A Computational Experiment Introducing Undergraduates to Geometry Optimizations, Vibrational Frequencies, and Potential Energy Surfaces

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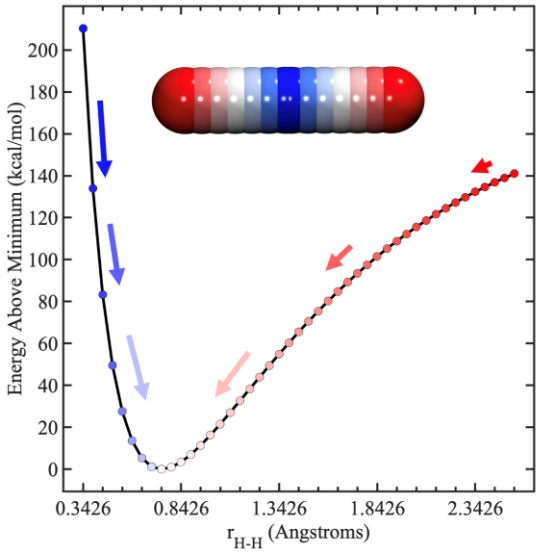
ABSTRACT

In this article, we describe a fully computational laboratory exercise that results in an increase of students' understanding of what quantum chemical geometry optimization calculations are doing to find minimum energy structures. This laboratory was conducted several times over multiple years at a small private undergraduate institution, St. Bonaventure University. Through this experiment, physical chemistry undergraduate students are exposed to chemical problems for which computations provide a necessary supplement to chemical intuition, thus cementing the importance of computational work in contemporary chemistry. Students apply their understanding of geometry optimizations to problems of complex 3-D molecular structures that stretch their intuition, including the geometries and isomers of closo-carboranes and of the hexamer of the co-catalyst methylaluminoxane. Students are also exposed to vibrational frequency calculations both as a diagnostic tool for determining whether structures represent energetic minima or transition states and are exposed to the vibrational zero-point energy correction.

GRAPHICAL ABSTRACT



KEYWORDS

Upper-Division Undergraduate, Physical Chemistry, Computer-Based Learning, Computational Chemistry, Constitutional Isomers, Molecular Modeling, Quantum Chemistry

INTRODUCTION

Finding the ground state equilibrium geometry is incredibly important to understanding a chemical system. By knowing the nuclear positions of a chemical system when it is lowest in energy, i.e. at equilibrium in the ground electronic state, one can begin to calculate essentially any property that relies on the ground electronic state. Furthermore, geometry optimization has a deep connection with experimental and theoretical techniques for materials characterization. For instance, structures determined with X-ray crystallography are the experimental equivalent of optimized geometries for extended materials, so understanding how and why these structures arise on a theoretical level is critical for students.[1] Moreover, determining optimized structures and their connections with physical characteristics of materials is a critical aspect of enterprises like the Materials Genome Initiative and the RCSB Protein Databank project.[2,3]

Determining an optimal geometry, however, can be somewhat taxing, since there are many different reasonable configurations of atoms that can be assembled. Today, commercial computational chemistry and physics software packages can be utilized to find the ground state equilibrium geometry, albeit in a relatively complex and opaque way. Several studies in this *Journal* have utilized the process

of geometry optimization, though mostly as a "black box" procedure in which the user does not see any details of the calculation nor a discussion of how it works.[4–10] The goal of this exercise is to illustrate some basic ideas of geometry optimizations while providing a practical introduction to computational chemistry for upper-level undergraduate physical chemistry students. The authors acknowledge that we are not completely unveiling the "black box" nature of quantum chemical software packages, as we neglect to discuss the self-consistent field (SCF) algorithms used for determining the electronic energy, gradients, etc. and the details of different algorithms used to conduct optimizations (steepest decent, BFGS, Newton's method, quasi-Newton methods, etc.).[11–13] We do, however, provide a surface-level and concise explanation of the theory behind this exercise.

A non-linear molecule with N nuclei has an electronic energy (E) that is dependent on the nuclear coordinates of the N nuclei. These nuclear coordinates are often called internal coordinates. The number of independent nuclear coordinates is given by $3N - 6$ ($3N - 5$ for linear molecules), where the value 6 is the result of three translational and three rotational degrees of freedom that do not change the electronic energy of an isolated molecule. The nuclear potential energy surface (PES) for a molecule gives E as a function of all the internal coordinates of the N nuclei that make up the molecule. The generation of accurate PESs for a variety of molecules is still a contemporary research topic in chemistry, particularly for complex systems such as those with hydrogen bonds.[14–17] Students often see simple PESs in general or organic chemistry courses that are also sometimes called reaction coordinate diagrams.[18] PES diagrams are also used in illustrating the dissociation of a chemical bond.[19,20] The calculation of E at a specific arrangement of atoms is called a single-point energy calculation, whereas a geometry optimization is a calculation that seeks to modify this arrangement of N nuclei to find the lowest possible E, which is also called the global minimum energy structure.[12] In practice, geometry optimizations find a local stationary point on the PES and one must conduct a large number of geometry optimizations to gain confidence that the global minimum has been determined. Furthermore, several studies in this journal have attempted to illustrate the portions of the PES relevant to chemical reactions in low-dimensional (i.e. visualizable) representations.[7,8,10,21]

As an example of a simple cut of a PES along one coordinate, a plot of energy versus torsional rotation angle about the C2-C3 bond in butane, is given in Figure 1. The *anti*-conformation, the

conformation where the C2-C3 bond is rotated so that the methyl groups on C1 and C4 are the furthest away from one another, is the lowest energy conformation.[18] Therefore, this conformation is the global minimum, assuming the other coordinates are optimized as well. The *gauche* conformation, in which the C1 and C4 carbons are staggered in a closer configuration than in the *anti*-conformation, is a bit higher in energy than the *anti*-conformation but is still a local minimum on the PES. The *eclipsed* conformations are all energetic maxima. These are considered transition states between the energetic minima on the PES. We will use this example to illustrate how a geometry optimization program finds molecular configurations of lower energy in the next paragraph.

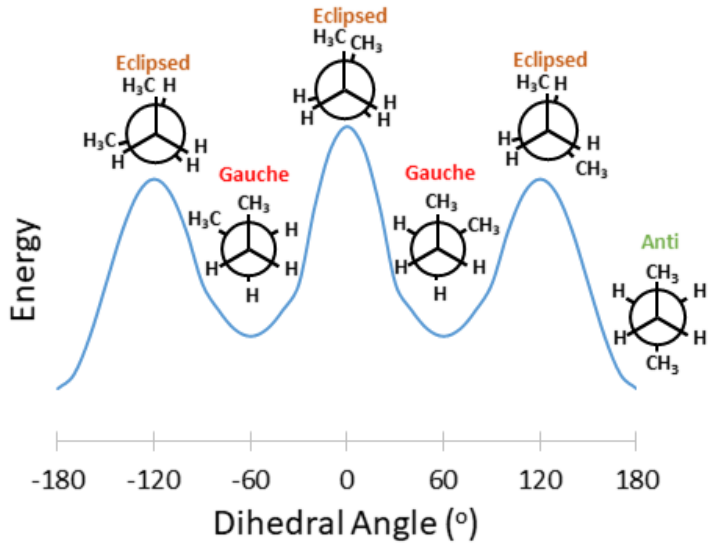


Figure 1: Energy versus the C1-C2-C3-C4 dihedral angle for butane (C_4H_{10}).

Geometry optimization programs utilize the gradient—or more intuitively, the slope—of the PES to determine the forces acting on the atoms, since the negative of the gradient of the potential energy is the definition of force in classical mechanics.[22] The atoms are then moved by these forces towards a state of lower energy and the process is repeated until an energy minimum is reached. The details of applying these forces, such as how far atoms are moved for a given force, are particular to the implementation of various algorithms in each program.[23] Often, these parameters can be modified by the user when dealing with pathological optimizations. The example in Figure 1 clearly shows how a geometry optimization program might start at a structure between two of the energetic maxima and find a minimum energy structure using the slope of the PES. During a geometry optimization, one would

hope to find the global minimum (e.g. the *anti*-conformation in the example from Figure 1) but, depending on the initial geometry and geometry optimization criteria, one may optimize to a local minimum (e.g. the *gauche*-conformation). How can we be sure if we have optimized a structure to a global minimum? The short answer is that we cannot know with absolute certainty that we have arrived at the global minimum. While this answer is unsatisfactory, it is true. Therefore, critical evaluation of the results of a quantum chemical calculations and use of chemical intuition to rationalize the results of these calculations is necessary.

It is also important to be able to check whether a given structure is a minimum energy structure, a transition state, or another point on the PES. This can be determined via a vibrational frequency calculation.[24] A minimum on the PES will have all real, positive vibrational frequencies while a transition state will have a single imaginary frequency. A system with more than one imaginary frequency is at neither a minimum nor a maximum energy. A diatomic molecule can be used as a simple example to illustrate why minimum energy structures have positive frequencies and transition states have an imaginary frequency, as shown in the notes for the instructor. It is important to note, however, that the diatomic molecule only gives a mathematical and not a physical model for imaginary frequencies, as a diatomic molecule will not display a negative concavity at its energetic extreme.

Vibrational frequencies can be also used to determine a zero-point energy (ZPE) correction to the electronic energy (E_{ZPE}) to find a zero-point corrected energy (E_{corr}):[20,24]

$$E_{corr} = E + E_{ZPE} \qquad [1]$$

This corrected energy is the energy that should be considered the ground state energy since the nuclei in a molecule are in constant motion and vibrate around their equilibrium position even at 0 K, as predicted by the Heisenberg uncertainty principle.[12,20] The zero-point energy correction can be approximately determined from a vibrational frequency calculation by adding up all the ground state vibrational energies under the harmonic oscillator approximation. Utilizing the ZPE corrected energy is required to get accurate estimates of differences between electronic energies.[25] While the ZPE will turn out not to make a qualitative difference to the results of this experiment, it is crucial that students build habits for considering the possible relevant factors for energetic differences in different molecules or different states within the same molecule since it will make a noteworthy difference in some contexts.[25]

Herein, we describe a computational experiment that uses these concepts of geometry optimization, vibrational frequencies, and the ZPE correction to study a range of problems in molecular geometry and structural/conformational isomerism. Crucially, this activity includes portions that align well with undergraduate chemical intuition, and portions that give insights into problems for which students will likely have no chemical intuition at all. This shows the utility of quantum chemical calculations as a means of answering questions for which there may not be readily available experimental or intuitive means to investigate.

OVERVIEW OF EXPERIMENT

STUDENT LEARNING OBJECTIVES

Students will:

(1) Demonstrate the utility of computational chemistry in analyzing molecular geometries and ranking constitutional/conformational isomers by ZPE corrected energies.

(2) Demonstrate the usefulness of computational chemistry in supplementing chemical intuition in cases where it is difficult to predict structures *a priori*, as evidenced by determining the structure of $(AlOCH_3)_6$.

(3) Better understand differences between electronic energy and ZPE corrected electronic energy as demonstrated by our pre-/post-test metrics.

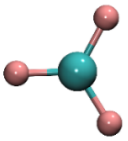
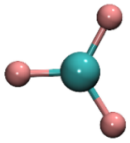
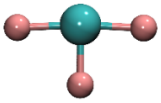
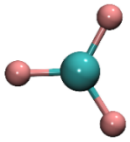
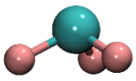
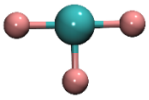
(4) Utilize graphical user interfaces (GUIs) to better conduct quantum chemical calculations and interpret their results as verified by correctly determining the most probable structure of various molecules.

During two four-hour lab periods, junior/senior physical chemistry students were taken through a three-part experiment including building molecules, running *ab initio* calculations, and interpreting results. Students utilized the Gaussian 16 program through WebMO version 18.1 for all calculations.[26,27] Calculations for the first and second parts of the experiment were readily completed during the first lab period, while some optimizations in the final part required additional time outside of class due to computational expense. The Beowulf computer cluster utilized in the experiment was equipped with 4 Dell PowerEdge R300 servers. These servers were equipped with 3.16 GHz quad-core processors and 16

GB of RAM. This was the second experiment conducted in the semester with the first being a tutorial on how to use WebMO. The 8 junior/senior level students conducted the exercise. All students had one full semester of the thermodynamics portion of physical chemistry (CHEM 401: Physical Chemistry I). Symmetry and point-groups were being covered concurrently in CHEM 441: Advanced Inorganic Chemistry, in which all students were enrolled. Irreducible representations were not covered at the time of the experiment.

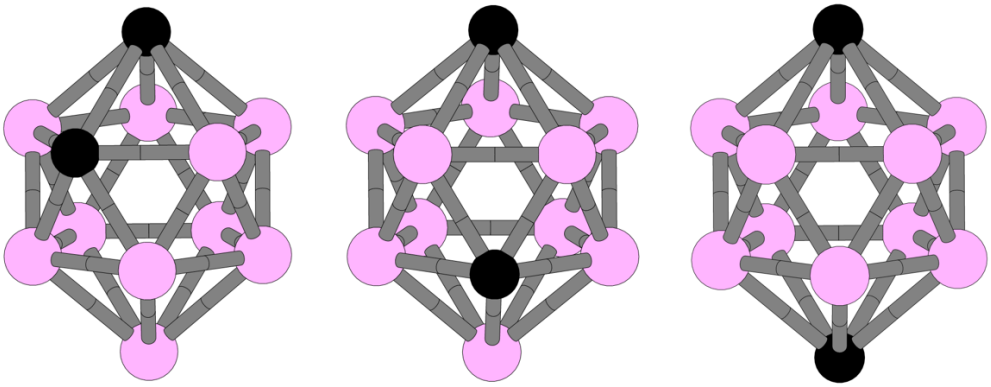
The first part of the experiment tasked students with predicting the VSEPR geometries of ClF_3 and the ClF_3^{2+} cation. Students then computed the optimized geometries and energies of various symmetrized versions of these molecules, as well as a vibrational ZPE. This allowed students to see if the most stable conformational isomer for each molecule is the one predicted by chemical intuition with VSEPR theory. The results of this procedure are shown in Table 1, with E_{corr} reported relative to the minimum energy structure for each species.

Table 1. Energetic data for ClF_3 and ClF_3^{2+}. Structures above the dashed bar are neutral, and structures below the bar are cationic. Structures marked with a † are those predicted by VSEPR theory

Species (Symmetry)	Ball & Stick Representation	Optimized E (kcal/mol)	ZPE (kcal/mol)	Relative E_{corr} (kcal/mol)
ClF_3 (D_{3h})		-476549.54	3.14	13.73
ClF_3 (C_{3v})		-476549.54	3.14	13.73
ClF_3 (C_{2v})†		-476564.49	4.35	0
ClF_3^{2+} (D_{3h})		-475761.71	2.62	73.69
ClF_3^{2+} (C_{3v})†		-475838.04	5.25	0
ClF_3^{2+} (C_{2v})		-475781.99	4.27	55.06

In the second part, students were tasked with determining the lowest energy constitutional isomer (*o*-, *m*-, or *p*-) of closo-carborane ($C_2B_{10}H_{12}$). Cartoon images of these structures, omitting the individual hydrogen atoms bound to each of the atoms shown, are given in Figure 2 to assist with visualization of the 3-D structure. The ZPE-corrected minimum energy structures could then be compared to the experimentally determined heats of formation to see if the geometry optimization matched with the experimental predictions. While a more detailed calculation of thermodynamic quantities such as the enthalpy, entropy, and free energy of each structure would be valuable, the early time that this experiment takes place in the semester precludes teaching students the requisite background for such calculations in addition to the new material for this experiment. The optimized

energies, along with ZPEs, are shown in Table 2, with E_{corr} reported relative to the minimum energy structure for each species.



o-closo-carborane *m*-closo-carborane *p*-closo-carborane

Figure 2. Cartoon representations of the closo-carboranes omitting the hydrogen atoms for clarity. Black spheres are carbon atoms and pink spheres are boron atoms.

Table 2. Energetic data for *o*-, *m*-, and *p*-closo-carborane

Species	Optimized E (kcal/mol)	ZPE (kcal/mol)	Relative E_{corr} (kcal/mol)
o-closo-carborane	-208395.54	111.35	18.65
m-closo-carborane	-208411.78	111.71	2.77
p-closo-carborane	-208414.66	111.82	0

Finally, in the third part of the experiment students were tasked with investigating the structure of one of the oligomers of the olefin polymerization co-catalyst methylaluminoxane (MAO). Students were asked to explore the structure of the hexamer, which has the chemical formula $(AlOCH_3)_6$.[28,29] This step ensured students could see the utility of quantum chemical optimizations on a system for which they likely have no chemical intuition at all. Students were tasked with building and optimizing a series of candidate structures of MAO, but with the methyl groups replaced with hydrogens for the initial optimizations. Students then would optimize the full structure by converting the hydrogens back to methyl groups in the initially optimized structure before optimizing the structure again. This gave students an opportunity to see whether a chemically simplified model system could be reliably compared

with the true system, both geometrically and in the energetic ranking of isomers. The currently agreed-upon ground state geometry of the MAO hexamer is presented in figure 3.

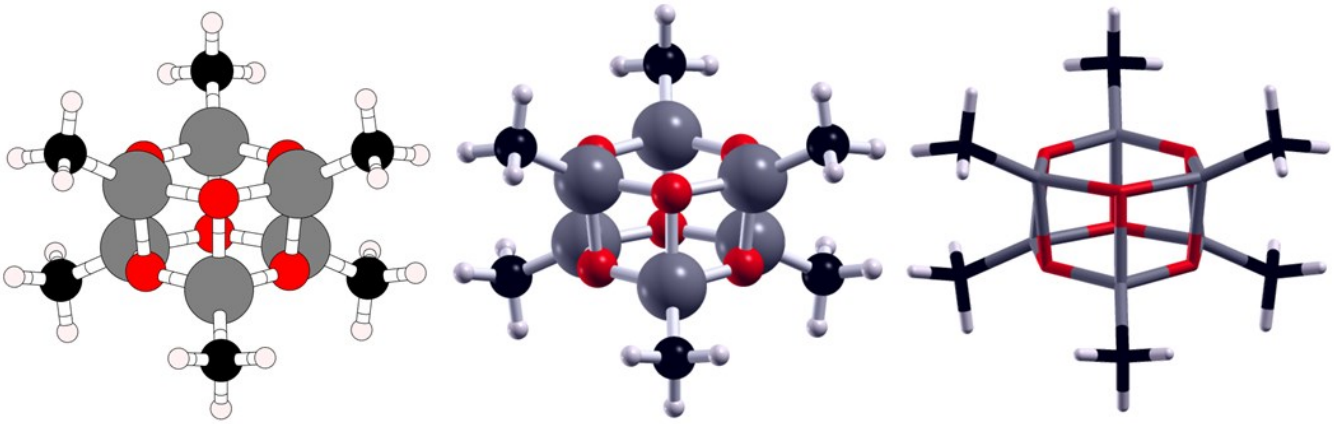


Figure 3. Cartoon (left) representation, ball-and-stick model (middle), and stick model (right) of $(AlOCH_3)_6$.

A full lab manual, pre/post-tests, and notes for the instructor for this experiment are included in the Supporting Information. Optimized structures of ClF_3 and ClF_3^{2+} for each symmetry, the optimized closo-carborane structures, and several optimized candidate structures of MAO, both with and without the hydrogen simplification, are included in the Supporting Information. The notes for the instructor include the optimized energies and ZPEs of all structures described above with high-quality images produced using the VMD software package.[30] The notes for instructor also include the total computational CPU time elapsed for each unique structure presented. The actual wall time is approximately four times less because the jobs were run on four parallel cores.

Common problems associated with this exercise include:

- Failure to visually inspect the optimized geometry to determine if the output geometry was correct. For example, some students constructed flat sp^3 carbon-containing molecules that optimized to planar geometries due to symmetry constraints.
- Students can often struggle with building reasonable initial structures for optimization, particularly with cage-like compounds such as the closo-carboranes.
- Geometry optimization calculations can sometimes fail to converge if a chemically non-sensible initial structure is chosen, or if methyl group rotations do not neatly stabilize. This can result in the energy "oscillating" rather than converging to a minimum, or the iterative calculation of the electronic energy failing altogether in extreme cases.
- Depending on available computational resources, students should not be allowed to submit an excessive number of candidate structures of MAO, as this could cause delays.

Additional topics that could be explored by instructors include:

- Investigation of different density functionals and corrections beyond B3LYP.
- Investigation of increasing/decreasing basis set size.

- Calculations of the enthalpy of formation of the closo-carboranes for comparison with the experimental values stated in the laboratory manual.
- Exploring other oligomers of MAO beyond $(AlOCH_3)_6$.

HAZARDS

There are no physical hazards involved with this experiment.

RESULTS AND DISCUSSION

Student learning of content was assessed at St. Bonaventure University by a pre-/post-assessment, a pre-laboratory quiz, and a summative laboratory report prepared by the students. The pre-assessment was administered prior to the laboratory experiment, while the post-test was administered a week after the second laboratory session when the summative laboratory report was due. The assessment questions, along with the percentage of correct student responses, is given in Table 3. Growth of student comprehension is clear from the increased rate of correct responses in the post-assessment. The most frequent error in the post-assessment was failing to mark "all of the above" for the second assessment question. Students instead marked one of the individual correct items as the sole correct answer. The majority of students could correctly describe a local minimum and global minimum on a PES, how to identify a local minimum/transition state, and explain why a negative force constant results in an imaginary frequency, as indicated by our post-assessment.

As previously described, in Section 1 of the exercise students were charged with determining the ground state structure for ClF_3 and the ClF_3^{2+} cation. All eight students correctly determined the lowest energy structure for the neutral and cationic state of chlorine trifluoride. Students quickly determined that they could get the desired symmetry by building a common molecule with the desired symmetry, then replacing the atoms with chlorine/fluorine. For example, students desiring a C_{3v} symmetry would build an ammonia molecule then replace the nitrogen/hydrogen with chlorine/fluorine, respectively. Each student determined that their VSEPR knowledge/prediction matched the outcome from the quantum chemical calculations.

As previously described, in Section 2 of the exercise students were charged with determining the ground state structure for *o*-, *m*-, or *p*-closo-carborane ($C_2B_{10}H_{12}$). All eight students determined the correct energy ranking for the series of $C_2B_{10}H_{12}$ isomers. Students struggled building the boron-carbon

icosahedron core of the closo-carboranes. Many resorted to finding a compound that could be imported from the Fragments implemented in WebMO. Most elected to use the twisted ferrocene molecules contained in the Symmetry Examples.

As previously described, in Section 3 of the exercise students were charged with determining the ground state structure of $(AlOCH_3)_6$, the MAO hexamer. Six of the eight students correctly identified the ground state structure. The two students who did not determine the correct structure did not test more than 3 possible structures, while successful students optimized 6 or more different structures. They determined that planar structures were higher in energy than those with higher dimensionality. Some students elected to optimize structures by modifying the number of square/hexagonal faces, leading them down the correct path to the accepted global minimum of the MAO hexamer. When considering the simplified system $(AlOH)_6$, most students found the energetic ranking of the structures matched that of their similar $(AlOCH_3)_6$ structures while the difference in relative electronic energy of the structures changed.

Table 3. Pre- and post-test evaluation results ($N = 8$)

Assessment Item	Pre-test Correct Response, %	Post-test Correct Response, %
What is meant by the terms local minimum and global minimum on a potential energy surface? Explain with words and pictures.	12.5	100
A vibrational frequency calculation can tell you: a. The zero-point energy b. The vibrational spectrum of a molecule c. If the geometry is a minimum or a transition state d. All of the above e. None of the above	37.5	75
Given the following equation: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, why does a negative force constant result in an imaginary frequency?	12.5	100
Draw the Newman projections for a local minimum, global minimum, and local maximum looking down the C2-C3 axis of 2-methyl-butane.	0	87.5
A minimum on the potential energy surface has how many imaginary frequencies?	25	87.5
A transition state on the potential energy surface has how many imaginary frequencies?	37.5	100

CONCLUSIONS

Physical chemistry students at a primarily undergraduate institution (PUI) conducted a computational exercise investigating potential energy surfaces (PES) utilizing density functional theory (DFT). The first section of the exercise explored the structure of a simple molecule/cation that could easily be predicted from VSEPR theory/general chemistry knowledge. Students explored the stability of closo-carboranes in the second section and compared the results to experimental thermodynamic data. In the final section of the experiment, students predicted the structure of the hexamer oligomer of the olefin polymerization co-catalyst methylaluminoxane (MAO) to show students how computations can be utilized to build chemical intuition for an unfamiliar system. Based on pre-/post-assessment data,

students improved in their abilities to identify energetic minima and transition states, and better understand basic concepts about PESs and vibrational calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX. [ACS will fill this in.] Example brief descriptions with file formats indicated are shown below; customize for your material.

Notes for Instructors (DOCX)

Laboratory Manual (DOCX)

Survey Instrument (DOCX)

Optimized Molecular Coordinates (ZIP)

Grading Guide (DOCX)

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