

## Lab 3: Calculating Vibrational Frequencies

CHE 525/PHY 567, Stony Brook University

### 1 Introduction

Electronic structure calculations are capable of computing many spectroscopically observable properties. For example, a common quantum chemical task is the computation of vibrational frequencies, which can be directly compared to infrared and/or vibrational Raman spectra in order to determine the presence or absence of a particular compound. Of course, quantum chemical calculations are approximate, and the available approximations vary significantly in accuracy.

In this exercise, you will compute the vibrational spectrum of a simple molecule (water) at several levels of theory. By comparing to experiment and reading relevant literature, you will assess the accuracy of several methods for this property. You will then choose a method to compute the vibrational frequencies of the reactant and product of a common organic reaction, the Paal-Knorr synthesis, to determine which spectroscopic features one would look for to determine whether the reaction has been successfully completed.

### 2 Procedure

The procedures and Python code you need to do this lab were mostly covered in Lab0 and Lab1. An example script for optimizing the geometry and calculating the vibrational frequencies of water at the HF/6-31G\* level can be found in `Lab3starter.py`. Follow the following procedure:

1. First you will practice visualizing vibrational frequencies in molden. Run the provided starter script (`Lab3starter.py`). A molden frequencies file (with the file extension `“.molden_normal_modes”`) will be created. Open it in molden. To visualize the normal modes, click on the “Norm. Mode” radio button at the top left of the Molden Control window. You may now visualize each mode by selecting it in the “Molden Frequency Select” window. Make a note of the chemical character of each mode (bend, asymmetric stretch, etc.) along with its vibrational frequency.<sup>1</sup>
2. Now you will compare several methods for computing the vibrational frequencies, using water as a benchmark system. In addition to Hartree-Fock (“scf” in Psi4) compute the frequencies using the following methods: 1) Møller Plesset second order perturbation theory (“mp2” in Psi4; a reasonably affordable correlated wave function method which we will soon discuss in class), 2) PBE0 (“pbe0” in Psi4; a common density functional method). Use the same (6-31G\*) basis in all cases. Record all computed frequencies. Look up the experimental gas phase vibrational frequencies of water (the NIST Webbook is an excellent free online source) as a point of reference. Which method is the most accurate?
3. In addition to vibrational frequencies, one can also use quantum chemistry methods to estimate how strongly light at the resonant frequency would be absorbed, or the “IR intensity.” Unfortunately, Psi4 does not yet have built-in functionality developed yet for calculating IR intensities for any methods except restricted Hartree-Fock. Fortunately for you, your instructors have developed code to do this! Use the `CHE525_Vib` package (`import CHE525_Vib` with `CHE525_vib.py` in the same directory as your main Python program) to calculate the vibrational intensities for the three vibrational modes of water for the same three methods you used above (SCF, MP2, PBE0). This package has two functions, `get_dipole()` and `dipder()`. The functions are documented in `CHE525_vib.py` and example usage is shown in the starter file. The function `get_dipole()` returns a vector for the molecule’s dipole moment. The function `dipder()` makes finite displacements of the molecule’s geometry along the normal mode coordinates and uses the resulting finite difference in the dipole moment to estimate the derivative  $d\vec{\mu}/dQ$  where  $\vec{\mu}$  is the dipole moment and  $Q$  is the normal mode coordinate. As we will discuss in class, the vibrational transition strength is proportional to  $|d\vec{\mu}/dQ|^2$ .
4. Now, using the more accurate of the methods you investigated in the previous step, you will investigate the spectroscopic signature of the reactants and products of the Paal-Knorr synthesis, a common reaction for creating heterocyclic organic molecules from 1,4-dicarbonyl compounds. Succinaldehyde is

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<sup>1</sup>If you find the Molden animation too fast for you to clearly see the vibrational motion, click the hourglass button to change the delay time between frames

the simplest 1,4-dicarbonyl, so here we will use it to represent the reactant. Compute the vibrational frequencies of succinaldehyde. Which frequencies are characteristic of the two aldehyde functional groups? The ring-closed product of the Paal-Knorr reaction of succinaldehyde would be furan. Compute the vibrational frequencies of furan. Which frequencies are characteristic of the unique functional groups of furan? Note that frequencies calculations on molecules of this size may take a few minutes, so be prepared to wait.

\*\*\*Important Note: When you look at the vibrational frequencies, are any of them listed as negative numbers in Molden? This is a problem! It indicates an “imaginary frequency,” which is another way to say that the curvature (second derivative) of the potential energy surface (PES) is negative in that direction. That is, you are not at a true local minimum on the PES, but instead the optimization got stuck on a saddle point. This often happens if your initial guess geometry has higher symmetry than the minimum energy structure. To fix this, you will need to rerun the optimization, starting from a new initial guess. Watch the vibrational motions in along the normal mode corresponding to the imaginary frequency. Use the Z-matrix editor in Molden to displace the molecule roughly along this coordinate (breaking the symmetry of the molecule), and then rerun the optimization and frequencies calculations from this new initial guess.

### 3 Deliverables

- Make a table of the vibrational frequencies of water according to the three levels of theory you performed above and according to experiment. Discuss the agreement with experiment. Also give the IR intensities in km/mol in your table. You should find the IR intensities to vary widely between the different normal modes. Why?<sup>2</sup> You may also find that the IR intensities depend strongly on the level of theory. Why?
- Scaling vibrational frequencies to achieve better agreement with experiment. Read the paper by Scott and Radom [J. Phys. Chem. **100**, 41 (1996), <https://pubs.acs.org/doi/10.1021/jp960976r>], and also check out the more comprehensive list that is hosted by NIST <https://cccbdb.nist.gov/vibscalejust.asp>. Create a new table, scaling your frequencies by the suggested scaling factors. Does this improve agreement with experiment? (Note that some of Scott and Radom’s notation is a little different from ours: “6-31G(d)” = “6-31G\*”; our MP2 method is his “MP2-fu”; “PBE0” is not included in Radom’s paper, but it’s listed on the NIST list as “PBE1PBE”)
- Explain which feature(s) of the vibrational spectra of succinaldehyde and furan that would allow you to discriminate between them in practice.

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<sup>2</sup>Think about how different deformations of the molecule change the dipole moment. It might be helpful to calculate the dipole moment for different geometries near equilibrium, but slightly distorted along the normal mode coordinates. For example, you might look at how the dipole moment changes when you bend the molecule vs. changing the OH bond lengths.