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**Ligated Metal-Chalcogenide and Aluminum Based Superatoms for
Superatomic Crystals with Tunable Functionalities**

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14. ABSTRACT Objectives: The key objective of the current proposal was to carry out theoretical studies on the effect of ligands on the redox properties of aluminum based superatomic clusters and carry out theoretical studies on recently discovered ligated metal-chalcogenide superatoms (composition MxEyLz; M: Transition Metal; E: Chalcogens; L: Ligand) and their assemblies. The metal-chalcogenide clusters, composed of a core of metal and chalcogen atoms surrounded by ligands, represent a new class of superatoms that are highly stable as individual motifs, whose properties can be controlled by changing the metallic core or the ligand, and can be assembled to form solids with diverse functionalities. Our objective is to offer insight into some of the recently observed unique features exhibited by such assemblies, to explore new potential applications of such assemblies in a two year program. The original work schedule was slightly delayed due to covid-19 problems but we accomplished all the proposed work and even carried out additional studies that have led to significant and important findings that are scientifically challenging and open doors to real applications. Our work was featured on the cover pages of three different journals. In the following, I briefly outline our objectives. (1) Controlling the redox properties of Aluminum based clusters and metal-chalcogenide clusters using donor and acceptor Ligands.			
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Summary of Accomplishments:

1. Controlling the Redox Properties of Aluminum based and Metal-Chalcogenide Clusters through Ligands

Organic ligands that protect the surfaces of clusters and nanoparticles against reactions and control the rate of growth are generally considered to be inert passive coatings. Through first principles studies, we have demonstrated that the ligands can also strongly affect the redox properties of clusters including the position of HOMO-LUMO gap. Our studies based on Al_{13} and MAl_{12} ($M = \text{B}, \text{C}, \text{Si}, \text{and P}$) clusters first showed that ionization energy can be modified by substituting an Al atom by C, Si, and P atoms. We then showed that the ionization energy of all the clusters can be substantially lowered by adding weakly bound N-ethyl-2-pyrrolidone ($\text{EP}=\text{C}_6\text{H}_{11}\text{NO}$) where we showed that the addition of ligands led to a dramatic lowering of the ionization energy independent of the shell occupancy of the cluster. We also showed that the electronic

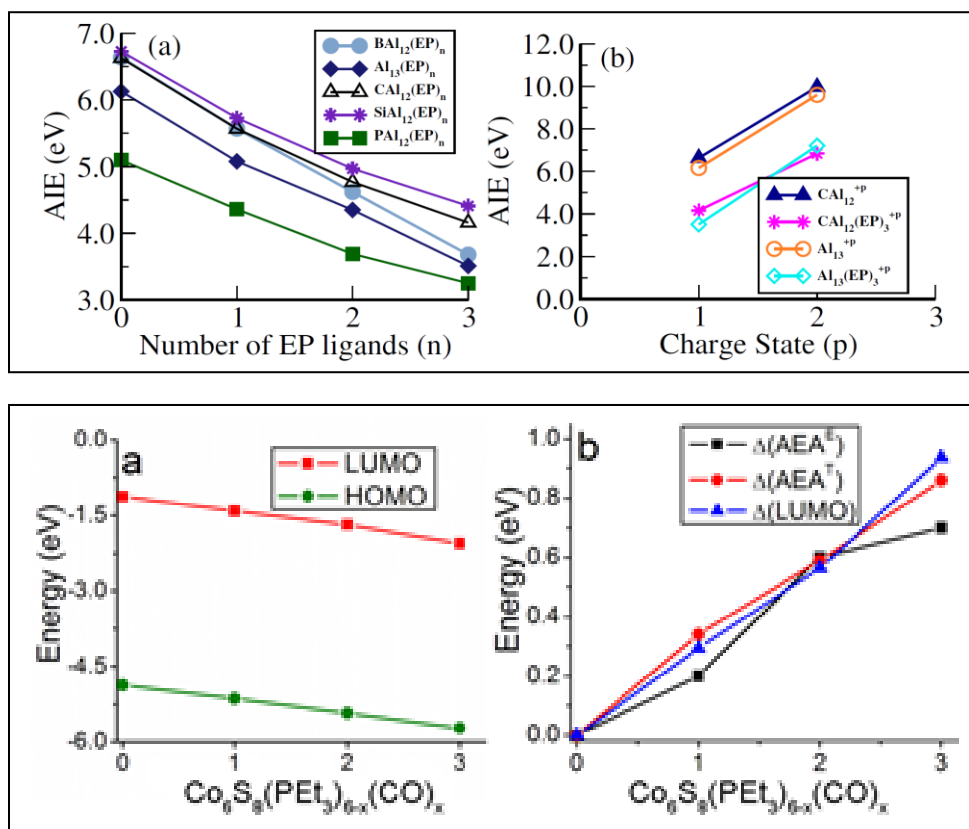


Fig. 1. Adiabatic Ionization Energies (AIE) as a function of number of ligands and as a function of charged state. The lower figure shows a comparison of adiabatic electron affinity (AEA) based on theory and experiments.

spectrum can be shifted up or down in energy by placing ligands that form charge transfer complexes. In a subsequent work, we showed that these effects are not specific to metal clusters but can be generalized to metal-chalcogenide clusters. To demonstrate this we undertook a synergistic study combining theoretical work at VCU and the experimental work at Johns Hopkins university (group of Prof. Kit Bowen) and Columbia university (group of Prof. Xavier Roy) to demonstrate these concepts by measuring the anion

photoelectron spectra of a series of Co_6S_8 clusters decorated with different ratios of electron-donating and electron-withdrawing ligands, $\text{Co}_6\text{S}_8(\text{PET}_3)_{6-x}(\text{CO})_x$ ($x = 0-3$). We find that $\text{Co}_6\text{S}_8(\text{PET}_3)_6$ has a low electron affinity (EA) of 1.1 eV, and that the successive replacement of PET_3 ligands with CO gradually increases its EA to 1.8 eV. Density functional theory calculations reveal that the increase of EA results from a monotonic lowering of the cluster highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). Our work provides unique insights into the electronic structure and tunability of superatomic building blocks.

2. Multiple-Valence Aluminum in Al_nO_m Clusters:

In a joint experimental/theory project, we examined the reactivity of cationic aluminum clusters with oxygen via a customized time-of-flight mass spectrometer (TOFMS). Unlike the etching effect for anionic aluminum clusters exposed to oxygen, here the cationic Al_n^+ clusters were found to react and produce a range of small Al_nO_m^+ clusters. Relatively large mass abundances were found for Al_3O_4^+ , Al_4O_5^+ , and Al_5O_7^+ at lower O_2 reactivity; while at higher O_2 concentration oxygen addition leads to Al_2O_7^+ , $\text{Al}_3\text{O}_{6,8,9,10}^+$ and $\text{Al}_4\text{O}_{7,9}^+$ showing relatively high abundance, and Al_5O_7^+ remains as a stable species dominating the Al_5O_m^+ distribution. In order to understand these results, we investigated the structures and stabilities of the Al_nO_m^+ clusters. First-principles theoretical investigations revealed the structures, HOMO-LUMO gaps, fragmentation energies, ionization energies, and Hirshfield charge of the Al_nO_m^+ clusters ($2 \leq n \leq 7$; $0 \leq m \leq 10$). Energetically, Al_3O_4^+ , Al_4O_5^+ , and Al_5O_7^+ were calculated to be most stable with high fragmentation energies, however they still allow for chemisorption of additional O_2 with large binding energies leading to clusters with higher O/Al ratios. The stability of the species is consistent with Al possessing three valence electrons while O typically accepts two, leading to the expectation that Al_3O_4^+ , Al_5O_7^+ , and $\text{Al}_7\text{O}_{10}^+$ are reasonably stable. In addition to this, Al_3O^+ , Al_5O_3^+ and Al_7O_5^+ were found to exhibit large HOMO-LUMO gaps associated with the different oxidation states of Al. The oxygen-rich species such as Al_2O_7^+ , $\text{Al}_3\text{O}_{10}^+$

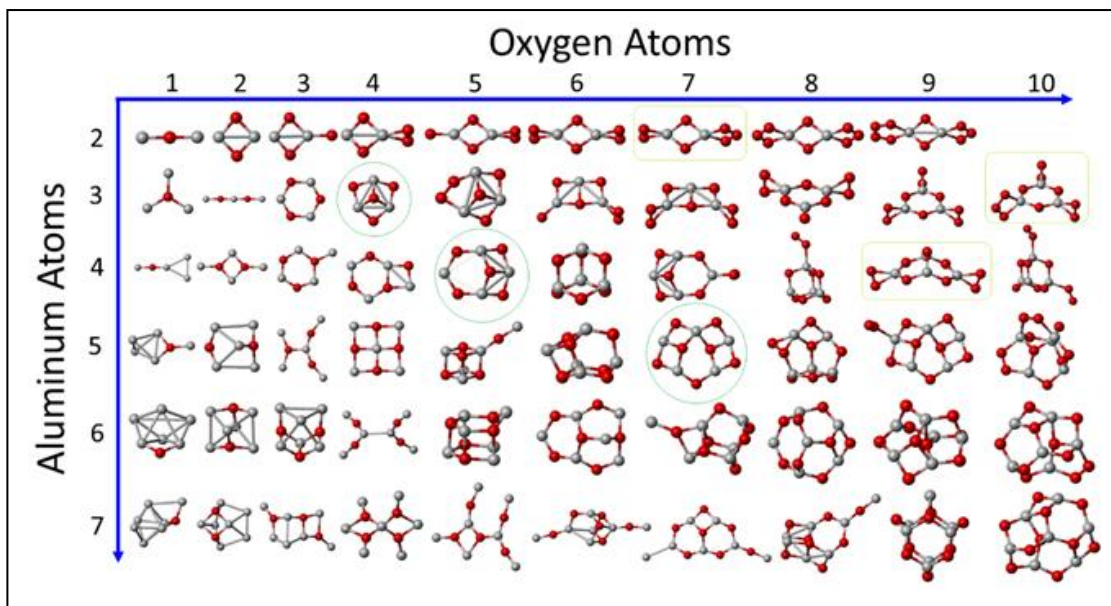


Figure 2. Optimized ground-state atomic structures of Al_nO_m^+ ($2 \leq n \leq 7$; $0 \leq m \leq 10$). Aluminum is gray, Oxygen is red.

and Al_4O_9^+ all display superoxide structures providing further insights into the oxidation of aluminum clusters.

3. Ligand Induced Homojunction between Aluminum Based Clusters: Separating Electron Hole Pairs for Photovoltaics Applications:

In a startling development that went beyond the original proposed work, we showed how ligated aluminum based clusters could be joined together to create large internal fields that could separate electron hole pairs upon the absorption of light offering the possibility for photovoltaic applications.

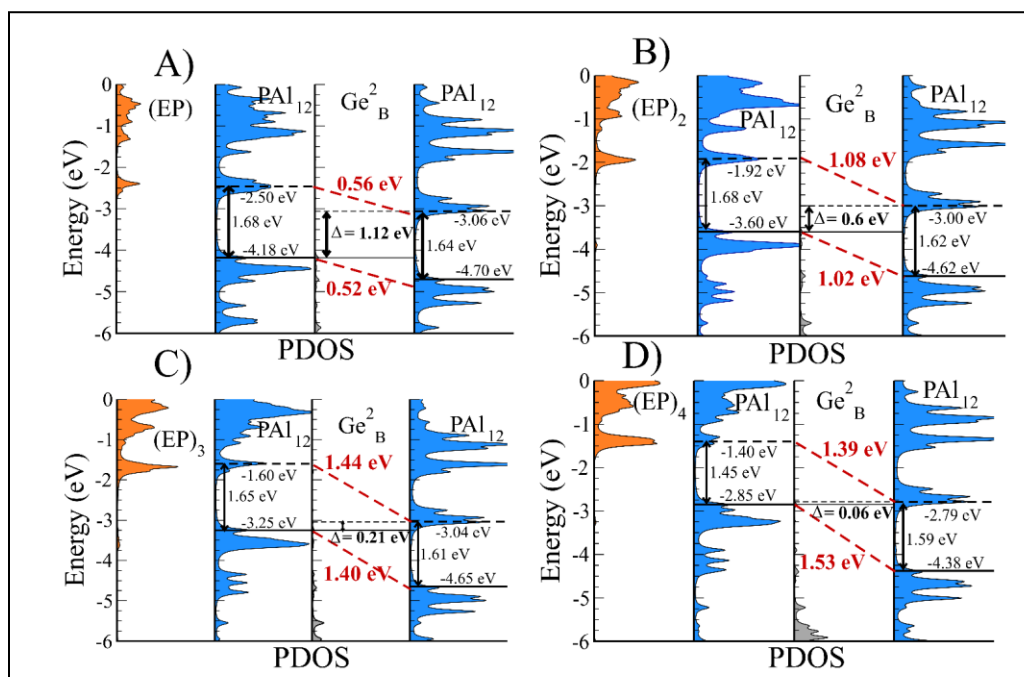


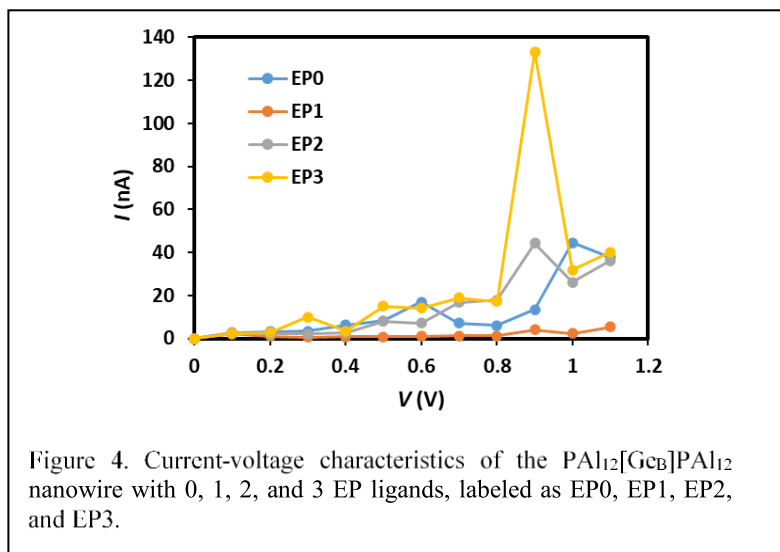
Figure 3. The density of states of the $(\text{EP})_n\text{PAI}_{12}[\text{Ge}^2_{\text{B}}]\text{PAI}_{12}$ for $n=1-4$. The projected density of states of both sides of the cluster are plotted separately with the ligated cluster on the left, and the non-ligated on the right. The red dotted lines indicate the shift of the HOMO and LUMO levels across the intercluster interface. HOMO-LUMO gaps in eV are given by Δ .

Our work focussed on a superatomic molecule formed by joining two PAI_{12} metallic clusters linked by an organometallic bridge. We showed that the combination can behave like a semiconductor and the addition of ligands can induce a significant shift between the conduction and valence band edges across the intercluster interface. The band alignment is induced by the N-ethyl-2-pyrrolidone ligands, and the placement of the ligands strongly affects the direction of the dipole moment, including the case where the dipole moment is parallel to the cluster interface. This provides an alternative strategy for constructing nanometer-scale electronic interfaces. The semiconducting features in the PAI_{12} clusters emerge from the grouping of the quantum states in a confined nearly free electron gas that creates a substantial energy gap. An organometallic $\text{Ge}(\text{CH}_3)_2(\text{CH}_2)_2$ bridge links the clusters while maintaining the cluster's electronic shell structure. The amount of band shifting between the bridged clusters can be changed by controlling the number of ligands. Attaching multiple ligands can result in the valence band edge of one cluster being aligned with the conduction band edge of the other bridged cluster. Furthermore, the singly ligated bridged

superatomic molecule was shown to exhibit promising features to separate the electron-hole pairs for photovoltaic applications.

4. Electron Transport through PAI₁₂-Based Cluster Complexes:

We also investigated the electronic transport through the PAI₁₂ superatomic dimer in discussed above. The electronic transport properties of PAI₁₂ based nanowires were investigated by density functional theory (DFT) in combination with the non-equilibrium Green's function (NEGF) method. Joining two PAI₁₂ clusters via a germanium linker creates a stable semiconducting nanowire with a large HOMO–LUMO gap. Sequential attachment of an electron-donating ligand, N-ethyl-2-pyrrolidone, to one of the two linked clusters results in the shifting of the electronic spectrum of the ligated cluster while the energy levels of the unligated cluster are mostly unchanged. Using this approach, one can eventually align the HOMO of the ligated cluster to the LUMO of the non-ligated cluster, thereby significantly reducing the HOMO–LUMO gap of the nanowire. As a result, the transport properties of the nanowire are highly dependent on the number of attached ligands. Although a single ligand is observed to generally decrease the current, the inclusion of two or more ligands shows a significant increase in the amount of current at most voltages. The resulting increase of the current can be attributed to two factors, first the reduction in the

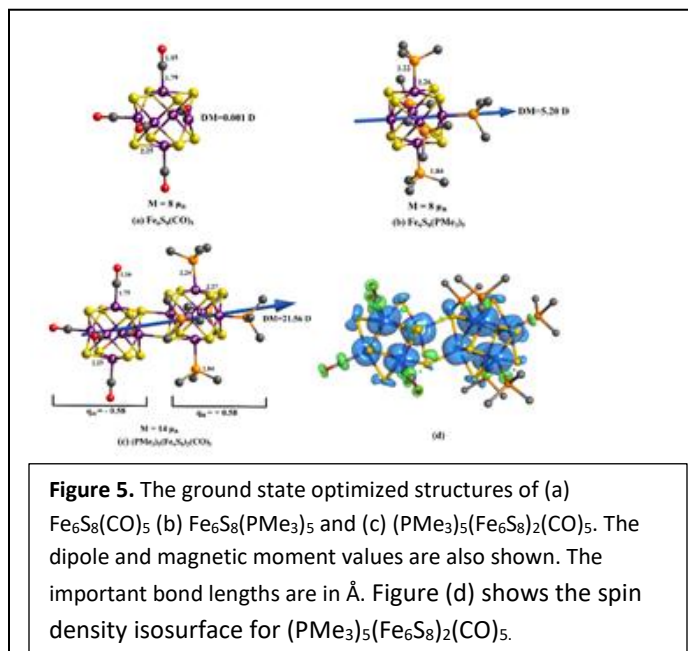


HOMO–LUMO gap due to ligand attachment which has moved the transmission orbitals into the bias window. Secondly, when two or more ligands are attached to the nanowire, the HOMO's become delocalized across the scattering region, and this significantly enhances the currents. Our results were featured on a cover page of Nanoscale Advances.

Magnetic Superatomic Dimer with Intense Electric Dipole Moment:

We then proceeded to examine if one could form a similar dimer that could be magnetic and also marked by intense internal electric field that could find applications in spintronix devices. To this end we investigated the electronic and magnetic properties of ligand decorated Fe₆S₈ cluster and fused superatomic dimer using the first-principles density functional theory. We first showed that the redox properties of the Fe₆S₈ cluster can be effectively controlled by altering the nature of the attached ligands. Donor ligands such

as phosphines reduce the ionization energy of the Fe_6S_8 cluster, whereas the acceptor ligands such as CO increase the electron affinity. Such variation in the redox properties of the Fe_6S_8 cluster is the result of the ligand-induced shift in the cluster's electronic levels, so the occupation number remains mostly unaffected,



leading to a marginal change in the spin magnetic moment of the cluster. A combination of two identical Fe_6S_8 clusters decorated by unbalanced ligands was shown to result in a superatomic dimer with a massive dipole moment and a large spin magnetic moment. Donor ligands on one side of the superatomic dimer with acceptor ligands on the other cause significant inter-cluster charge transfer. The resulting superatomic dimer offers an interesting motif for spintronics-related applications. Our work was featured on the cover page of the J. Phys. Chem. A.

5. Metal Chalcogenide Clusters as catalysts for CO_2 Dissociation and conversion to useful materials:

An important problem currently facing humanity is the climate changes resulting in an increase in temperature, floods, droughts, rising sea levels, and melting glaciers due to greenhouse gases. Carbon dioxide (CO_2) is considered the major greenhouse gas produced by the combustion of fossil fuels and industrial processes. Removal of CO_2 and, in particular, the conversion of CO_2 into useful chemicals is, therefore, one of the most consequential and challenging problems of the modern era. During the course of this proposal, we addressed two critical issues related to first thermochemical dissociation of CO_2 and then conversion of CO_2 to formic acid. Our first attempt was to investigate if metal chalcogenide clusters can be used for thermochemical dissociation of CO_2 .

As a first step thermochemical dissociation of CO_2 on pure, ligated, and mixed transition metal (W, Cu) chalcogenide clusters was investigated using the first-principles gradient corrected density functional approach. It was shown that although the pure and ligated metal chalcogenide clusters exhibit significantly high barriers for CO_2 dissociation, the computed barriers for the mixed clusters are relatively lower. The lowest barrier was obtained for the $\text{Cu}_3\text{W}_3\text{Se}_8$ cluster, which

showed a dramatically reduced barrier height of only 0.41 eV. Detailed analysis revealed that the substitution of W by Cu sites leads to a charge transfer from Cu to W sites resulting in locally active W sites. The lowering of the CO₂ dissociation barriers can be attributed to the facile transfer of charge from the locally active W sites and also due to the alteration of the binding energy of CO₂ to the charged W sites. Our studies provide an alternate strategy to design novel thermochemical catalysts for CO₂ adsorption and subsequent dissociation. Our work was featured on the cover page of the journal

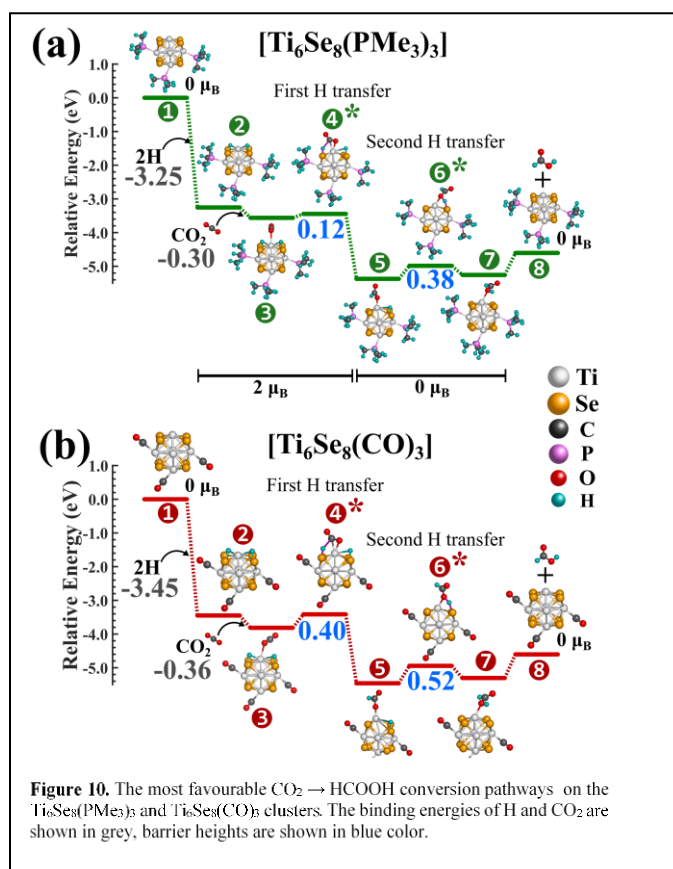


Figure 10. The most favourable CO₂ → HCOOH conversion pathways on the Ti₆Se₈(PMe₃)₃ and Ti₆Se₈(CO)₃ clusters. The binding energies of H and CO₂ are shown in grey, barrier heights are shown in blue color.

Fig. 6. Conversion barriers for various steps for transforming CO₂ to formic acid.

In a subsequent paper, that is being submitted, we investigated the conversion of CO₂ into useful chemical formic acid. First-principles theoretical studies were carried out to investigate the formation of formic acid via the hydrogenation of CO₂ using bare and ligated Ti₆Se₈ clusters as catalysts. We have examined PMe₃ ligands that act as donors and the CO ligands that act as acceptors. It is shown that these ligands lead to a raising or lowering of the electronic spectrum of the cluster, thereby transforming the Ti₆Se₈ cluster into an effective donor or acceptor. The initial addition of H atoms leads to absorption where the H atoms occupy sites close to Se atoms leaving the Ti sites available for effecting the catalytic conversion. The reaction barriers for the addition of first and second hydrogen to the CO₂ cluster are shown to be sensitive to the number and nature of ligands. Detailed studies indicate various mechanisms that lead to the change in barriers. First,

the donor clusters are found to bind H more weakly, thereby facilitating the H transfer to CO₂. Secondly, the donor clusters are found to be better charge donors to the CO₂ molecule at the transition state, enabling a lower barrier to bind H atoms. Finally, the raising of the electronic levels in donor clusters reduces the effective binding of CO₂ in the pre-reaction complex, thereby reducing the barrier. These studies provide unique opportunities to control the reaction rates by using a combination of donor/acceptor ligands.

6. Infrared and optical absorption spectra of metal chalcogenide clusters: Examination of Periodic Trends

We had proposed to investigate the optical and vibrational properties of the metal-chalcogenide clusters. Our objective was not only to investigate these properties but also to examine the periodic trends that could allow us to extend the superatomic concept to these clusters. With this objective, we investigated the optical absorption, infrared spectra, binding energies, and other cluster properties to investigate whether periodic trends can be observed in the electronic structure of transition metal chalcogenide clusters ligated with CO ligands. Our studies demonstrated the existence of several periodic trends in the properties of pure and mixed octahedral metal chalcogenide clusters, TM₆Se₈(CO)₆, (TM=W-Pt). We find that octahedral metal-chalcogenide clusters with 96, 100, and 114 valence electrons have larger excitation energies, consistent with these clusters having

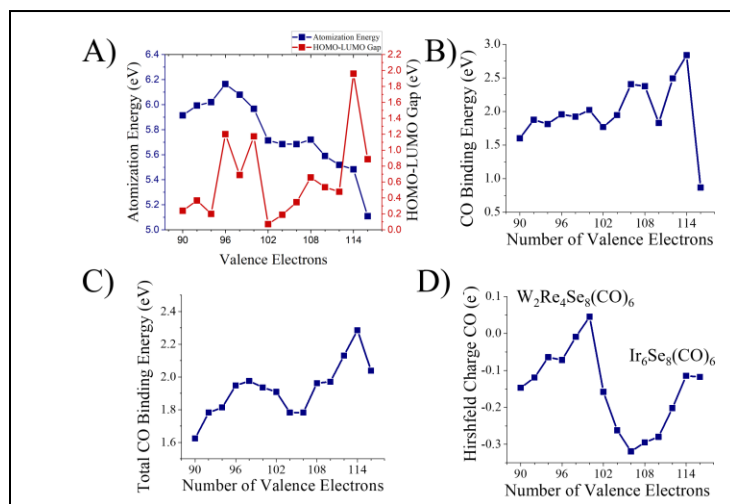


Figure 7: A) The atomization energy, B) CO removal energy energy, C) Total CO binding energy, and D) Hirshfeld charge on the CO molecules for the TM₆Se₈(CO)₆ clusters.

closed-electronic shells. Periodic trends were observed in the infrared spectra, with the CO bond stretch having the highest energy at 100 and 114 valence electrons due to the closed-electronic shell minimizing back-bonding with the CO molecule. A periodic trend in the antisymmetric TM-C stretch was also observed, with the vibrational energy increasing as the valence electron count increased. This is due to decrease in the TM-C bond length resulting in a larger force constant. In addition to providing information on the vibrational spectra and optical properties, these results reveal that periodic trends seen earlier in simple or noble metal clusters can be observed in symmetric transition-metal chalcogenide clusters, showing that the superatom concept in metal

chalcogenide clusters goes beyond electronic excitations, and can be seen in other observable properties.

Impacts:

Development of the principle discipline of the project.

The work completed during the project is going to have tremendous impact in numerous areas. First, the ability to control redox properties by attaching charge transfer ligands will lead to super donor and super acceptor clusters that will have applications in a variety of areas including as chemical dopants to synthesize p- and n- type semiconductors via deposition on surfaces. This is extremely important since the conventional doping involves replacement of atoms whereas the surface doping does not require introducing defects in underlying structure. More importantly, the ability to control placement of energy levels is critical to creating nano p-, n- junctions that could absorb light and separate electron hole pairs.

Our studies on using metal chalcogenide clusters as catalysts are unique as they will allow thermochemical conversion of CO₂ to formic acid thus reducing greenhouse gases and converting them to useful products.

Our studies on vibrational and optical spectra are valuable in identifying periodic trends thus enabling extension of superatomic framework to metal chalcogenide clusters.

Other Disciplines:

As outlined above, our findings are significant in areas of nano transport and catalysts to convert greenhouse gases into useful products.

Impact on the Development of Human Resources

The student carrying out studies on vibrational and optical spectra is a minority undergraduate student who just graduated but wanted to do important research before joining the graduate school. He is currently being interviewed at other places for a Ph.D. program.

Impact on teaching and Educational Practices:

I am co-developing an undergraduate course on nanoscience and most of the findings during the current proposal have been incorporated into the new course.

Impact on physical, institutional, and information resources

We have carried out theoretical studies.

Impact on Society beyond science and technology

The rapid increase of the CO₂ level in the atmosphere has become a serious concern to mankind in recent times. One of the direct solutions to the problem is utilizing porous or mesoporous adsorbents as a medium for CO₂ capture. However, the higher cost associated with storage and transport restricts such procedures from large-scale industrial applications. As an alternative, the conversion of CO₂ into useful chemicals represents a relatively cost-effective strategy. Aside from reducing CO₂ concentration in the atmosphere, the converted products can also be utilized as a resource for higher value-added chemicals. Among the assortment of chemicals that CO₂ can be chemically converted into, formic acid (FA) represents a compelling choice for a multitude of reasons. As a chemical, formic acid is extensively used as feedstock material and can also be transformed into higher value-added products with relative ease. As an energy-dense material, it can also be used as an alternative to fossil fuels, thereby being effective in reducing the carbon footprint. Our work demonstrating that ligated clusters can lead to thermochemical conversion is an important discovery.

Changes:

Changes in Approach; None

Problems or Delays: No cost extensions were approved due to delays associated with Covid-19.

Expenditure Impacts: None

Significant Changes in the use of human subjects: Not Applicable

Changes in primary place of performance: None

Technical Updates:

Our work was featured on the cover of three journals. Copies of the cover are included herewith.

