions for cluster models of the studied materials. Finally, we will compare the theoretical results with available experimental data to assess the accuracy and validity of the theoretical predictions.

2:45pm **AS-TuA-3 Theory as a Guide to Electrocatalysis: An Experimentalist's Point of View*, Jeffry Kelber,*** University of North Texas **INVITED**

In situ and *operando* XPS – in concert with experimental electrocatalysis and absorption spectroscopy – provide detailed understanding of interactions at the electrolyte/solid interface regarding studies of N_2 and nitrate reduction to NH_3 (NRR and NO_3RR, respectively). In such work, Hartree-Fock (HF)-based cluster calculations have provided specific interpretations of experimental near-ambient pressure XPS spectra, leading to important conclusions regarding the significance of stabilizing vanadium oxide cation surface sites in V(+3) oxidation states for NN and NO bond activation. DFT-based calculations have been critical in interpreting electrochemical and XPS data regarding NRR and NO_3RR reaction mechanisms – including the absence of the widely-supposed Mars van Krevelen mechanism in transition metal oxynitrides. Such DFT-based studies have also provided broad insight concerning catalyst reaction mechanisms, as well as the potential catalyst selectivity for, e.g., NRR vs hydrogen evolution. Thus, computational studies have served to not only better understand experimental results but also served as a strategic guide to future experimental studies.

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3:15pm **AS-TuA-5 Fourier Denoising of XPS Data: An Algorithm for Automating the Identification of the Cutoff of the Gauss-Hermite Filter in Reciprocal Space and Feature Identification in XPS Spectra*, Alvaro J. Lizarbe,*** *Matthew R. Linford, Kristopher S. Wright, Garrett Lewis,* Brigham Young University*; David E. Aspnes,* North Carolina State University*; David J. Morgan,* Cardiff University, UK*; Mark Isaacs,* University College London*; Jeff Terry,* Illinois Institute of Technology*; Stanislav Průša,* Brno University of Technology

Introduction

Especially in X-ray Photoelectron Spectroscopy (XPS), large amounts of data and information are collected in its various modes that include imaging, depth profiling, stability, and operando studies. We recently published a paper[1] introducing Fourier analysis with a Gauss-Hermite filter function as a way to denoise X-ray Photoelectron Spectroscopy (XPS) data. While we always advocate for high quality data to be collected, Fourier analysis offers ways to improve collected data when the best possible signal-to-noise ratios cannot be obtained. Imperfect data are commonly obtained in sample damage studies due to changes in the sample, when elemental concentrations or low, when weak photoemission cross sections (seen in HAXPES) exist, when large numbers of spectra are collected in imaging studies, or when there is limited instrument time available. In such cases, Fourier analysis offers a mathematical approach to reduce noise and enhance signal quality, making it a valuable tool for XPS data analysis. We recommend that the original and smoothed data always be shown together. The Gauss-Hermite filter is a type of low-pass filter that applies a gradual, sigmoidal cutoff to low and high frequencies, allowing for a smooth transition between noise and signal. Currently, the position of this cutoff is adjusted manually by the analyst.

Work to be Presented.

The user must select the cutoff for the Gauss-Hermite filter we use to Fourier denoise XPS data. While the approximate location for this cutoff is generally clear from the shape of the Fourier coefficients in reciprocal space, it would be advantageous to be able to automate this process. In this talk, we describe an algorithm that successfully identifies the cutoff for the Gauss-Hermite filter, which should make this general approach to data denoising more widely applicable. This cutoff is based on statistical analyses of the fits. As a useful expansion to this capability, we show how this general approach can be applied when a high-order polynomial is used to fit carbon Auger data for D-parameter calculations.[2]

(1) Lizarbe, A. J.; Wright, K. S.; Lewis, G.; Murray, G.; Austin, D. E.; Terry, J.; Aspnes, D. E.; Linford, M. R. The case for denoising/smoothing X-ray photoelectron spectroscopy data by Fourier analysis. *J. Vac. Sci. Technol. A* **2025**, *43* (3). DOI: 10.1116/6.0004167

(2) N. Fairley, G. Compagnini, V. Scardaci, J. Baltrus, A. Roberts, A. Barlow, P. Cumpson and J. Baltrusaitis, Surf. Interface Anal. 55 (3), 165 (2023).

4:00pm **AS-TuA-8 Fourier Denoising of XPS Data: Application of the Gauss-Hermite Filter Function to Carbon Auger D-Parameter, HAXPES, and LEIS data, and an Improved Algorithm for Reducing End-Point and Slope Discontinuity Artifacts*, Matthew R. Linford,*** *Alvaro J. Lizarbe, Kristopher S. Wright, Garrett Lewis,* Brigham Young University*; David E. Aspnes,* North Carolina State University*; David J. Morgan,* Cardiff University, UK*; Mark Isaacs,* University College London, UK*; Jeff Terry,* Illinois Institute of Technology*; Stanislav Průša,* Brno University of Technology, Czechia

A general trend in surface and material characterization is the collection of larger amounts of data and information. In X-ray photoelectron spectroscopy (XPS), large numbers of spectra are often collected in imaging, depth profiling, damage, and operando studies. These large quantities of data present challenges to the analyst who always has limited time for data analysis. Accordingly, mathematical tools for XPS data analysis should become more relevant and important, not less. We recently presented the case for the Fourier denoising of XPS data (Lizarbe, A. J.; Wright, K. S.; Lewis, G.; Murray, G.; Austin, D. E.; Terry, J.; Aspnes, D. E.; Linford, M. R. *J. Vac. Sci. Technol. A* **2025**, *43* (3)). The highest quality data should be collected whenever possible, and mathematical 'tricks' aren't, in general, a viable way to clean up extremely poor data. However, it's not always possible to collect data with the best possible signal-to-noise ratios. Imperfect data are often collected, when an element or chemical state of an element is present at a very low concentration, when cross section for photoemission is low, like in HAXPES, when many spectra must be collected in a short period of time, as in imaging studies, or when instrument time is simply expensive. For these reasons, noise removal from adequate data has a place in XPS data analysis. We showed that the traditional Savitzky-Golay and Boxcar smooths are lacking in their ability to successfully remove noise from data. These deficiencies, when observed in reciprocal space, demonstrate that these common smooths don't fully remove noise (high frequencies) from XPS data. A better approach to XPS data smoothing is with the Gauss-Hermite filter, which is applied in reciprocal space and has a sigmoidal shape. Below a user-selected cutoff, it preserves all the low-frequency information in a spectrum (low-index Fourier coefficients, signal), while removing high-frequency information.

In this talk, we describe an extension of these approaches to calculating the carbon Auger D-parameter and to smoothing HAXPES data. In addition, we show Fourier smoothing of data from a different technique: low-energy ion scattering (LEIS) data. LEIS spectra can present a challenge to data analysis because of their high sputter backgrounds at low energies. Finally, because numerical artifacts are introduced by Fourier denoising when there are end-point or slope discontinuities in the data, we show an improved algorithm for Fourier denoising via the Gauss-Hermite filter. This approach uses an improved function over what is currently in the software, which substantially reduces the current slope discontinuity in the current procedure.

4:15pm **AS-TuA-9 Identification of Materials from TOF SIMS Spectra via Machine Learning**, ***Lev Gelb***, *Amy Walker,* University of Texas at Dallas

We present progress towards analysis of TOF SIMS data using machine learning (ML) methods. We posit that TOF SIMS is not more widely used because the data is complex and hard to interpret without expert knowledge, and investigate how machine learning might help. We primarily train models on simulated "big" data sets constructed by combining and modifying experimental spectra, with a focus on neural-network (NN) architectures.

Two applications are considered: identification of (presumed) homogeneous samples (which could be even a single pixel in a TOF SIMS image), and separation of multicomponent mixtures. In both cases, the sample consists of compound(s) which appear in some reference library, which is the basis for training. Complicating factors include statistical noise, background, calibration errors, and the likely case that the reference spectra were not taken under exactly the same conditions (primary ion, ion energy, instrument manufacturer, etc.) as the data to be analyzed.

In the first application, we focus on the extent to which improved spectral resolution helps (or hinders) analysis, the effect of reference library size on model performance, the effects of background counts and contamination by other species, and ways to have the model indicate that the sample is *not*described in the library. The NN approach is also compared with more straightforward spectral overlap-based methods and alternative machine-learning algorithms.

In the second application, the sample is assumed to consist of at least two components contained in the reference library. In addition to the complicating factors already mentioned, the presence of matrix effects can significantly complicate automated analysis. As in the first application, NN model performance is quantified and compared with overlap-based methods.

4:30pm **AS-TuA-10 Benefits of a Modern File Format for ToF-SIMS Imaging**, ***Alex Henderson***, University of Manchester, UK **INVITED**

ToF-SIMS data is typically acquired into the proprietary file format of the instrument vendor. The vendor's software has visualisation tools and data analysis routines that are tuned to that format, and that can be sufficient for the end-user. But what if we want to do something the vendor has yet to implement? What about those machine-learning or deep-learning AI methods we read about? Can we share our data with our collaborators? Can we publish it openly, as mandated by most academic funding providers?

Most vendors offer one or two data export options. Sometimes these are only suitable for single spectra, or images of pre-selected ions. Often the file format is something thought up by the vendor, or can be missing important metadata.

For SIMS there are only a limited number of open file formats, each with their limitations. Examples include ISO 14976 (the "VAMAS format") for spectra and maps, and imzML, originally developed for MALDI, for hyperspectral imaging. Each of these has issues with the size of files generated by modern instrumentation, or modalities such as image depth profiling.

In this presentation we will explore formats from other 'big data' domains such as climate science and astronomy, to see whether these can be adapted to our data. In the course of this, we will explore peak detection, data compression, out-of-core data access, visualisation, and machine learning.

We will also present open questions regarding metadata and invite the community to be involved in the process of developing a common format suitable for our requirements.

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