

Monday Evening, December 12, 2022

Charles S. Fadley Memorial Session

Room Naupaka Salon 4 - Session CF-MoE1

Charles S. Fadley Memorial Session I: Advances in X-ray Spectroscopy and Analysis

Moderators: Gregory S. Herman, Oregon State University, Boris Sinkovic, University of Connecticut

5:40pm **CF-MoE1-1 Pursuing Chuck Fadley's Ideas a Scientific Lifetime: Photoelectron Recording with Maximum Parallelization, Gerd Schönhense**, Institut für Physik, Johannes Gutenberg-Universität, Germany
INVITED

In 1988-89 the author had the great pleasure of doing postdoctoral work in the Fadley group. Experiencing the impressive work with an electron spectrometer with a multi-channel detector (VG ESCALAB5) [1] initiated decades of thinking about a further parallelization of photoelectron recording techniques. Today we find powerful implementations that extrapolate those early ideas that have resulted in orders of magnitude increased recording efficiency.

Thanks to the excellent time structure of modern photon sources such as lasers, HHG sources, Synchrotrons and FELs, time-of-flight (ToF) detectors can record a wide energy band in parallel. Additional full-field imaging of (k_x, k_y) momentum patterns has led to a novel ARPES technique, termed ToF momentum microscopy (ToF-MM). A fast delay-line detector records (x,y) position and ToF for each electron with count rates up to 8×10^6 cps. ToF-MM enabled new types of experiments, such as fast tomographic-like Fermi surface and -velocity mapping [2].

The developments had a dramatic impact on experiments with very low signal intensities. In particular, spin-resolved experiments suffer from the low figure-of-merit of spin detectors. Significant advances have been made with the advent of multichannel spin recording [3]. Bulk-sensitive photoemission using hard X-ray excitation suffers from low cross sections and enhanced phonon scattering. The ToF-MM approach was extended to energies >7 keV and an order of magnitude higher (E_B, k_x, k_y) phase-space acceptance. This led to new types of (H)ARPES [4] and X-ray photoelectron diffraction (XPD) experiments [5]. The large k-field-of-view provides 4D bulk spectral functions $\rho(E_B, \mathbf{k})$ in a single measurement without scanning the photon energy.

In fs time-resolved photoemission (tr-ARPES), weak signals of transient excited states are recorded with high efficiency, both for FELs [6] and HHG sources [7]. In parallel to the tracking of the electronic structure, rapid changes in the geometric structure can be observed using tr-XPD. Resolving the intrinsic time scale of ultrafast processes and further parameters like pump-laser fluence coined the term "multidimensional photoemission" for such experiments. For further reading, see current reviews [4,5,7].

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6:20pm **CF-MoE1-3 The State of Interpretation for Multiplet Splitting and Shake-Up Satellites in Transition Metal Compound XPS: Fe₂O₃ and NiO, Christopher R. Brundle**, C. R. Brundle and Associates; *B. Crist*, XPS Library; *P. Bagus*, University of North Texas

We discuss the understanding of multiplet splitting and shake-up satellite structure for transition metal compounds. Chuck Fadley was an early pioneer for the former (1).

Gupta and Sen (2) expanded atomic multiplet splitting theory to include spin orbit coupling, providing predictions for the 2p XPS splitting features for TM cations. Such calculations do not include ligand-field or bonding effects in solids. Later semi-empirical approaches attempted to include such effects by scaling parameters and by invoking a charge transfer model to describe shake-up satellites. A free program, CTM4XAS (3), incorporates all this to simulate the cation 2p XPS spectrum.

Though CTM4XAS may roughly describe the BE spread in the cation 2p XPS, it completely disagrees with the description obtained from our full ab initio cluster calculations (Fe₂O₃ and NiO) of the electronic characteristics of the major features. The strong experimental satellite intensity for the Fe2p spectrum of Fe₂O₃ and other high spin Fe(III) compounds, at ~8.5 eV, has long been assigned to shake-up; and has been used to verify the presence of Fe(III) (4). Similarly, in the Ni2p spectrum of NiO, the satellite at ~6.5eV is

used to verify the presence of Ni(II). Our calculations confirm that these satellites do have a large amount of shake character, and that the leading edge of the "main" peak (lowest BE) is essentially "normal", ie it has no shake involvement (5, 6). CTM4XAS reverses these assignments, claiming that main peak is a shake state (charge transfer in their parlance) and the intense satellite represents the "normal" transition. Furthermore, our calculations show that once shake excitation is included, the intensity distribution of all structure in the 2p spectrum is highly modified, and there is no region, except the leading edge of the main 2p_{3/2} peak, that is 100% "normal" (5). Everywhere else there is significant mixing of "normal" and shake. We expect this mixing to hold for other TM compounds.

References

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2. R. P. Gupta and S. K. Sen, *Phys. Rev. B*, 1974, **10**, 71-77; P. Gupta and S. K. Sen, *Phys. Rev. B*, 1975, **12**, 15-19.
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4. C. R. Brundle, T. J. Chuang, and K. Wandelt, *Surface Sci.* **48**, 29 (1974).
5. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, N. Lahiri, and K. M. Rosso, *Phys. Chem. Chem. Phys.*, 2022, **24**, 4562-4575.
6. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, E. S. Ilton, N. Lahiri, and K. M. Rosso, *Inorganic Chemistry* in press.

6:40pm **CF-MoE1-4 Zinc and Cadmium: Chemical State Determination Through XPS Analyses of Standard Samples, Jeffrey D. Henderson, S. Buchanan, L. Grey, M. Biesinger**, Surface Science Western, Canada

Zinc, cadmium, and their related compounds have a myriad of applications, including, but not limited to, automotive manufacturing, batteries, photovoltaic devices, corrosion protection, and pigments. From a research perspective, the ability to accurately speciate different compounds is critical to understanding how surface chemistry can influence material properties. This ability allows for the advancement of our mechanistic understanding. It has been repeatedly demonstrated that X-ray photoelectron spectroscopy (XPS) is a powerful analytical tool for the study of changes in surface chemistry. Typically, speciation is achieved through the careful analysis of photoelectrons, and occasionally, Auger electrons. Since the main photoelectron binding energies of many zinc and cadmium compounds overlap, the modified Auger parameter must also be utilized to reliably detect chemical shifts. While the binding energies and Auger parameter data can be found in the literature for some zinc and cadmium compounds, in most cases, the available data lacks consistency, certainty, and reproducibility. Notably, Auger parameter data is often underreported in the existing literature, despite its proven utility. Additionally, many of these sources do not provide the variety of compounds needed to perform accurate chemical state analyses.

In this presentation, recent work to extend upon previously published XPS reference data and curve-fitting procedures will be detailed for a wide range of high-purity zinc- and cadmium-containing compounds. This will include a summary of literature data, carefully excluding those which contain issues related to reliability. Lastly, the applicability of peak fitting Auger lines will be explored for the analyses of mixed species systems.

7:00pm **CF-MoE1-5 X-Ray Spectroscopic Identification of Strain and Structure-Based Resonances in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane, Trevor Willey, J. Lee**, Lawrence Livermore National Laboratory; *D. Brehmer, O. Paredes Mellone*, SLAC National Accelerator Laboratory; *L. Landt*, Lawrence Livermore National Laboratory; *P. Schriener, A. Fokin, B. Tkachenko*, Institute of Organic Chemistry, Justus Liebig University, Germany; *A. de Meijere, S. Kozhushkov*, Institute for Organic and Biomolecular Chemistry, Georg-August-University, Germany; *T. van Buuren*, Lawrence Livermore National Laboratory

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes, or defects within or at the surfaces of diamond nanoparticles) significantly alter the electronic states of the nanocarbon material. Understanding the effects of steric strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how strain affects electronic structure in a benchmark series of some

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fundamental saturated carbon cage compounds. Adamantane, C₁₀H₁₆, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of this series. Twistane also is a C₁₀H₁₆ isomer but the fixed cyclohexane twist conformation of the central ring introduces some strain into the cage. Octahedrane, (CH)₁₂, and cubane, (CH)₈, are considerably much more strained, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. First, a broad C–C σ^* resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C–H σ^* in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as in octahedrane, even though these two molecules have only tertiary carbons, with chemical formula (CH)_x. The spectral differences are entirely due to the shape of the molecules; in particular, in cubane, the features arise from a high degree of p-p interaction between parallel C–C bonds. In contrast to the conventional wisdom that near-edge X-ray absorption is primarily an atomically localized spectroscopy, molecular shape and associated bond strain lead to the dominant features in spectra acquired from this fundamental series of carbon cage structures.

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