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Computational Studies of Fundamental Organic Transformations Catalyzed by Metal Oxides
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OVERVIEW

Exploration of metal oxide mediated reactions is critical to expanding the development of new approaches for organic transformations, which are essential in the petroleum industry. The objective of this project is to explore fundamental aspects of structure in metal oxide and related species to gain insight to the catalytic function such systems serve in fundamental organic transformations. This PRF award has provided the PI and his group the opportunity to develop experience in the theoretical study of structure and bonding of metal oxide and related systems. Importantly, the work carried out as part of this project will contribute significant contributions to two Ph.D. students' dissertations in the new future. It is also notable that this new direction research effort has motivated and informed a broader research program in the PI's group and continues to have a positive impact on his career and those of the students and postdoc that have engaged in these projects.

CURRENT AND ONGOING WORK

In the second project year, we made progress in two important areas. First, we began examining the intriguing structure and bonding of lanthanide oxides. Second, we showed that a new model for describing electron detachment can be used to understand the complex photoelectron spectra of the mixed-metal MoVO₂ clusters, which serves as a model of Mo-doped vanadium oxide catalysts. This work has benefitted from a strong collaboration with experimentalist Prof. Caroline Chick Jarrold of Indiana University.

Examination of Cerium Species

Motivated by intriguing catalysis of transition metal oxides on cerium oxide and similar species, we have explored the structure of CeO₂B_x (x=2, 3). We have also examined the CeB₆ cluster, which is expected to serve as a model of edge and corner sites of bulk cerium boride. This work involved a number of open-shell species and benefitted from our group's increasing expertise in treating such systems.

Boronyl (B=O) ligands have garnered much attention as isoelectronic and isolobal analogues of CO and CN, yet successful efforts in synthesizing metal boronyl complexes remain scarce. DFT calculations were employed to investigate two small CeO₂B_x (x=2, 3) complexes identified by our experimental collaborators using laser ablation of a mixed Ce/B pressed powder target. Anion photoelectron spectra reveal markedly different bonding upon incorporation of an additional B atom. Calculations show that CeO₂B₂ has a Ce(I) center coordinated to two monoanionic boronyl ligands in a bent geometry. This result was unexpected as previous studies suggest electron-rich metals are most suitable for stabilizing such ligands. Introducing another B atom, however, favors a much different geometry in which Ce(II) coordinates an O₂B₃³⁻ unit through both the O and B atoms, which was evident in the markedly different PE spectra. Importantly, simulations of the photoelectron spectra using the computationally determined structures show excellent agreement with experimental spectra (see Fig. 1).

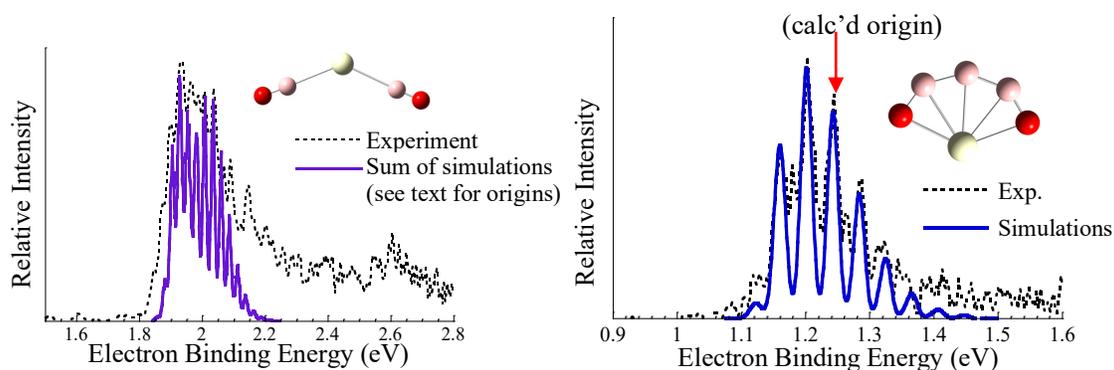


Figure 1. Comparisons of experimental and computational photoelectron spectra for CeB₂O₂ and CeB₃O₂.

We have also probed the electronic and molecular structure of the CeB₆ molecular unit using DFT calculations to gain insight into structural and electronic relaxation on edge and corner sites of ionic material. These efforts were informed by experimental photoelectron results collected by the Chick Jarrold Lab. While boron in bulk lanthanide

hexaboride materials assumes octahedral B_6^{3-} units, the monomer assumes a less compact structure to delocalize the charge. Two competitive molecular structures were identified for the anion and neutral species, which include a boat-like structure and a planar or near-planar teardrop structure. Ce adopts different orbital occupancies in the two isomers; the boat-like structure has a $4f$ superconfiguration while the teardrop favors a $4f6s$ occupancy. The B_6 ligand in these structures carries a charge of -4 and -3, respectively. The teardrop structure, which was calculated to be isoenergetic with the boat structure, was most consistent with the experimental spectrum. B_6 -local orbitals crowd the energy window between the Ce $4f$ and $6s$ (HOMO) orbitals. A low-lying transition from the B-based orbitals is observed slightly less than 1eV above the ground state. The results suggest that edge and corner conductivity involves stabilized, highly diffuse $6s$ orbitals or bands rather than the bulk-favored $5d$ band. High-spin and open-shell low-spin states were calculated to be very close in energy for both the anion and neutral, a characteristic that reflects how decoupled the $4f$ electron is from the B_6 $2p$ - and Ce $6s$ -based molecular orbitals.

Toward a New Model for Electron Detachment

Attempts to reconcile simulated photoelectron spectra of $MoVO_4^-$ clusters are complicated by the presence of very low energy barriers in the potential energy surfaces of the lowest energy spin states and isomers. Transition state structures associated with the inversion of terminal oxygen ligands are found to lie below, or close to, the zero point energy of associated modes, which themselves were found to be of low frequency and thus likely to be significantly populated in the experimental characterization. Our simulations used Boltzmann averaging over low-energy coordinates and full mapping of the PES to obtain simulations in excellent agreement with the experimental spectra previously reported. Molecular orbital analysis of accessible final spin states revealed the existence of low energy two-electron transitions in which the final state is obtained from a finite excitation of an electron along with the main photodetachment event. This analysis was carried out using the so-called Natural Ionization Orbitals model, which specifically developed in the PI's group to understand processes of this sort that we have recently investigated with thanks to support from this PRF award. The NIOs for this system's photodetachment channels show that the lowest energy transition involves a two-electron process – electron detachment accompanied by metal-to-metal charge transfer. The NIO model allowed us to explain the large difference in intensity between different bands present in the photoelectron spectrum. Additional studies using this model are ongoing.

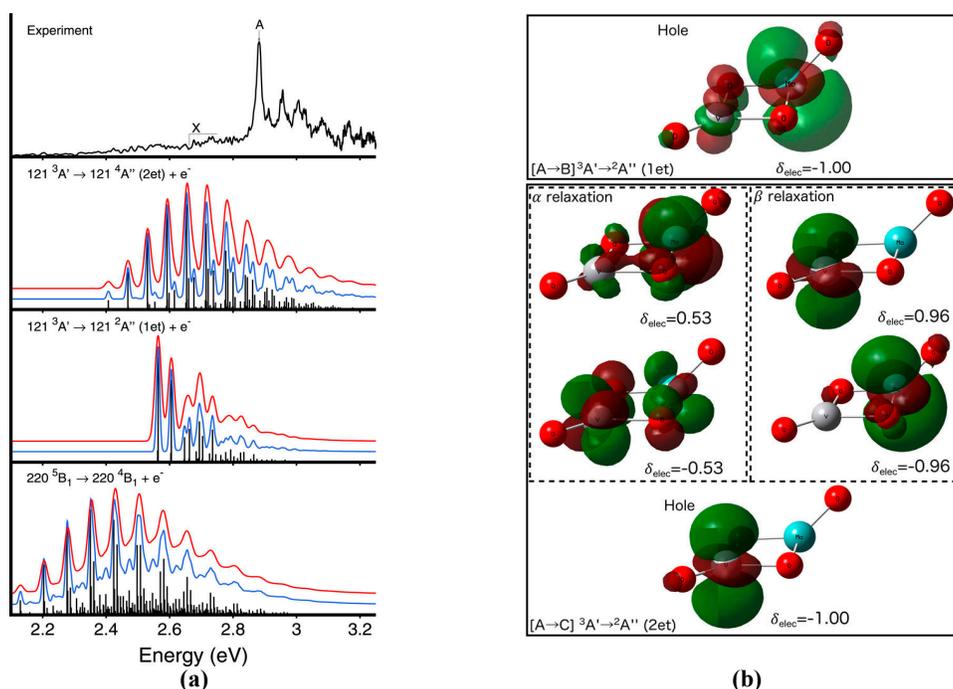


Figure 2. Results from a computational study of anion photo-detachment from $MoVO_4^-$. It was found that the reported spectrum results from a convolution of two electron detachment processes (a). Using the Natural Ionization Orbitals model (b), it was determined that the lowest energy transition corresponds to a pseudo-two-electron transition and is forbidden and is thus a minor contributor to the observed spectrum.