IR and NMR Spectra

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Description:
In this lab we will be computing molecular properties by considering derivatives of the energy. In particular, we will calculate the IR and NMR spectra of several small organic molecules, and use the calculated spectra to help identify an unknown molecule.

**Suggested level:** graduate/advanced undergraduate.

Learning objectives: Learn how compute IR and NMR spectra and how to relate them to molecular structure; review harmonic and anharmonic oscillators; review point group symmetry of molecular structures and vibrations.

I. BACKGROUND

Many properties of a molecule can be determined from derivatives of the energy with respect to some external parameter. For example, derivatives with respect to nuclear coordinates, R_i, can be used to determine equilibrium and transition structures and are characterized by the derivatives of the energy being zero

$$\frac{\partial E}{\partial R_i} = 0 \qquad (1)$$

These structures correspond to critical points on the potential energy surface (PES):
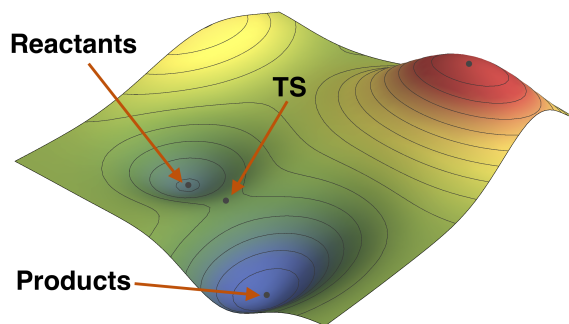

We can determine the nature of a critical point by considering the signature of the Hessian matrix:

$$H_{ij} = \frac{\partial^2 E}{\partial R_i \partial R_j} \qquad (2)$$

This is the multidimensional analog of a second derivative, which you may remember using to determine if a curve is concave up, or concave down in single-variable calculus. The signature of a matrix gives the number of positive and negative eigenvalues. If the Hessian has:

- Zero negative eigenvalues, the critical point is a local minimum which corresponds to an equilibrium structure.

- One negative eigenvalue, the critical point is a first-order saddle point which corresponds to a transition structure.

The Hessian can also be used to predict the infra-red (IR) spectrum of a molecule. We invoke the harmonic approximation, which assumes that, around a minimum, we can model the PES locally by a parabola:
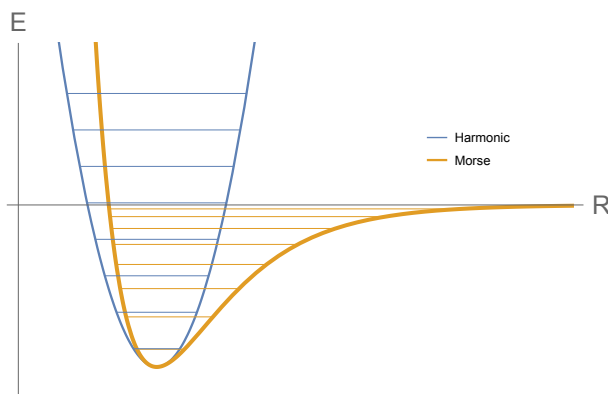
This approximation is usually adequate for the fundamental band ($\nu = 1 \leftarrow 0$), but begins to break down for overtones and large-displacement modes (such as weakly-bound systems). Diagonalization of the (mass weighted) Hessian yields the eigenvalues, which give the harmonic frequencies, and the eigenvectors, which show the nuclear displacements for each mode.

A common practice is to optimize a structure at a particular level of theory and then perform a frequency calculation (at the same level of theory!) to verify that a minimum has been obtained. If a saddle point has been found, the negative eigenvalue will show up as an imaginary frequency in the calculation. The eigenvector corresponding to this imaginary frequency show in which direction the molecule wants to distort in order to lower its energy.

Note: many quantum chemistry packages report imaginary frequencies as negative frequencies, and consequently many people refer to them as such. This is not correct, they are in fact imaginary.

Nuclear shielding constants, σ_{ij}, are another property that can be computed via derivatives:

$$\sigma_{ij} = \frac{\partial^2 E}{\partial B_i \partial M_j} \tag{3}$$

where B_i is a component of the external magnetic field, and M_j the nuclear magnetic spin of the nucleus. Nuclear shielding is very sensitive to the electronic environment of the nucleus and therefore NMR provides a high-resolution technique for resolving the structure of a molecule.

If the shieldings for a reference (such as tetramethylsilane, TMS) are available, then we can compute chemical shifts and use these to predict the NMR spectrum for the molecule.

II.   METHOD

In this lab, we will consider the following eight isomers of $C_6H_4O_2$:

(1) (2) (3) (4)

(5) (6) (7) (8)
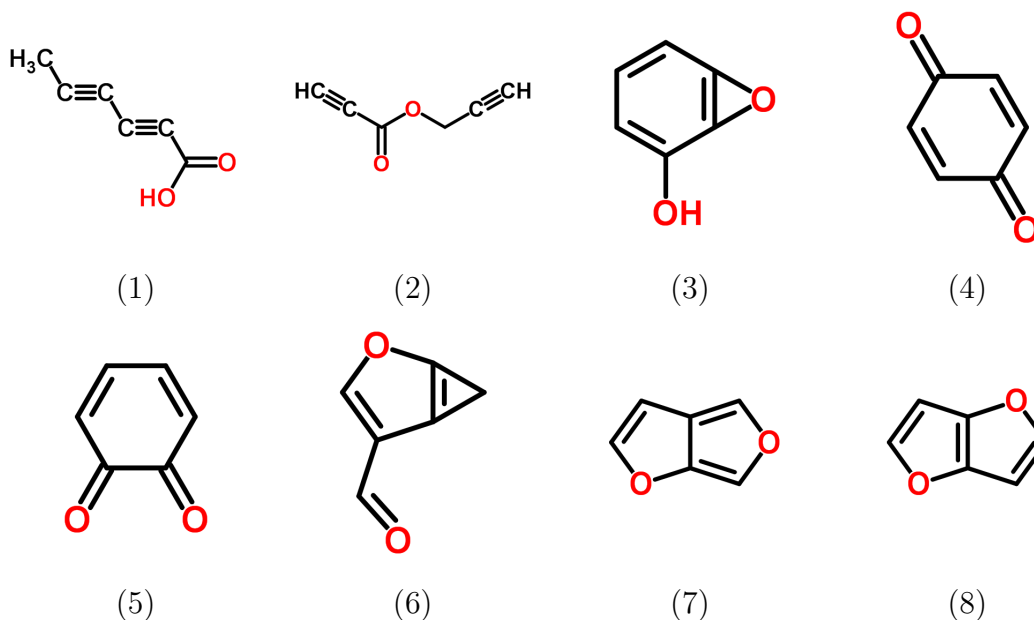
For each of these structures, carry out the following steps:

1. Build the structure and clean it up by minimizing and symmetrizing using IQMOL. Make a note of the point-group symmetry.

2. Use Q-CHEM to refine the geometry at the B3LYP/3-21G level and compute the frequencies. You can do this in just one calculation as follows:

   (a) Set 'Basis' to 3-21G and 'Method' to B3LYP.
   (b) Select Geometry for the 'Calculate' option.
   (c) Click on the ⊞ button to add a new job section to the input. You will now be editing options for the second job section. To change between active job sections, you can use the 'Job Section' combo box at the top-left of the QUI. The active job section is displayed in darker text in the right-hand panel of the QUI dialog.
   (d) The 3-21G basis and B3LYP method will be copied across to the second job section, but you should select Frequencies for the 'Calculate' option.
   (e) Submit the job as usual.

   This will ask Q-CHEM to optimize the geometry and then read in the optimized geometry for the frequency calculation, which is exactly what we want.

3. When the job has finished, record the final optimized energy. This is will be the final energy listed in the 'Geometries' item in the Model View.

4. Open the Frequencies configurator by double-clicking the Frequencies item in the Model View. Make a note of the frequency of the most intense mode. Animate this mode by double-clicking the mode in the table and describe it.

5. If you find you have imaginary frequencies, animate the imaginary mode to determine how to distort the geometry to find a minimum. Ask a demonstrator how to do this if you are unsure. Resubmit your calculation (optimization + frequency) to obtain a minimum.

For structure (1), predict the number of peaks in the ^{1}H and ^{13}C NMR spectra. Compute the NMR chemical shifts at the B3LYP/6-31G* level to confirm your predictions. (Click the reset button in the QUI before setting up the job to remove the extra job sections.) Save images for each of these spectra, you will need these to answer the questions.

Note: If you are using version 2.8 of IQMOL you will be able to right-click on the spectra to save images. For older versions you will need to take screen shots. On a Mac this can be accomplished by *cmd-shift-4* and then selecting the desired region using the cross-hairs.

III.   EXERCISES

You report should contain a table of results containing:

- The isomer identifier
- The optimized energy and nuclear repulsion energy (report total energies in hartrees, with 6 decimals)
- Point group
- Number of IR *inactive* modes
- The frequency of the most intense mode
- A description of the most intense mode
- Energies of isomers relative to the most stable structure (report energy differences in kcal/mol and/or kJ/mol)

and answers to the following questions:

1. Which isomer is least stable? Explain why.
2. For which isomer(s) did you encounter imaginary frequencies? How did you alter the geometry to obtain the minimum?
3. Explain why isomer (8) has IR silent modes, whereas (7) does not.
4. The following spectrum was taken from the NIST website. Determine which isomer of $C_6H_4O_2$ it corresponds to giving reasons for your choice. Use your frequency calculation to assign the four main bands in the spectrum.
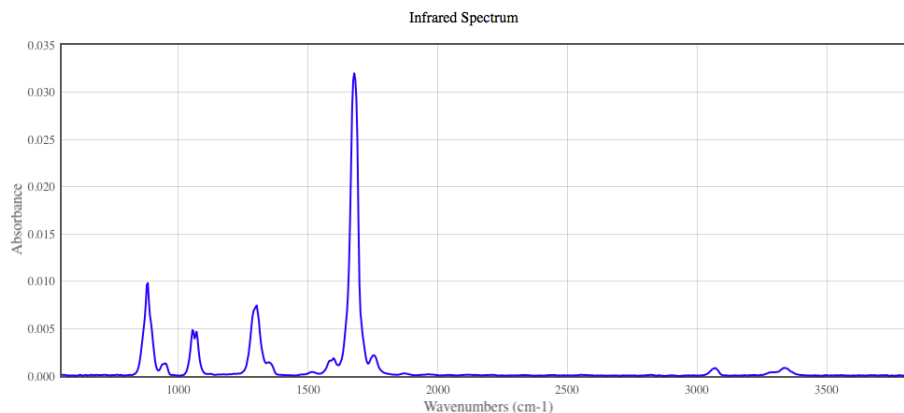
5. Assign the bands in your NMR spectra of isomer (1). Why are there more signals in the ^{1}H spectrum that you would expect experimentally.