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The term of this grant, from 9/15/2009 – 11/14/2016, saw several notable scientific, technical, and organizational accomplishments. Below, we address these by the indicated category headings.

I Publications

Ten papers have appeared in print, and three additional manuscripts (discussed below) are in final stages of preparation. These will be submitted outside the support window but will acknowledge support from the present award. Papers in print are:

1. Katherine M. Davis, Brendan T. Sullivan, Mark Palenik, Lifen Yan, Vatsal Purohit, Gregory Robison, Irina Kosheleva, Robert W. Henning, Gerald T. Seidler, Yulia Pushkar, "Rapid Evolution of the Photosystem II Electronic Structure during Water Splitting," *submitted,* Science (2015).
2. Scott Jensen, Katheine Davis, Brendan Sullivan, Daniel Hartzler, Gerald T. Seidler, Diego Casa, Elina Kasman, Hannah Colmer, Allyssa Massie, Timothy Jackson, Yulia Pushkar, "X-ray emission spectroscopy of biomimetic Mn coordination complexes," *submitted*, Journal of the American Chemical Society (2017)
3. D.R. Mortensen and G.T. Seidler, "Robust optic alignment in a tilt-free implementation of the Rowland circle spectrometer," Journal of Electron Spectroscopy and Related Phenomena **215**, 8 (2016).
4. G.T. Seidler, D.R. Mortensen, A. Ditter, N. Ball, and A. Remesnik, "A Modern Laboratory XAFS Cookbook," Journal of Physics: Conference Series **712,** 012015 (2016).
5. D.R. Mortensen, G.T. Seidler, A.S. Ditter, P. Glatzel, "Benchtop Nonresonant X-ray Emission Spectroscopy: Coming Soon to Laboratories and Beamlines Near You," Journal of Physics: Conference Series **712,** 012036 (2016).
6. K.M. Davis, M. Palenik, Lifen Yan, P.F. Smith, G.T. Seidler, G.C. Dismukes, Y. Pushkar, "X-ray emission spectroscopy of Mn coordination complexes towards interpreting the electronic structure of the Oxygen Evolving Complex of Photosystem II," Journal of Physical Chemistry C **120,** 3326 (2016).
7. G.T. Seidler, D.R. Mortensen, A.J. Remesnik, J.I. Pacold, N.A. Ball, N. Barry, M. Styczinski, O.R. Hoidn, "A Laboratory-based Hard X-ray Monochromator for High-Resolution X-ray Emission Spectroscopy and X-ray Absorption Near Edge Structure Measurements," Review of Scientific Instruments **85**, 113906 (2014).

8. Joseph I. Pacold, David S. Tatum, Gerald T. Seidler, Kenneth N. Raymond, Xiaoyi Zhang, Andrew B. Stickrath, and Devon R. Mortensen, "Direct Observation of 4f Intrashell Excitation in Luminescent Lanthanide Complexes by Time-Resolved X-ray Absorption Near Edge Spectroscopy," Journal of the American Chemical Society **136**, 4186 (2014).
9. K.M. Davis, I. Kosheleva, R.W. Henning, G.T. Seidler, Y. Pushkar, "Kinetic Modeling of the X-ray-induced Damage to a Metalloprotein," Journal of Physical Chemistry B **117**, 9161 (2013). (DOI: 10.1021/jp403654n).
10. Matthew Gliboff, Hong Li, Kristina M. Knesting, Anthony J. Giordano, Dennis Nordlund, Gerald T. Seidler, Jean-Luc Bredas, Seth R. Marder, and David S. Ginger, "Competing Effects of Fluorination on the Orientation of Aromatic and Aliphatic Phosphonic Acid Monolayers on ITO," Journal of Physical Chemistry C **117**, 15139 (2013). (DOI: 10.1021/jp404033e)
11. Matthew Gliboff, Lingzi Sang, Kristina M. Knesting, Matthew C. Schalnat, Anoma Mudalige, Erin L. Ratcliff, Hong Li, Ajaya K. Sigdele, Joseph J. Berry, Dennis Nordlund, Anthony Giordano, Gerald T. Seidler, Jean-Luc Brédas, Seth R. Marder, Jeanne E. Pemberton, David S. Ginger, "Orientation and Order of Phenylphosphonic Acid Self-assembled Monolayers on Transparent Conductive Oxides: A Combined NEXAFS, PM-IRRAS and DFT Study," Langmuir **29**, 2166 (2013).
12. Stefan G. Minasian, Jason M. Keith, Enrique R. Batista, Kevin S. Boland, Joseph A. Bradley, Scott R. Daly, Stosh A. Kozimor, Wayne W. Lukens, Richard L. Martin, Dennis Nordlund, Gerald T. Seidler, David K. Shuh, Dimosthenis Sokaras, Tolek Tyliszczak, Gregory L. Wagner, Tsu-Chein Weng, and Ping Yang, "Covalency in Metal–Oxygen Multiple Bonds Evaluated Using Oxygen K-edge Spectroscopy and Electronic Structure Theory", Journal of the American Chemical Society **135,** 1864 (2013).
13. Brian A. Mattern and Gerald T. Seidler, "Theoretical Treatments of the Bound-Free Contribution and Experimental Best Practice in X-ray Thomson Scattering from Warm Dense Matter," Physics of Plasmas **20**, 022706 (2013) (doi: 10.1063/1.4790659).
14. S.M. Heald, G.T. Seidler, D. Mortensen, B. Mattern, J.A. Bradley, N. Hess, M. Bowden, "Recent Tests of X-ray Spectrometers Using Polycapillary Optics," in Advances in X-Ray/EUV Optics and Components VII, edited by Shunji Goto, Christian Morawe, Ali M. Khounsary, Proc. of SPIE Vol. 8502 (2012), article number 85020I (doi: 10.1117/12.929960).
15. K.M. Davis, B.A. Mattern, J.I. Pacold, T. Zakharova, D. Brewe, I. Kosheleva, R.W. Henning, T.J. Graber, S.M. Heald, G.T. Seidler, Y. Pushkar, "Fast Detection Allowing Analysis of Metalloprotein Electronic Structure by X-ray Emission Spectroscopy at Room Temperature," Journal of Physical Chemistry Letters **3**, 1858 (2012).
16. B.A. Mattern, G.T. Seidler, J.J. Kas, J.I. Pacold, J.J. Rehr, "Real-Space Green's Function Calculation of Compton Profiles," Phys. Rev. B **85**, 115135 (2012).
17. J.A. Bradley, K.T. Moore, M. J. Lipp, B.A. Mattern, J.I. Pacold, G. T. Seidler, P. Chow, E. Rod, Y. Xiao, and W. J. Evans, "4*f* electron delocalization and volume collapse in praseodymium metal, " Phys. Rev. B **85**, 100102 (2012).
18. J.I. Pacold, J.A. Bradley, B.A. Mattern, M.J. Lipp, G.T. Seidler, P. Chow, Y. Xiao, E. Rod, B. Rusthoven, and J. Quintana, "A miniature X-ray emission spectrometer (miniXES) for high-pressure studies in a diamond anvil cell," J. Synch. Rad. **19**, 245 (2012).
19. B.A. Mattern, G.T. Seidler, M. Haave, J.I. Pacold, R.A. Gordon, J. Planillo, J. Quintana, B. Rusthoven, "A Plastic Miniature X-ray Emission Spectrometer (miniXES) based on the Cylindrical von Hamos Geometry," Rev. Sci. Instrum. **83**, 023901 (2012).

20. J.A. Bradley, A. Sakko, G.T. Seidler, A. Rubio, M. Hakala, K. Hamalainen, G. Cooper, A.P. Hitchcock, K. Schlimmer, K.P. Nagle, "Revisiting the Lyman-Birge-Hopfield Band of N_2," Physical Review A **84**, 022510 (2011).
21. Subhra Sen Gupta, J. A. Bradley, M. W. Haverkort, G. T. Seidler, A. Tanaka, and G. A. Sawatzky, "Coexistence of Bound and Virtual-bound States in Shallow-core to Valence Spectroscopies," Physical Review B **84**, 075134 (2011).
22. A. F. Tillack, K. M. Noone, B. A. MacLeod, D. Nordlund, K. P. Nagle, J. A. Bradley, S. K. Hau, Hin-Lap Yip, Alex K.-Y. Jen, G. T. Seidler, and D. S. Ginger, "Surface Characterization of Polythiophene:Fullerene Blends on Different Electrodes using Near Edge X-ray Absorption Fine Structure," ACS Applied Materials and Interfaces **3**, 726 (2011).
23. R.A. Gordon, G.T. Seidler, T.T. Fister, K.P. Nagle, "Studying low-energy core-valence transitions with bulk sensitivity using q-dependent NIXS," J. Elect. Spect. Related Phenom. **184**, 220 (2011).
24. D.W. Liu, Y.Y. Liu, A.Q. Pan, K.P. Nagle, G.T. Seidler, Y.H. Jeong, G.Z. Cao, "Enhanced Lithium-Ion Intercalation Properties of V_2O_5 Xerogel Electrodes with Surface Defects," Journal of Physical Chemistry C **115**, 4959 (2011).
25. J.A. Bradley, Ping Yang, E.R. Batista, K.S. Boland, C.J. Burns, D.L. Clark, S.D. Conradson, S.A. Kozimor, R.L. Martin, G.T. Seidler, B.L. Scott, D.K. Shuh, T. Tyliszezak, M.P. Wilkerson, and L.E. Wolfsberg, "Experimental and Theoretical Comparison of the O *K*-Edge Nonresonant Inelastic X-ray Scattering and X-ray Absorption Spectra of $NaReO_4$," Journal of the American Chemical Society **132**, 13914 (2010).
26. J.A. Bradley, G.T. Seidler, G. Cooper, M. Vos, A.P. Hitchcock, A.P. Sorini, C. Schlimmer, K.P. Nagle, "Comparative Study of the Valence Electronic Excitations of N_2 by Inelastic X-ray and Electron Scattering," Physical Review Letters **105**, 053202 (2010).
27. A. Sakko, C. Sternemann, Ch.J. Sahle, H. Sternemann, O.M. Feroughi, H. Conrad, F. Djurabekova, A. Hohl, G.T. Seidler, M. Tolan, and K. Hamalainen, "Suboxide interface in disproportionating a-SiO studied by x-ray Raman scattering," Physical Review B **81**, 205317 (2010).
28. J.A. Bradley, S. Sen Gupta, G.T. Seidler, K.T. Moore, M.W. Haverkort, G.A. Sawatzky, S.D. Conradson, D.L. Clark, S.A. Kozimor, and K.S. Boland, "Probing Electronic Correlations in Actinide Materials Using Multipolar Transitions," Physical Review B **81**, 193104 (2010).

II. A Rejuvenation of Laboratory-based High-Resolution X-ray Spectroscopies

In October 2013 we commissioned a new type of inexpensive lab-based spectrometer for high-resolution x-ray studies, including x-ray absorption fine structure (XAFS) and x-ray emission spectroscopy (XES). In the subsequent year we have fine-tuned our experimental technique and now regularly achieve data that is in essentially perfect agreement with synchrotron-based results, see Fig. 1. The instrumentation paper for our lab spectrometer has been submitted to the Review of Scientific Instruments.

The startling performance of this modest instrument has garnered significant interest that, we emphasize, has been solely focused on DOE-priority research issues and that does not have the character of competition with synchrotron facilities. In addition to providing a true introductory capability that can help attract and educated entire new user communities, laboratory-based XAFS enables measurements that, for reasons of long duration, sample preparation complexity, chemical hazards, or radioisotope hazards, cannot be performed with regularity or certainty at synchrotron light sources. To this end, under funding from the University of Washington, we have used the technology developed under support from this award to build a mid-scale lab XAFS user facility for the UW Clean Energy Institute (CEI). The CEI-XAFS facility will see extensive use in long-baseline studies of electrical energy storage that cannot, due to the long experimental duration, be completed with regularity at synchrotron beamlines. Commissioning is proceeding well, and all performance milestones for flux and energy resolution have been achieved.

We are also assisting collaborators at LANL and ANL with the design and construction of XES spectrometers for the lower-energy range of 2-4 keV, e.g., for S XES in Li-S batteries or in air-sensitive actinide-sulfur compounds that cannot be reliably transported to the light source. In support of the effort to extend lab-based XES to lower energies we have successfully developed an inexpensive x-ray camera for the 2-4 keV ‘tender’ x-ray range. [Hoidn and Seidler, RSI 2015]

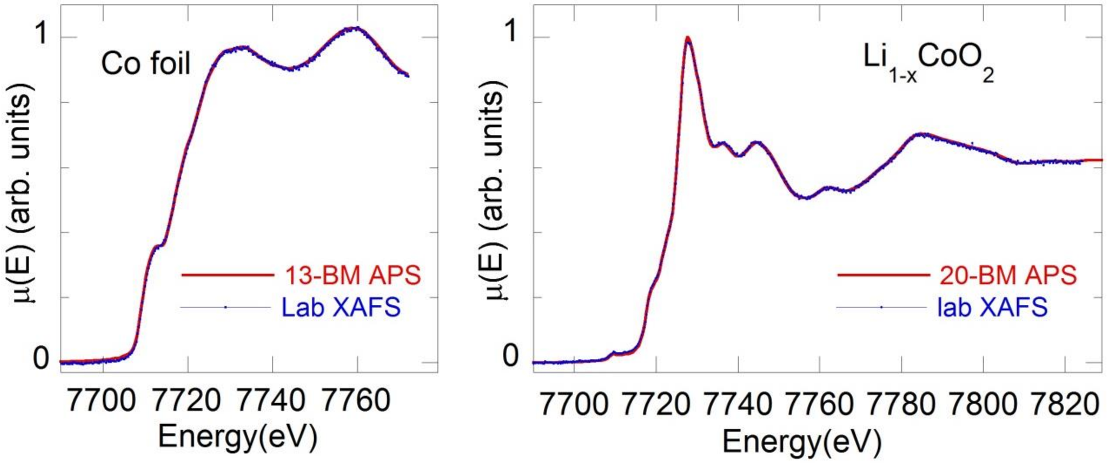

Fig. 1: XANES spectra for a reference Co foil and for a partially discharged $LiCoO_2$ battery electrode (*ex situ*), measured at the Advanced Photon Source and with our lab-based spectrometer.

III. X-ray Heating Studies at LCLS/MEC

The recent LD67 and LK20 campaigns at LCLS/MEC was led by the PI. While this beamrun emphasized laser-shock heating of multicomponent targets (supported by a grant from DOE/FES), complementary x-ray heating experiments were also performed as part of the WDM research under the present award. The results are still under analysis, but show interesting effects in the electronic structure of metallic and more complex intermediate-Z alloys and compounds. For example, the ability to compare response across multiple intermediate-Z species in alloys will allow a detailed interrogation of the correct theoretical treatment of the electronic structure of isochorically heated matter. Studies at LK20 found new effects in x-ray diffraction that can be used to interrogate finite-T DFT in crystalline matter at elevated temperatures.

IV. Time-resolved Studies of Energy Transfer and Electron Correlations

Lanthanide compounds and coordination complexes are responsible for a wide range of light-gathering and light-emitting applications, including as commercial phosphors in lighting applications, as tools to better match the solar spectrum to the function of photovoltaic devices, and as a critical component in many bioassays. In this lattermost role, an organic 'antenna' acts as a strong near-UV photoabsorber before nonradiatively transferring energy to a chelated, trivalent lanthanide ion via a 4f-4f intrashell excitation. This dipole-forbidden excitation subsequently decays through the so-called 'hypersensitive' pseudo-quadrupolar decay, giving light at delays of order msec after the initial excitation due to the long lifetime for the 4f excitation. This long time-delay allows simplest time-gate filtering of the emission from the luminescent lanthanide complex from that of the host biological system.

The microscopic physics underlying each step in the energy transfer pathway in the luminescent lanthanides, and indeed in all materials used for the applications described above, remain incompletely understood. Our recent work at the Advanced Photon Source on luminescent lanthanide complexes demonstrate an unexpected, but clear expression of the 4f instrashell excitation in the time-resolved x-ray absorption near-edge spectrum (XANES) of the lanthanide ion.[Pacold, et al., JACS 2014] Our leading explanation requires a surprisingly dynamic coupling between the 4f and 5d orbitals of the lanthanide ion. In any event, this discovery opens up new opportunities to use the LCLS to directly monitor the energy transfer onto the lanthanide species, giving an important complement to studies of the de-excitation of multiple ligand states by transient optical absorption.

We have recently extended this project with time-resolved x-ray excited optical luminescence (TR-XEOL) studies performed at the Advanced Photon Source. The high flux-density of the 20-ID microprobe endstation allowed us to reach a nonlinear XEOL regime where the time scales for different steps in the energy relaxation cascade in Bi-sensitized Y_2O_3:Eu phsophors can be separated. This became a capstone chapter in a student dissertation and is still part of a manuscript in preparation.

IV. Miniature Spectrometer Development

During the term of this award, we further developed a new approach to high-throughput x-ray emission spectroscopy at synchrotron light sources. This resulted in two instrumentation papers [Mattern et al Rev Sci Instrum 2012, Pacold et al J. Synch. Rad. 2012], the development of a large number of spectrometers for use at the Advanced Photon Source, and a long-standing collaboration on XES of phototsystem II [Davis et al 2015; Jensen et al 2017; Davis et al 2016; Davis et al 2013; Davis et al 2012]. The work on PSII proved important for groundwork for LCLS studies and also has strong relevance for recent proposals of novel charge-transfer mechanisms.

V. The electronic structure of warm dense matter

Matter at solid-like and higher densities that is also at temperatures of order a few eV to somewhat past the Fermi energy is frequently referred to as 'warm dense matter' (WDM). In this regime, all but the lightest species will still be partially (rather than fully) ionized, resulting in a highly complex admixture of the physics typical of plasmas and that of condensed phases. This regime, whose fundamental interest is seasoned by strong technical relevant for fusion science and direct representation of the thermodynamic conditions of several astrophysical and planetary phenomenon, is seeing emergent interest from both the plasma and condensed phase communities.

However, the highly transient nature of such experiments at large-scale laser facilities and x-ray free electron lasers poses unique challenges for the determination of even the most basic state variables (*e.g.*, pressure, temperature, density, and ionization state). This limitation is critically impeding progress toward understanding of the equation of state or toward any consequent, comprehensive microscopic treatment. As a case in point, WDM thermometry is in a uniquely difficult situation compared to any other regime of quasi-equilibrium matter: no thermometry from other fields of science is applicable to WDM, and the dominant methods used in WDM (specifically, based on inelastic x-ray scattering) are extremely sensitive to models of electronic structure that (to date) have inherently poor applicability outside of the WDM regime.

During this award term, we developed improved theoretical tools of atomic and condensed-phase effects can actually be validated against ambient-condition, high-resolution IXS results collected at synchrotron light-sources before being applied to the much poorer-quality IXS spectra that are typical of WDM studies at major laser-plasma facilities and x-ray free electron lasers. Our work includes a real-space Green's function treatment of the valence contribution to the IXS spectrum [Matternet al 2012], a reinvestigation and gross correction of methods used to treat the core contribution to IXS in WDM experiments,[Mattern et al 2013] and a comprehensive comparison of methods from solid-state physics and from the plasma community for the treatment of the valence electronic structure in a 'tepid' regime, at low, but nonzero, levels of ionization.[Mattern et al 2013].

VI. Multi-electron Excitation and X-ray Emission from Ni

Making use of the lab-based spectrometer (see above), we have completed a study of of the nonresonant x-ray emission spectroscopy (XES) from Ni metal in an energy range spanning the Kβ, valence-to-core, and double-ionization (DI) satellites that appear the single-particle Fermi level. A special feature of the laboratory-based x-ray spectrometer allows us to collect both x-ray emission and x-ray absorption measurements so as to accurately aligning the XES and x-ray absorption spectra to a common energy scale. This careful alignment of energy scales is prerequisite to correcting of the strong sample absorption above the Ni K-edge energy – the first time that such effects have been quantified and corrected. The successful correction of absorption effects allows a determination of the branching ratios for the [1s3d], [1s3p], [1s2p] and [1s2s] satellites with respect to their corresponding diagram lines. Comparison of our branch ratio results with several predictions can be used to distinguish between different theoretical treatments. The central experimental data is shown in Figure 2, below.

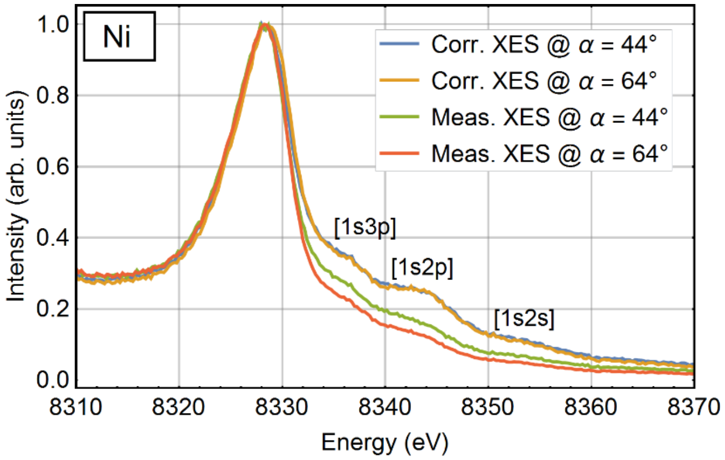

Figure 2 | Absorption-Corrected Nickel Valence Emission. This figure shows both the uncorrected and corrected spectra of Ni valence emission. Obtaining the correct intensity of multi-electron peaks, identified via the Z+1 approximation, is critical for theory comparison.

These results demonstrate that lab-based XES can be an important complement to synchrotron-based studies of multi-electron excitations. A manuscript [Valenza et al 2017] is nearing submission and will attribute the present award as the main funding support.

VI. Benchmark Results and Theoretical Treatment of Valence-to-Core XES

As the capstone project in a student dissertation (Mortensen 2016) we completed a study of the valence-to-core x-ray emission for a broad family of Fe-rich and Zn-rich compounds. These results were critically compared to calculations from multiple theoretical treatments (Rehr group at UW, Prendergrast group at LBNL, Govind team at PNNL) to determine the relative importance of treatments of core-hole effects and especially quadrapole contributions. A resulting manuscript is nearing submission and will attribute the present award as the main funding support. One of the main results is presented in the figure below.

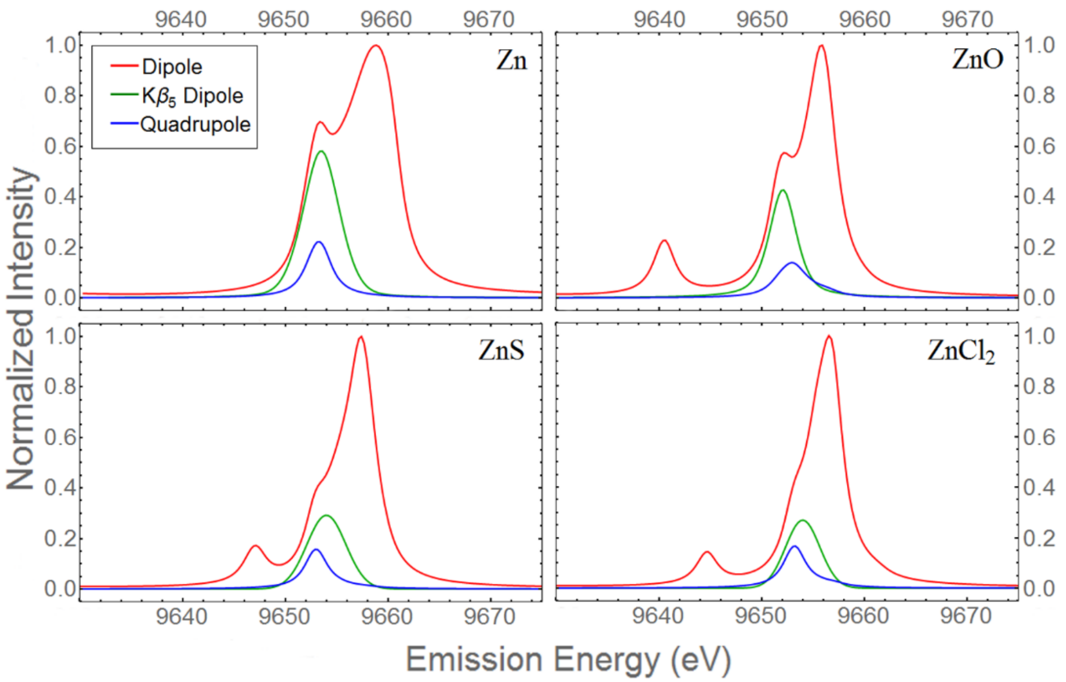

Figure 3. The full dipole (red), isolated Kβ5-dipole term (green) and quadrupole (blue) contributions to the FEFF calculation for ZnO. These calculations indicate the Kβ5 term originates from states of both metal 4p and 3d character.

These results address a long-standing question about the magnitude of quadrapole contributions to valence-to-core XES in transition-metal systems, with significant consequences for future work at synchrotrons and XFELs.

VII. Further development of Inelastic X-ray Scattering for Molecular and Solid Systems

The earliest years of this award saw substantial work aimed at the further development of inelastic x-ray scattering methods at synchrotron light sources, especially as regards the use of nonzero momentum transfer effects to more fully interrogate the density of states outside the dipole selection rule. This includes numerous publications, and two student dissertations (Bradley and Nagel). A highlight of this work was the critical comparison of IXS and electron energy loss spectroscopy to the problem of low-energy excitations in N_2 gas. [Bradley et al, PRL 2011] In that study. We demonstrated a more reliable determination of the momentum-transfer dependence of the oscillator strength for the Lyman-Birge-Hopfield resonances that have been the subject of enduring theoretical interest due to the difficulty in addressing the N2 triple-bond. We find that our results agree well with the most recent theoretical effort but that EELS results spanning several decades have been contaminated by effects outside of the first Born approximation.