

Chapter 11. Integrated Molecular Modeling, Synthesis, and Characterization Experiments for the Undergraduate Inorganic Chemistry Laboratory.

Results and Discussion

We have developed a series of integrated molecular modeling, synthesis, and characterization laboratory experiments. These allow students to use the results of molecular modeling experiments to make predictions about the physical properties of compounds, and compare these predictions to experimental data. This approach was designed to allow the students to develop molecular modeling skills within a context that allows for rapid testing of the molecular modeling results. The traditional synthesis and characterization aspects essential to an upper level undergraduate laboratory course are maintained. This project of developing a new curricular approach to using computer-assisted methods has been evaluated using a comprehensive, standardized student interview format. This process of evaluation was selected to obtain detailed evaluation data, and to minimize bias from the evaluation design.

Design of the Lab Exercise.

Our junior/senior level inorganic laboratory course was selected for the initial implementation of this experiment. Molecular modeling programs can be of great benefit to students in inorganic chemistry courses because many of the properties of inorganic molecules are explained in terms of molecular orbitals. Students frequently have a difficult time understanding this topic. When visualized, molecular orbital theory may be easier for undergraduates to understand. Despite this benefit, few undergraduate inorganic laboratory experiments have been published utilizing molecular modeling.^{139, 164,165} Additional factors important in choosing the inorganic laboratory were the low total course enrollment (approx. 25 students) which simplifies logistical aspects.

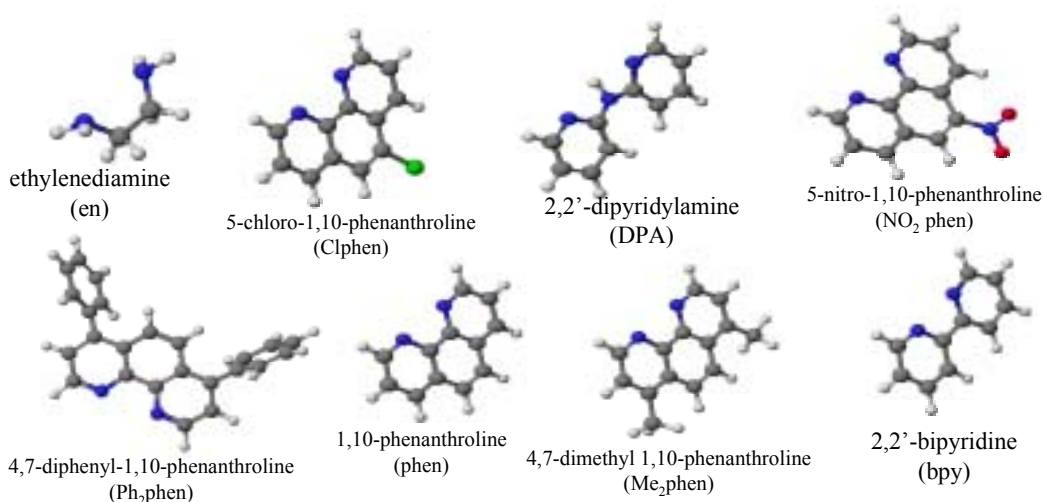
This integrated project requires students to use the chemical literature to design synthetic methods and to learn about molecular modeling techniques. This is done with the help of WWW based tutorials and exercises.

The use of lab groups was implemented based on the data supporting cooperative learning in the classroom and laboratory.^{138,139} I felt that by using partners, discussion of laboratory technique and the associated theories would be facilitated. The use of lab pairs is also beneficial to the students in making the correlations and predictions regarding molecular modeling results and characterizational techniques. Laboratory reports are prepared individually.

A Schematic outlining the design of the integrated molecular modeling, synthesis, and characterization laboratory experiment is found in Scheme 10.1 (page 96). This experiment is open-ended and student driven. (Step 1) Students are presented with a brief oral introduction to experimental design. This serves to provide student with background on the molecular modeling, characterization, and theory necessary to perform this experiment. (Step 2) Each pair of students selects two N-N ligands for use in the study of the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes. Students are permitted to use any two N-N ligands (N-N = bidentate, nitrogen donor ligands) for investigation in this experiment. Many different suitable N-N ligands are commercially available at low to moderate cost, or are easily prepared, see Figure 11.1 for examples. (Step 3) A feasible synthesis (either photochemical or thermal) for each complex is developed by the students and must be approved by the instructor before the student can proceed. Syntheses are adapted from the chemical literature, examples of both a thermal⁹⁶ and photolytic⁷⁹ procedure are provided to the students in their laboratory manual. (Step 4) The reagents and supplies necessary to complete both syntheses are located. (Step 5) Students complete the WWW tutorials to learn about molecular modeling and the CAChe software package. This software was selected for its ability to perform molecular orbital calculations on organometallic complexes, its “user friendly” interface, and the data output is visual/structural in nature. This allows the students to explore the CAChe program at their own pace and serves as an introduction to molecular modeling. CAChe allows for molecular mechanics energy minimizations of the Mo complexes as well as the Extended Huckel and ZINDO molecular orbital calculations. (Steps 6 and 7) The students then model the two complexes they have selected using the CAChe software package. Calculations performed and properties measured are based on the predictions that the students wish to

test. Students then select the physical properties that they wish to investigate in the laboratory and select calculation types that will provide useful information for correlation. (Step 8) Students make predictions (hypothesis) about the relative properties of the two compounds based upon calculated data from the modeling.

Figure 11.1. Examples of N-N Ligands that Form $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complexes.



(Step 9) After completing the modeling section of the experiment, the students submit a report. This outlines the modeling they performed, the properties they chose to model, the modeling results, and the predictions of the expected relative properties of the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems (hypothesis). The format of this report has varied from year to year. This has been done either as a formal laboratory report, or as a poster presentation. It should be noted that student predictions must be made, and this initial report submitted prior to beginning the synthesis of the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes. The first (modeling) part of the experiment (Steps 1-8) takes the students between one and two three-hour laboratory periods to complete.

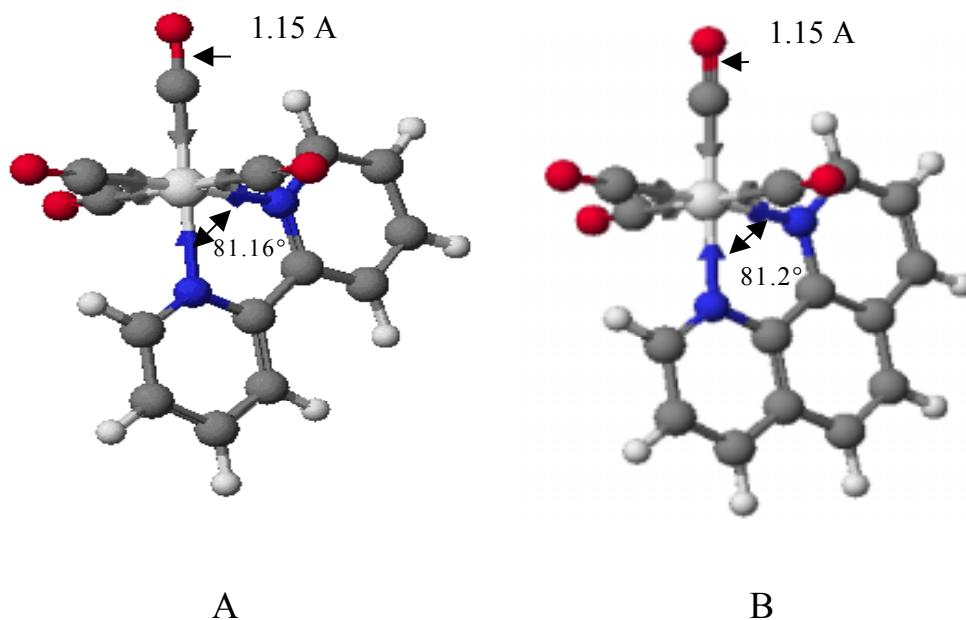
In the second part of the experiment (synthesis and characterization), (Step 10), the students synthesize the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems they modeled, and test their molecular modeling based predictions. Two general methods of preparing compounds of the form $[\text{Mo}(\text{CO})_4(\text{N-N})]$ are provided for the students to use in designing their preparations, thermal⁹⁶ and photochemical⁷⁹ (Scheme 7.1, page 67). (Step 11) After synthesizing the compounds, the students characterize them to demonstrate that the desired compounds were prepared. (Step 12) Then they compare the physical data obtained for the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ compounds to their calculation-based predictions (hypothesis). (Step 13) The synthesis, characterization, and analysis of their predictions are the subject of a second report. This report has always been a formal laboratory report in Inorganic Chemistry format. The second (synthesis and characterization) portion of the experiment requires between two and three three-hour laboratory periods to complete.

Molecular Modeling.

The following discussion of molecular modeling results and correlations details my research in the computational aspect of developing the integrated experiment. Information on the specific aspects of molecular modeling, as well as the relationships tested between synthetic and computational data for the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes are presented.

Geometry optimization of the compounds using the molecular mechanics routine was performed with the CAChe software. These showed the expected octahedral geometries around the molybdenum atoms, Figure 11.2 and Appendix XX (pp 159 – 161). The molecular mechanics geometry optimization allows viewing of bond angles and bond lengths for the complex being modeled (Figure 11.2). The values obtained computationally can be compared to X-ray crystallography data. For $[\text{Mo}(\text{CO})_4(1,10\text{-phenanthroline})]$, the Mo-C bond lengths deviate only slightly from the experimental lengths (by about 0.02-0.05 Å).⁹⁷ The Mo-N bond lengths were found to be substantially different in the calculated structure (0.15 Å). The C-Mo-C angles for cis-CO ligands deviated by between 3° from the experimental structure. This difference is probably due to the error in the N-Mo-N angle (81° calculated vs. 74° experimental).

Figure 11.2. Geometry Optimization of $[\text{Mo}(\text{CO})_4(\text{bpy})]$ (A) and $[\text{Mo}(\text{CO})_4(1,10\text{-phen})]$ (B) by Molecular Mechanics Energy Minimization.



Atom Types: blue = nitrogen, gray = carbon, white = hydrogen, red = oxygen.

ZINDO was also used to calculate partial charges, bond orders, molecular orbitals, electron density, orbital energies, and UV-vis spectra of the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes, Figure 11.3 and Appendix XXII (pp 167-171). The $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems geometry was optimized first using a molecular mechanics calculation, then the desired ZINDO calculation was completed. This was due to the fact that attempts to optimize the geometry with ZINDO resulted in the structures containing a four-membered carbon ring composed of the carbons from the carbonyl ligands. This is a documented problem with the ZINDO algorithm (small strained rings are calculated to be very stable).¹⁰³ The ZINDO calculated partial charges and bond orders, and electron density isosurface for $[\text{Mo}(\text{CO})_4(\text{bpy})]$ are shown in Figure 11.4.

Figure 11.3. HOMO and LUMO Frontier Orbitals of $[\text{Mo}(\text{CO})_4(\text{bpy})]$ (A) and $[\text{Mo}(\text{CO})_4(1,10\text{-phen})]$ (B) Calculated with the ZINDO Algorithm. Atom Types: blue = nitrogen, gray = carbon, white = hydrogen, red = oxygen.

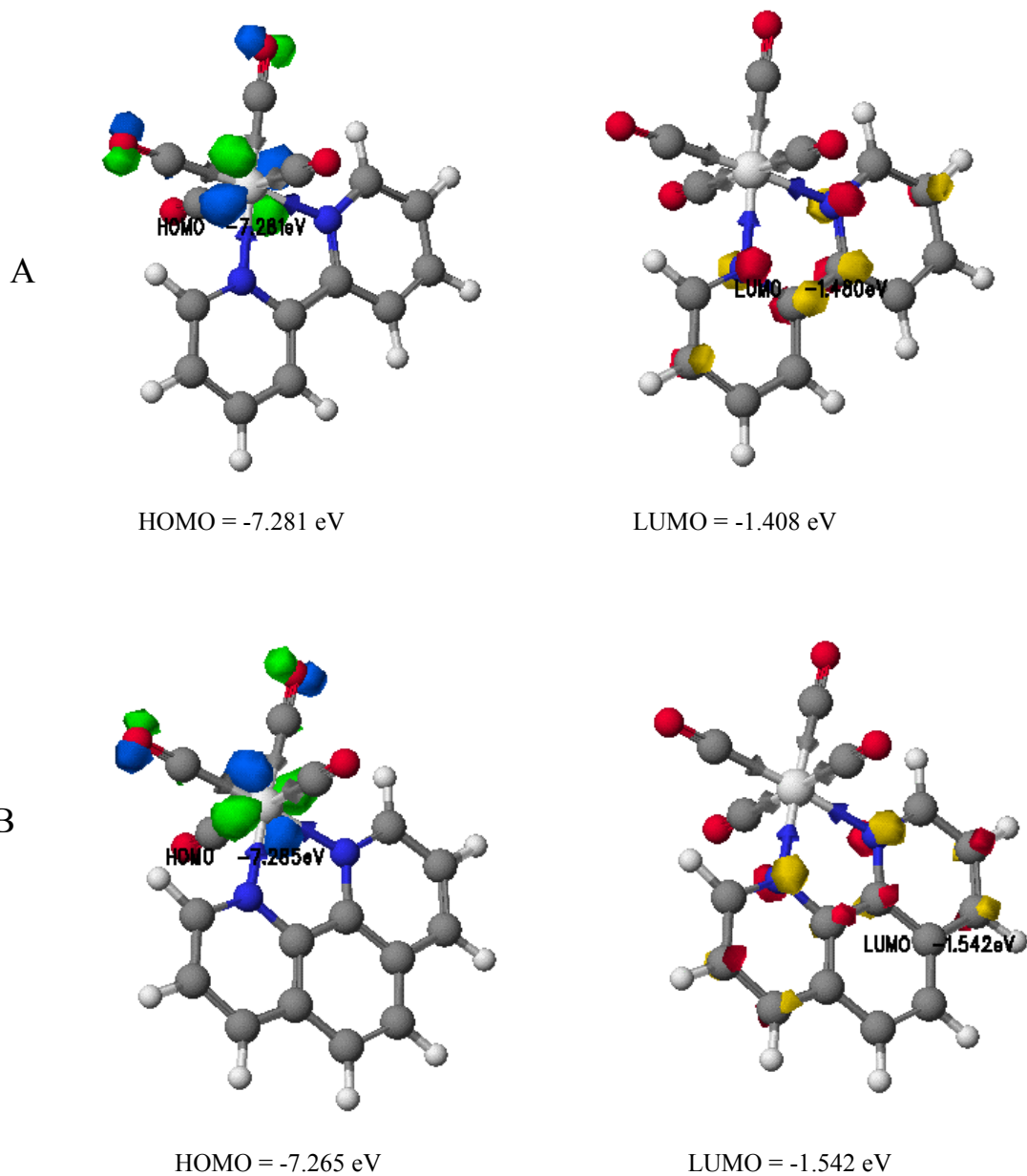
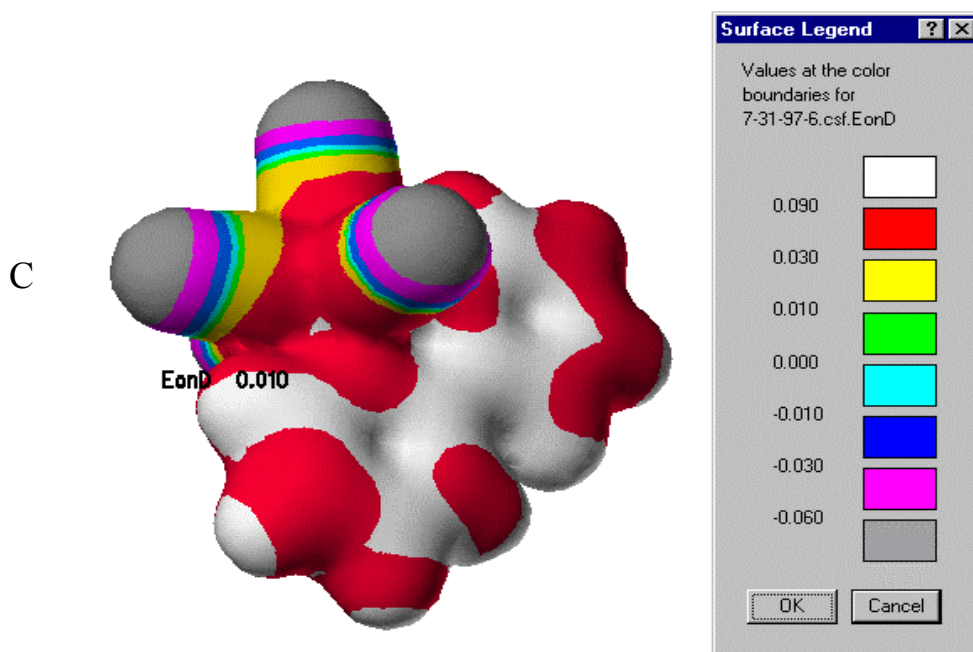
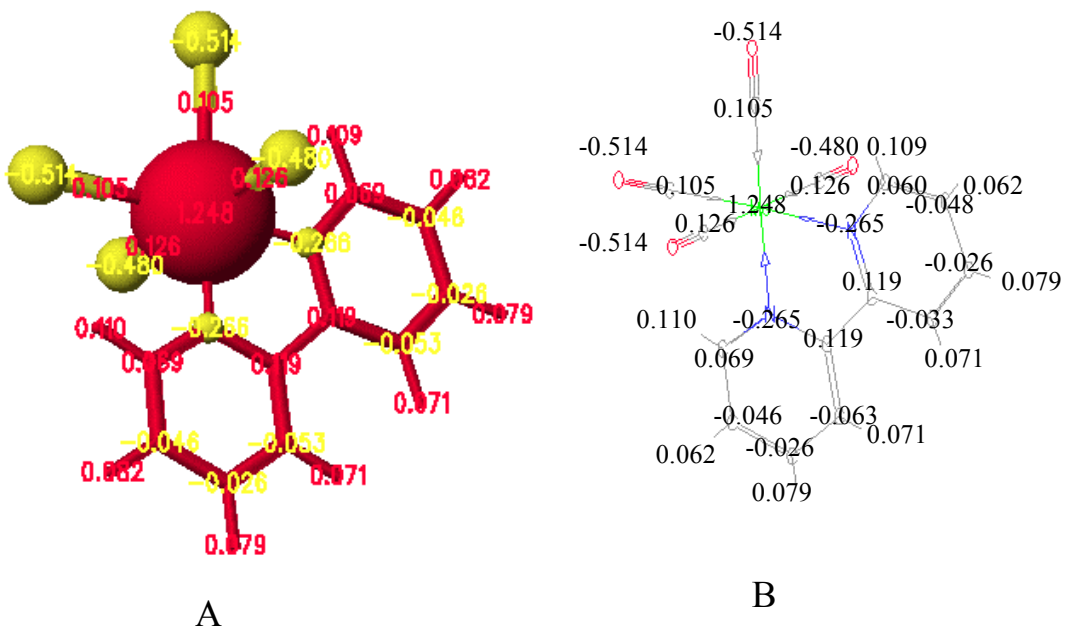


Figure 11.4. ZINDO (INDO/1) Calculated Partial Charge and Bond Order (A and B) and Electron Density Isosurface (C) for $[\text{Mo}(\text{CO})_4(\text{bpy})]$.



Extended Huckel calculations were also completed on the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes to calculate partial charges, bond orders, molecular orbitals, electron density, and orbital energies, Figures 11.5, 11.6, and Appendix XXI (pp 162 – 166). As with the ZINDO calculations, $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes geometry was optimized first using a molecular mechanics calculation, then the desired Extended Huckel calculation was completed. The Extended Huckel algorithm does not provide geometry optimization; therefore the molecule must first be optimized using molecular mechanics.¹⁰⁴

Figure 11.5. HOMO and LUMO Frontier Orbitals of $[\text{Mo}(\text{CO})_4(\text{bpy})]$ (A) and $[\text{Mo}(\text{CO})_4(1,10\text{-phen})]$ (B) Calculated with the Extended Huckel Algorithm. Atom Types: blue = nitrogen, gray = carbon, white = hydrogen, red = oxygen.

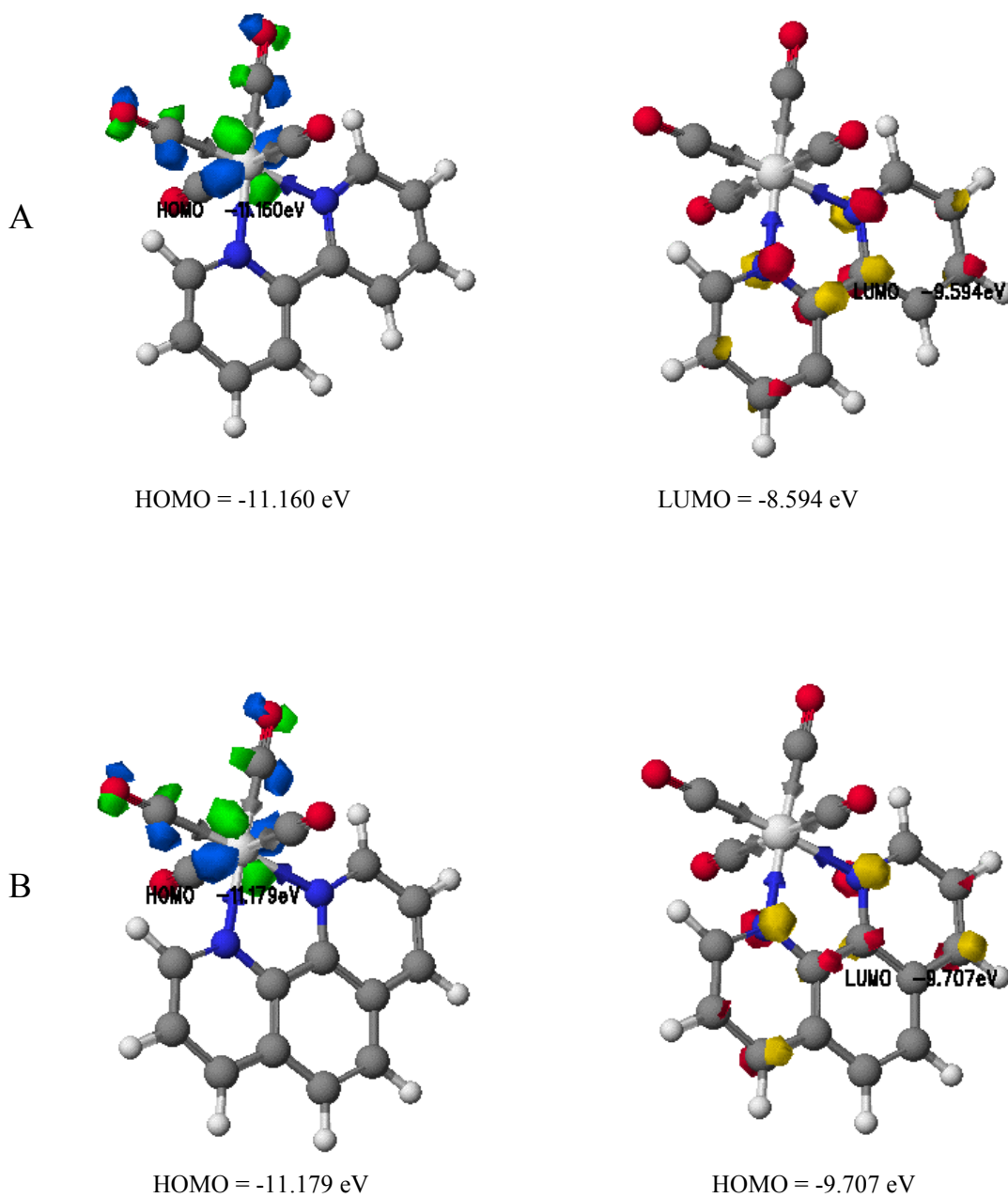
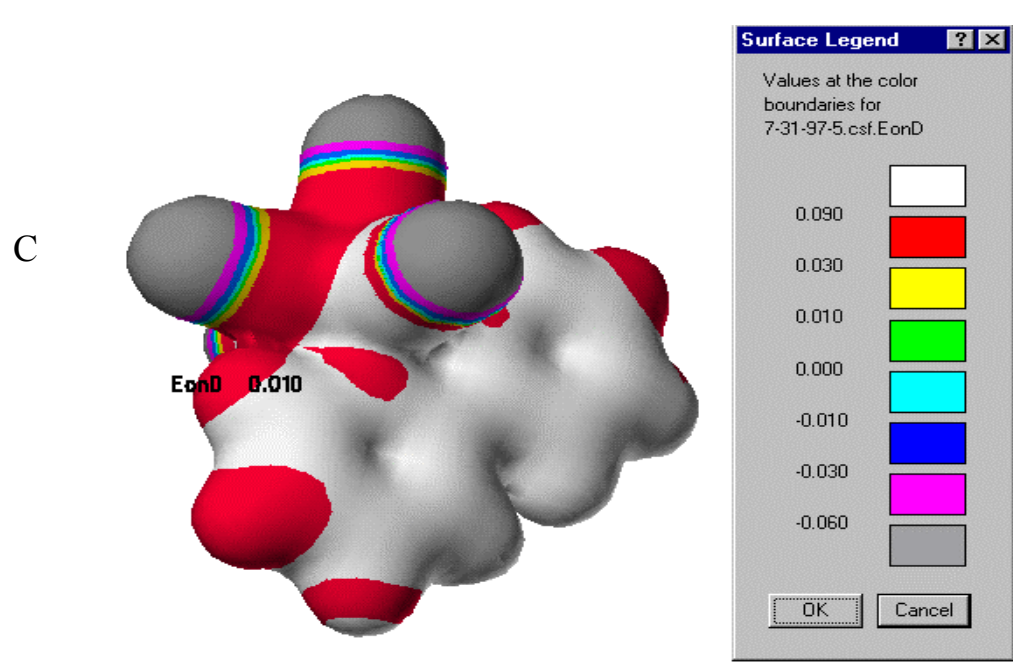
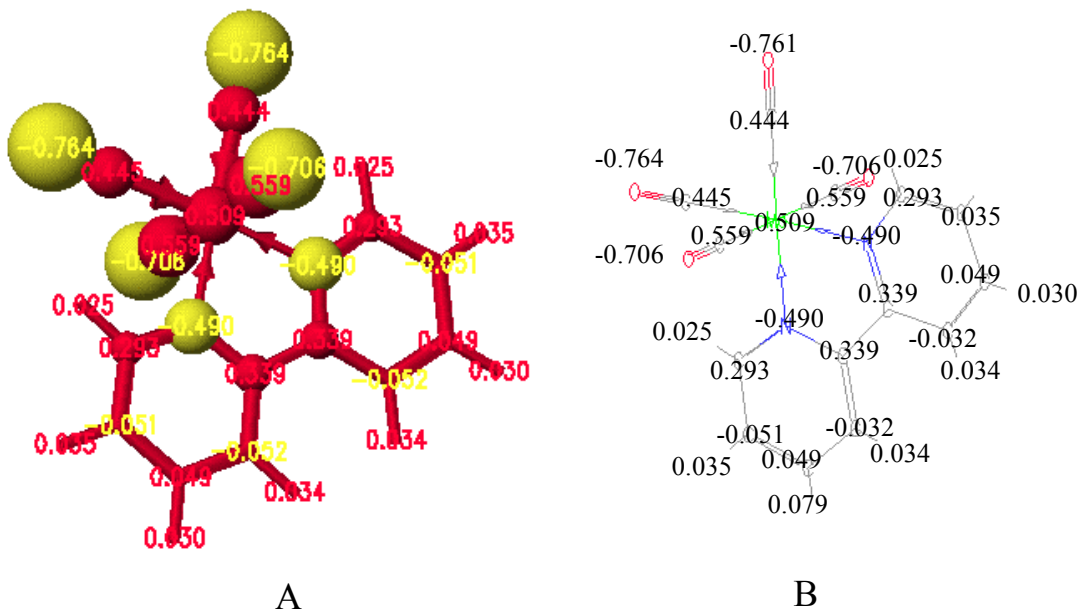


Figure 11.6. Extended Hückel Calculated Partial Charge and Bond Order (A and B) and Electron Density Isosurface (C) for $[\text{Mo}(\text{CO})_4(\text{bpy})]$.



When comparing the ZINDO and Extended Huckel calculations of the same molecule, $[\text{Mo}(\text{CO})_4(\text{bpy})]$, similarities and differences between the results are noted. Both the ZINDO and Extended Huckel algorithms find the HOMO to be primarily a molybdenum $d\pi$ orbital. The LUMO orbital is an N-N ligand (bpy) π^* antibonding orbital for both methods. The shape of the calculated HOMO and LUMO for $[\text{Mo}(\text{CO})_4(\text{bpy})]$ is the same with both techniques. The ZINDO orbital energy values (HOMO -7.281 eV, LUMO -1.480 eV) differ significantly from those calculated at the Extended Huckel level (HOMO -11.160 eV, LUMO -9.594 eV). The difference between the HOMO and LUMO energies for the two algorithms varies dramatically: ZINDO (Δ HOMO/LUMO 5.801 eV), Extended Huckel (Δ HOMO/ LUMO 1.566 eV). These orbital energy differences are closely tied to physical observations that the students can investigate. As the ZINDO and Extended Huckel algorithms calculate very different values for the HOMO and LUMO, correlations between computational and physical data are expected to yield different results.

In viewing the partial charge and calculated bond order for $[\text{Mo}(\text{CO})_4(\text{bpy})]$ as calculated at both the ZINDO and Extended Huckel level, easily visible differences appear in the results (Figures 11.4 and 11.6). These differences arise especially in the calculation of the partial charges for the molybdenum, carbon, and oxygen atoms. For example, the ZINDO algorithm calculates the partial charge of oxygen (-0.480 and -0.514) and carbon (0.125 and 0.105), whereas Extended Huckel calculates the partial charge of oxygen (-0.764 and -0.706) and carbon (0.559 and 0.544). Partial charge can also be used to correlate with characterization data.

Correlations: Computational versus Characterizational Data.

Correlations were tested between the computational results and the physical (characterizational) data for the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes, Table 11.1.

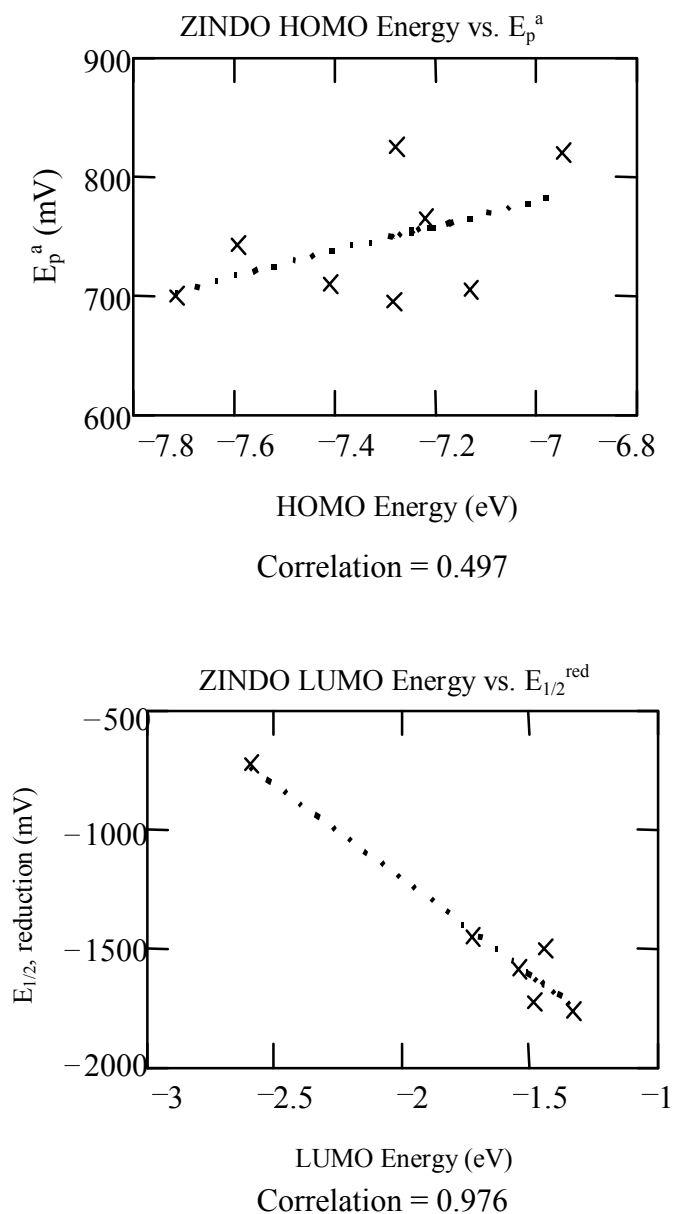
Table 11.1. Relationships Tested Between Computational and Characterizational Data for the Series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complexes.

Characterizational Data	Molecular Modeling Result
Electrochemistry $E_p^{\text{a oxidation}}$ $E_{1/2, \text{reduction}}$	Orbital Energies HOMO Energy LUMO Energy
MLCT Energy for Electronic Absorption Spectroscopy	HOMO-LUMO energy gap
Electronic Absorption Spectroscopy	Calculated Electronic Absorption Spectroscopy
^1H NMR Chemical Shift	Partial Charges on H Nuclei

The first set of correlations tested were between the $E_p^{\text{a oxidation}}$ and $E_{1/2}^{\text{red}}$ obtained with cyclic voltammetry, and the calculated HOMO and LUMO energies. The cyclic voltammograms of the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes are described by an irreversible metal based oxidation and a reversible ligand based reduction. Full details of the cyclic voltammetry of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes are reported in Chapter 7. The electrochemically obtained values are compared with computationally obtained HOMO and LUMO energy results. This was done for the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes, using both the ZINDO algorithm (Figure 11.7) and the Extended Huckel algorithm (Figure 11.8).

Figure 11.7 shows the relationship between the HOMO energy calculated at the ZINDO level and the $E_p^{\text{a oxidation}}$ (A), and the LUMO energy calculated at the ZINDO level and the $E_{1/2}^{\text{red}}$ (B). The HOMO energy versus $E_p^{\text{a oxidation}} (\text{Mo}^{0/+})$ plot (A) shows a

Figure 11.7. Correlation Between ZINDO HOMO Energy and E_p^a (A) and ZINDO LUMO Energy and $E_{1/2}^{\text{red}}$ (B) for the Series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complexes, where E_p^a = peak oxidation potential, $E_{1/2}^{\text{red}}$ = reduction potential. N-N ligands used include: ethylenediamine, 5-nitro-1,10-phen, 5-chloro-1,10-phen, 4,7-Ph₂-1,10-phen, 1,10-phen, bpy, 4,4'-Me₂-bpy, and DPA.



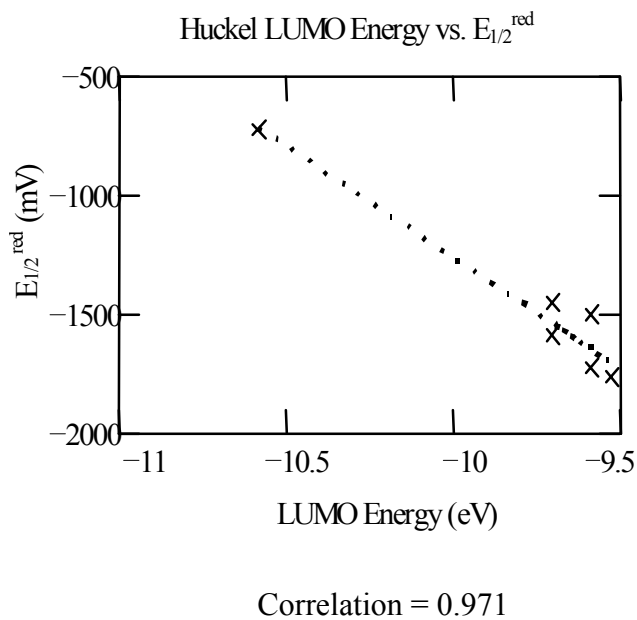
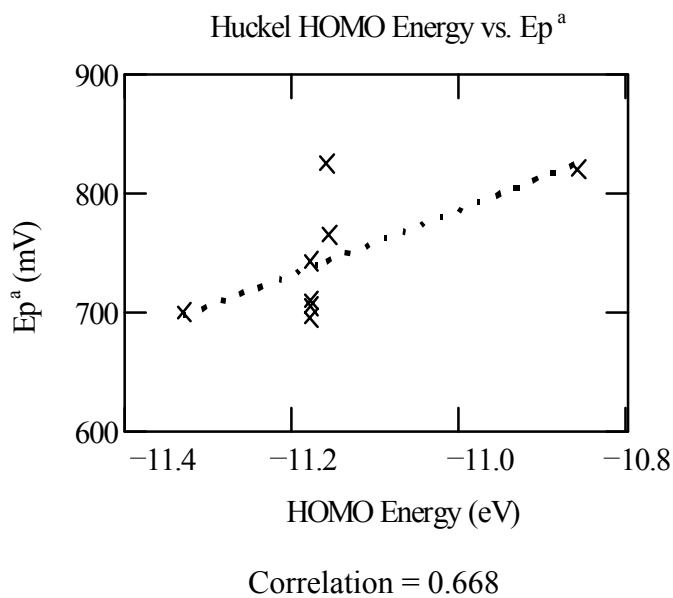
correlation coefficient of 0.497. E_p^a for irreversible processes are typically not good measures of E^0 . Throughout the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems, although the N-N ligand is being varied, there is not a large change in the $\text{Mo}^{0/+}$ oxidation potential, spanning 120 mV. When calculating the metal-based HOMO energy level, the ZINDO algorithm appears to exaggerate the effect of changing the N-N ligand (1000 mV). Thus, it is difficult to draw conclusive correlations between the HOMO energy versus E_p^a .

The LUMO energy versus $E_{1/2}^{\text{red}}$ Figure 11.7 plot (B) contains two less data points as the $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems where N-N= ethylenediamine and DPA do not display ligand-based reductions in cyclic voltammetry measurements. A correlation is seen (0.976). Both the electrochemical process and the calculated LUMO orbital are ligand-based. As the N-N ligand is varied throughout the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes, there is a substantial change in reduction potential (1100 mV) and the LUMO energy values (1200 mV from 5-nitro-1,10-phen to bpy). This larger effect may enhance the correlation between experimental and theoretical data. This data had an outlying point 5-nitro-1,10-phen which when omitted leads to a correlation = 0.739.

Figure 11.8 shows the relationship between the HOMO energy calculated at the Extended Huckel level and the E_p^a (A), and the LUMO energy calculated at the Extended Huckel level and the $E_{1/2}^{\text{red}}$ (B). The HOMO energy versus E_p^a plot (A) shows a lack of correlation (0.668), but displays quite interesting results. The HOMO energy calculation at the Extended Huckel level yields almost identical energies for the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes, except for $[\text{Mo}(\text{CO})_4(\text{ethylenediamine})]$ and $[\text{Mo}(\text{CO})_4(\text{DPA})]$. This lack of variation in the HOMO energies leads to a poor correlation with the varied E_p^a potentials.

As with the ZINDO algorithm, the LUMO energy calculated at the Extended Huckel level versus $E_{1/2}^{\text{red}}$ (Figure 11.8 B) displays a good correlation (0.971).

Figure 11.8. Correlation Between Extended Huckel HOMO Energy and E_p^a (A) and Extended Huckel LUMO Energy and $E_{1/2}^{\text{red}}$ (B) for the Series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complexes, where E_p^a = peak oxidation potential, $E_{1/2}^{\text{red}}$ = reduction potential. N-N ligands used include: 1,10-phen, 5-chloro-1,10-phen, 5-nitro-1,10-phen, 4,7-Ph₂-1,10-phen, bpy, 4,4'-Me₂-bpy, ethylenediamine, and DPA.



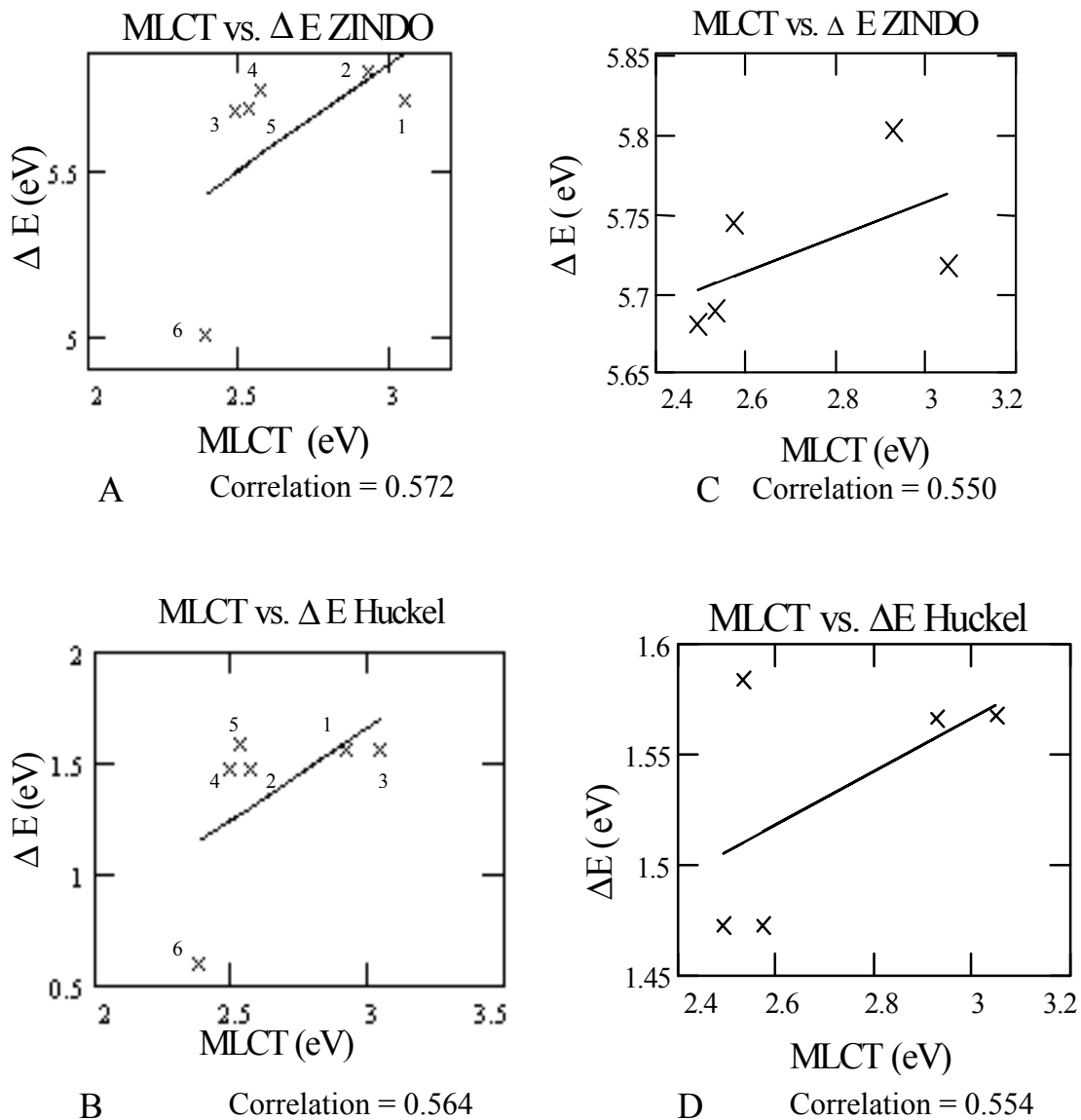
Although the ZINDO and Huckel methods gives different values for the orbital energies and HOMO – LUMO ΔE , they provide similar correlations with experimental data.

The next set of correlations tested was between the experimentally measured MLCT energy from the lowest lying transition in the electronic absorption spectroscopy and the calculated HOMO-LUMO gap, Figure 11.9.

In viewing both (A) and (B) in Figure 11.9, it is clear that the addition of the electron withdrawing nitro group to $[\text{Mo}(\text{CO})_4(1,10\text{-phen})]$ has a significant, measurable affect on the electron absorption spectrum, but a much smaller affect on the computational results. However, removal of this outlying $[\text{Mo}(\text{CO})_4(5\text{-nitro-}1,10\text{-phen})]$ point does not improve the correlation value, as illustrated in C and D in Figure 11.9. This is attributed to the fact that the values being compared span such a small numerical region (≈ 1 eV), making correlations between a small number of points difficult.

Molecular orbital calculations do not always yield HOMO and LUMOs that can be accurately compared with MLCT values. The MLCT is a spectroscopic transition from occupied metal based $d\pi$ orbitals to an empty ligand based (π^*) orbital. Molecular orbital calculations at both the ZINDO and Extended Huckel level sometimes find a HOMO/LUMO result that does not match this transition, as proper orbital overlap is needed for the optical process, Figure 11.10. The HOMO and LUMO are displayed in (A) for $[\text{Mo}(\text{CO})_4(\text{bpy})]$. The calculated HOMO is not of the appropriate symmetry to overlap the LUMO, making an MLCT transition possible. The HOMO –1 energy (B), however, is of the proper symmetry and should be used for comparison between the computational and MLCT data.

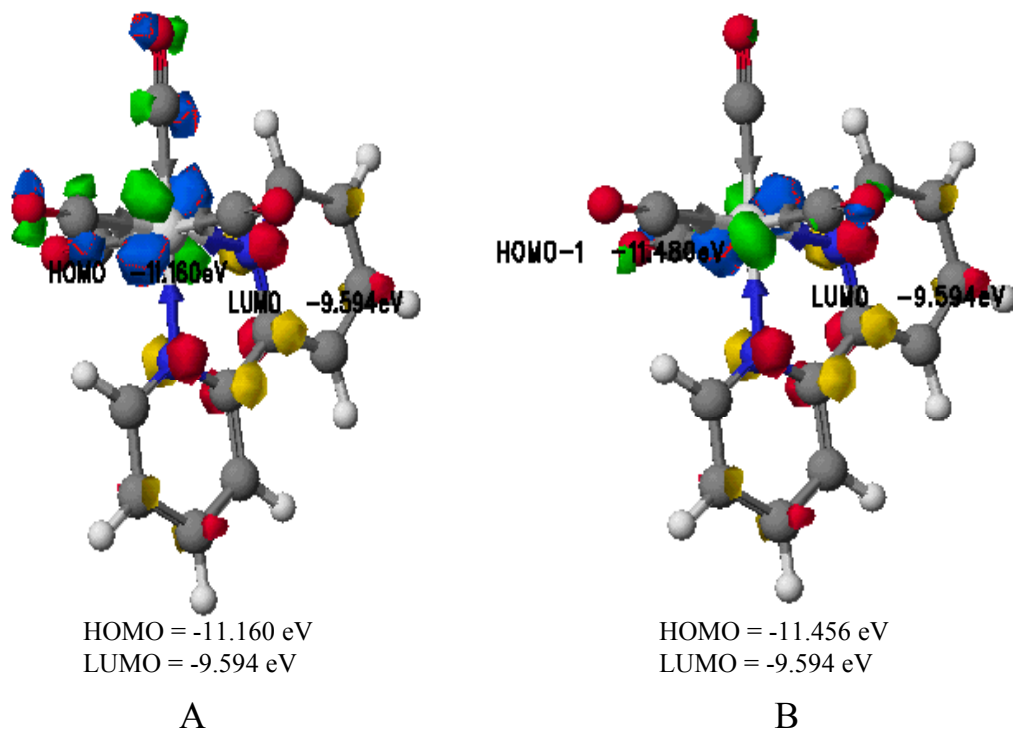
Figure 11.9. MLCT vs. HOMO-LUMO Gap Calculated at the ZINDO (A), and Extended Huckel (B) Levels, Omitting the Point for 5-nitro-1,10-phen (ZINDO) (C), Omitting the Point for 5-nitro-1,10-phen (Extended Huckel) (D). Each Point is Labeled as to which $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complex it Represents.



$[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complex

1. bpy
2. phen
3. 4,7-Me₂ phen
4. 5-Cl
5. 4,7-Ph₂ phen
6. 5-Nitro

Figure 11.10. Extended Huckel Molecular Orbital Calculation Results Depicting the Inappropriate Symmetry Match (A) and Appropriate Symmetry Match (B) of HOMO – LUMO to Correlate to Observed MLCT Optical Transitions.



Atom Types: blue = nitrogen, gray = carbon, white = hydrogen, red = oxygen.

UV-visible spectra calculations were completed for the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes using the ZINDO algorithm at current geometry/CI (Configuration Interaction) (Figure 11.10 and Appendix XXIII (pp 172 – 179)). The calculated data have been tabulated, and the correlations between the calculated and experimental MLCT energy tested (Table 11.2 and Figure 11.11, respectively). CAChe calculates reasonable electronic absorption spectra and is able to show the orbital involved in the electronic transitions. However, calculated electronic absorption transitions are consistently blue shifted from actual values, with differences being most prominent in the ultraviolet region. The $\lambda_{\text{max}}^{\text{abs}}$ MLCT calculated spectra do not take into consideration solvent effects, which can be quite large in charge transfer spectroscopy

Table 11.2. Experimental Electronic Absorption Spectroscopy and ZINDO based Calculation Lowest Lying MLCT for $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complexes.

$[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complex	Expt. MLCT $\lambda_{\text{max}}^{\text{abs}}$ in nm (eV)		Calc. MLCT $\lambda_{\text{max}}^{\text{abs}}$ in nm (eV)	
$[\text{Mo}(\text{CO})_4(\text{phen})]$	482	(2.57)	395	(3.14)
$[\text{Mo}(\text{CO})_4(5\text{-Cl-phen})]$	498	(2.49)	412	(3.01)
$[\text{Mo}(\text{CO})_4(5\text{-NO}_2\text{-phen})]$	520	(2.38)	434	(2.86)
$[\text{Mo}(\text{CO})_4(4,7\text{-Me}_2\text{-phen})]$	450	(2.75)	396	(3.13)
$[\text{Mo}(\text{CO})_4(4,7\text{-Ph}_2\text{-phen})]$	490	(2.53)	410	(3.02)
$[\text{Mo}(\text{CO})_4(\text{bpy})]$	474	(2.62)	419	(2.96)

Figure 11.11. The ZINDO Calculated (A) and Experimentally Obtained (B) Electronic Absorption Spectrum for $[\text{Mo}(\text{CO})_4(\text{bpy})]$, where bpy = 2,2'-bipyridine.

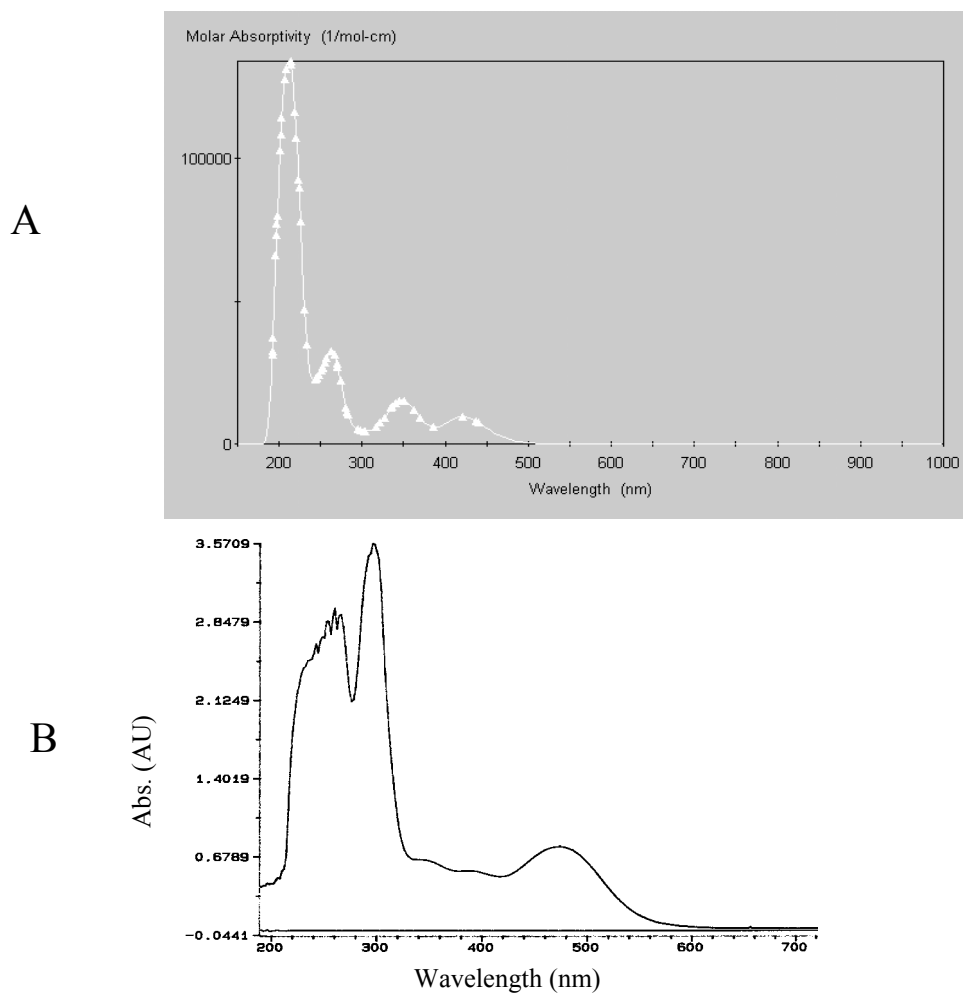
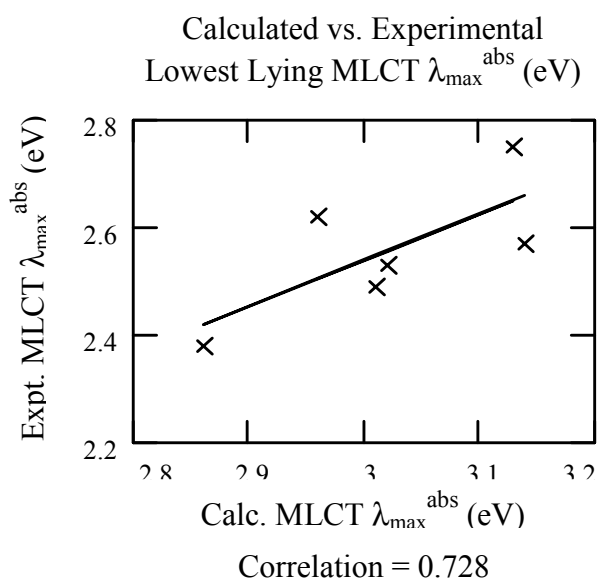


Figure 11.12 gives the correlation between the calculated UV-visible $\lambda_{\max}^{\text{abs}}$ using the ZINDO and the experimental value. The full series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes were considered, resulting in a plot with a correlation value of 0.728. There is a fair correlation between the calculated and characterizational $\lambda_{\max}^{\text{abs}}$ values for these transitions.

Figure 11.12. ZINDO Calculated Lowest Lying MLCT vs. Laboratory Obtained Lowest Lying MLCT for the Series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complexes.



The correlation between the partial charge calculated at the ZINDO level and the ^1H NMR chemical shift has been explored. This was done for $[\text{Mo}(\text{CO})_4(1,10\text{-phen})]$ and the substituted $[\text{Mo}(\text{CO})_4(1,10\text{-phen})]$ complexes at the consistently unsubstituted 3, 6, and 8 H positions (Figure 11.15). The numbering scheme used for the 1,10-phen derivatives is shown in Figure 10.1. Substituting at positions on the 1,10-phen ligand will affect the electron density of the hydrogens at the other positions. This is measured experimentally in the ^1H NMR chemical shift and is calculated by looking at the partial charges. It was found that at all three hydrogen positions (3, 6, and 8), some correlation could be drawn between calculated partial charge and ^1H NMR chemical shift.

Plot D in Figure 11.15 shows all of the partial charges versus ^1H NMR chemical shift for the three hydrogen positions (3,6, and 8). It can be seen from this plot that all of the data points that they provide a poor correlation. This plot (D) illustrates that a positive relationship can not be drawn between the partial charges versus ^1H NMR chemical shift for the three hydrogen positions taken collectively.

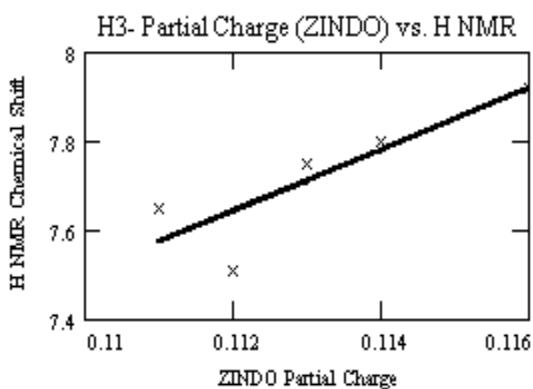
Evaluation of Student Response.

We assayed student response to this new instructional method. Our evaluation method used a standardized interview strategy.^{129,130,133} This style minimizes the researcher bias, maintains objectivity, and provides valuable feedback that would inform future modifications. Professor Darrel Clowes from the Education Department at Virginia Tech assisted in the design of our evaluation method, including interview format, questions, and analysis. The interviews were tape recorded, subsequently transcribed, and then reviewed several times and “rendered” to extract themes.¹³³ The themes and student comments obtained from the interview process were then used to make course modifications for future offerings.

The small class size for inorganic chemistry laboratory leads to large fluctuations in student background, class standing, and career goals. Within the course population many variables and personal biases exist which could impact student responses. Due to the small course enrollment, it was intended that the entire class be sampled. Since many of these students were graduating, this was difficult to achieve. Therefore, as many interviews were completed as could be scheduled with the students. Standardized student interviews were completed at the end of the spring semester in both 1998 and 1999. Basic sample statistics are presented below, and are tabulated in Table 11.3.

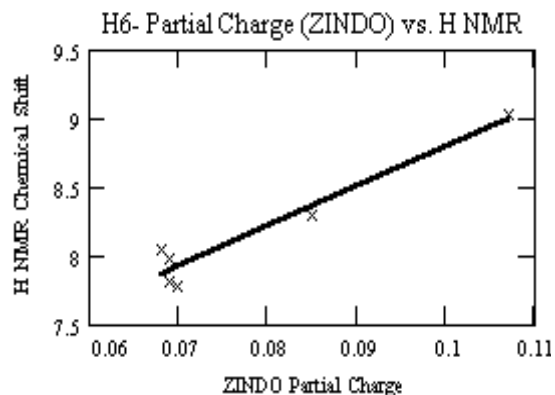
In 1998, of the seventeen students interviewed (90% of course population), seven were senior and ten were junior BS chemistry majors. Ten students were female and seven were male. For these seventeen students, ten had a career goal of graduate school, six industry, and four had other goals.

Figure 11.13. Partial Charge Calculated at the ZINDO Level Versus ^1H NMR Chemical Shift at the H3 (A), H6 (B), H8(C) for the Series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ Complexes; All H-Positions (3,6,8) Plotted Together (D). N-N ligands used include: 1,10-phen, 5-chloro-1,10-phen, 5-nitro-1,10-phen, 4,7-Ph₂-1,10-phen, 4,7-Me₂-1,10-phen, 2,9-Me₂-4,7-Ph₂-1,10-phen.



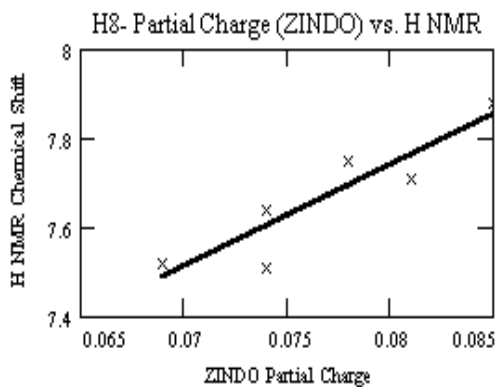
Correlation = 0.859

A



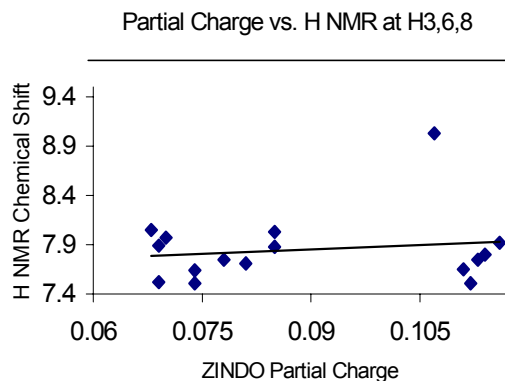
Correlation = 0.967

B



Correlation = 0.909

C



Correlation = 0.023

D

In 1999, of the fourteen students interviewed (93% of course population), two were senior and twelve were junior BS chemistry majors. Nine were female and five were male. For these fourteen students, five had a career goal of graduate school, three industry, and six had other goals.

One factor that might influence student success and perception with respect to this integrated experiment was completion of instrumental analysis. This instrumental analysis laboratory course (IA) is a degree requirement for all students pursuing the BS degree in chemistry. IA is typically taken in the senior year (12% of students interviewed had completed this course). All students who had completed instrumental analysis indicated they felt that this was to their advantage in the inorganic laboratory.

Rendering of the student responses to the interviews elucidated several common themes.¹²⁹ These themes included a series of positive comments on the benefit of this type of integrated approach and experimental design. A selection of positive comments from the student interviews is given in Table 11.4.

Table 11.3. Student Evaluation Sample Statistics, 1998 and 1999.

	1998	1999
Course Enrollment	19	15
Sample Number	17 (90%)	14 (93%)
Gender – Male	7 (41%)	5 (36%)
Gender – Female	10 (59%)	9 (64%)
Senior BS Majors	7 (41%)	2 (13%)
Junior BS Majors	10 (59%)	12 (87%)
Completed Instrumental Analysis	3 (18%)	1 (7%)
Career Goals*:		
Graduate School	10 (59%)	5 (36%)
Industry	6 (35%)	3 (21%)
Other	1 (6%)	6 (43%)

*Students were placed into career goal categories based on the following: graduate school (directly into a graduate program in chemistry); industry (employment in the chemical industry after graduation); other (graduate studies in other fields, professional school, military employment, etc.).

Table 11.4. Positive Comments, Responses from Student Interviews.

With respect to the WWW tutorials, students said:

“...I thought that they were very helpful...they were very self-explanatory.”

“They laid everything out for you, and you could go back and refer to them if there was something that you forgot.”

“I thought that they were very helpful...they were very self-explanatory.”

“They were helpful and definitely did provide adequate information to use CAChe.”

“...it was quite easy to do. There were nice pictures of the screens, this is what it is supposed to look like. It was perfect.”

With respect to molecular modeling, students said:

“It was very interesting even just to know that something like this was out there, because I had no clue that we had that kind of technology.”

“It’s a very, very good experiment. I can see it’s [molecular modeling] relevance now because I’m doing a ligand synthesis using the same principles, predicting IR, NMR, etc. Now I see the usefulness of it.”

With respect to the integrated laboratory experiment, students said:

“...I did not (even) have a basis before. I did not know what HOMO and LUMO were. I did not have any of that before I did this lab.”

“I liked the exposure of doing the synthesis both ways [photolytically and thermally]. I wish that there were actually more experiments that could have been done that way.”

“I thought that it was really neat. I had never done anything like that before. It was surprisingly easy.”

Rendering of the student responses led to the following conclusions:

1. The students generally found the integrated molecular modeling, synthesis, and characterization experiment to be interesting and educational. 92% of students interviewed felt that this was a worthwhile and informative experience, and an effective

way to gain exposure to molecular modeling.

2. Every student interviewed felt that the WWW tutorials used to teach the CAChe molecular modeling program were both helpful and an adequate/effective teaching tool. Specifically,

A. The students felt the detailed approach of the tutorials included was helpful. The picture by picture guide to the modeling result that the students see saved a lot in terms of guesswork.

B. The students felt that without any previous molecular modeling experience, one can complete the tutorials and then readily use the CAChe software program. They saw as an advantage of the WWW tutorial that they can review necessary materials out of class time.

3. Few students had previous exposure to molecular modeling. The students enjoyed the experiment and felt that the exposure to molecular modeling was very important. They viewed molecular modeling as a valuable skill to obtain during their BS degree program and that the CAChe system was appropriate for this purpose.

4. Many students commented that from completing this integrated laboratory experiment they now have a much better understanding of the relationship between orbital properties (calculated values) and characterization data. They viewed this skill of understanding orbital properties and their relationship to characterizational data as valuable.

5. Students viewed their exposure to photochemical reactions used in the synthesis of some $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes as valuable. They felt that this would be an interesting facet to expand into other experiments as well.

The students took advantage of this interview process to provide detailed and thoughtful suggestions for improvement. Some of the most common are highlighted below. A selection of responses regarding suggestions for improvement is given in Table 11.5.

Table 11.5. Student Responses, Suggestions for Improvement.

With respect to WWW tutorials, students said:

“I wish that there had been something like a handbook, maybe to use along side. I think that that would have been more comprehensive, along with the tutorials.”

“...maybe one general handout, one sheet of paper in addition to the tutorial.”

With respect to molecular modeling and the integrated laboratory experiment, students said:

“I did not know how to go from the molecular modeling result to the characterizational data.”

“...I did not really understand how to correlate, especially how we were supposed to compare CAChe to our actual results.”

“...working with the Brewer group and doing undergraduate research helped out a lot [with my understanding].”

“...we went in there on the first day of lab and boom- here is the tutorial, go for it. In physical inorganic we did not start going over this stuff until the end of April, which would have been too late.”

Rendering of the student responses led to the following conclusions:

1. The students felt that generating a separate short document in the lab manual or on the WWW that covers the basics of the CAChe system, such as toolbars and calculation types would be helpful. This suggestion was based on the feeling that easy access to this information after the tutorials were completed would be useful in the students' own molecular modeling experiment.

2. Every student interviewed felt that a “pre-lab type” presentation involving basic molecular orbital theory (HOMO/LUMO) and characterization (especially electrochemistry and electronic absorption spectroscopy) techniques would be helpful.

3. Some students felt that they needed more information on how modeling results are correlated to characterizational data. They felt that an example of this correlation

would be helpful. While providing more information on characterization techniques and molecular modeling is possible, giving specific examples of these correlations would defeat one of the main purposes of this experiment: having the students discover the correlation of orbital properties from molecular modeling to characterization data. This discovery process allows them to explore the impact and importance of orbital properties in inorganic systems, and is aimed at generating a more effective learning environment.

4. Students commonly perceived that success with this experiment depended to a certain degree on prior coursework. Not only are data interpretation skills necessary for the integrated modeling, but also for other experiments throughout the course. The students who had completed the instrumental analysis course (Chemistry 4114) seemed more confident in their understanding of the correlations between the molecular modeling and characterization; such students were generally seniors having completed other additional coursework. Students who have actively pursued undergraduate research also perceived greater success with this experiment. Most students who had difficulty in understanding characterization methods worked through those difficulties with the assistance of the graduate teaching assistants and professor.

5. This experiment typically started in the beginning of the semester. Some students suggested that postponing the integrated experiment until the end of the semester to allow other courses to have touched on difficult topics would be beneficial, such as molecular orbital theory. Other students, however, voiced some doubt about this, noting that these topics were introduced late in the semester in other lecture courses (in the last few weeks of the semester in physical chemistry and inorganic chemistry lectures, co- and prerequisites to this laboratory). As this experiment is completed in two parts, moving it to the end of the semester is not feasible.

Modifications of Experimental Design.

Several modifications have been made to this integrated experimental design as a result of student feedback. New WWW tutorials have been developed to discuss characterizational methods and briefly introduce molecular modeling theory. A short group of presentations on characterization methods has been added at the beginning of

the semester, and is presented as a series of short pre-lab discussions. This is done by showing the students the use of the instruments and some basic theory, and by introducing data analysis skills. A short description of molecular modeling orbital representations has been developed as a pre-lab discussion. Students are encouraged to use the NIH web site to learn more about these techniques.