

“The ability of quantum mechanics calculations to predict vibrational spectra.”

In lecture, we learned about 1D Harmonic Oscillator solutions to the Schrödinger equation, $\Psi_v(x)$, $v = 0, 1, 2, \dots$, for a particle subjected to a harmonic potential $V(x) = \frac{1}{2}kx^2$. We found the energies of each vibrational state to be

$$E_n = \left(v + \frac{1}{2}\right) h\nu \quad (1)$$

where h is Planck's constant, and $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ is the harmonic oscillator frequency, which depends on the force constant k (units $N.m^{-1}$) and the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ (assuming the vibration is for a two-particle system of masses m_1 and m_2). Let's explore how well this simple harmonic approximation compares to more detailed quantum calculations of diatomic molecules.

Procedure

Part A. Let's consider the diatomic molecule CO, carbon monoxide. Spartan has a database of experimental vibrational spectra for a small number of molecules, and CO is one of them. Perform the following steps:

1. Build the molecule, and optimize its geometry

- Build $C \equiv O$ molecule.
- Setup > Calculations....
- Calculate Equilibrium Geometry for the Ground State, using **DFT-B3LYP** with a modest basis set **6-31G***. Set total charge to “**Neutral**” with **0** unpaired electrons, and make sure the checkbox for **Vibrational Modes** is selected.
- The calculation should complete quickly.

2. Inspect the calculated vibrational spectra.

- Go to the Display > Spectra menu.
- Click on the plus icon and add the **Calculated IR spectrum and Experimental IR spectrum**. You should see good agreement between the two spectra. Clicking and dragging near the computed spectral peak will “lock on” to the peak and display a numerical value for the predicted peak, and animate the bond-stretching vibrational mode. Note that these spectra are reported in wavenumbers (cm^{-1}), which is very typical

of chemical spectroscopic measurements. The wavenumber $\bar{\nu}$ is the reciprocal of the wavelength, $\bar{\nu} = \frac{1}{\lambda}$. Thus, the frequency in Hz (s^{-1}), $\nu = c\bar{\nu}$, can be obtained simply by multiplying $\bar{\nu}$ by the speed of light, $3 \times 10^{10} \text{ cm.s}^{-1}$.

Part B. Vibrational Modes. It can be shown that there are $3N-6$ and $3N-5$ vibrational modes (in which N is the number of atoms in molecule) for non-linear and linear molecules; respectively. For example, we have 1 vibrational mode for CO molecule—as it is a linear molecule and $N=2$ —which corresponds with $C \equiv O$ bond-stretching.

For this part, let's try to evaluate vibrational modes of H_2O and HCN ($H - C \equiv N$) molecules. To do so, calculate Equilibrium Geometry for the Ground State of these molecules, using **DFT-B3LYP** with a modest basis set **6-31G***. Set total charge to “**Neutral**” with **0** unpaired electrons, and make sure the checkbox for **Vibrational Modes** is selected.

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Part A: In part A, you found the wavenumber corresponded to CO bond-stretching using DFT method. Convert the wavenumber $\bar{\nu}$ of the predicted peak to frequency ν .

Answer (ν from DFT):

Now, let's compare this frequency to the frequency of light we expect to be absorbed for excitation from the $v = 0 \rightarrow v = 1$ states of a **Harmonic Oscillator**, given in Equation (1). The reported force constant for CO is $k = 1820 \text{ N.m}^{-1}$. To calculate the reduced mass, assume that the masses of the carbon and oxygen atoms are $12 m_p$ and $16 m_p$, where $m_p = 1.672 \times 10^{-27} \text{ kg}$ is the mass of the proton. Are these results comparable to the quantum mechanical calculations?

Answer (ν from Harmonic Oscillator calculation):

Part B: Based on your results, complete the following table for H₂O and HCN molecules.

<i>Molecule</i>	<i>Wavenumber $\bar{\nu}$ (cm^{-1})</i>	<i>Which atoms are involved in each vibrational mode? Also, classify each one in terms of Symmetric-stretch, Asymmetric stretch, and Bending.</i>
<i>H₂O</i>	$\bar{\nu}_1 =$	
	$\bar{\nu}_2 =$	
	$\bar{\nu}_3 =$	
<i>HCN</i>	$\bar{\nu}_1 =$	
	$\bar{\nu}_2 =$	
	$\bar{\nu}_3 =$	
	$\bar{\nu}_4 =$	