**Determination of O-H Stretching Frequency by Isotopic Substitution Using Infrared Spectroscopy (IR)**

Different regions of the IR spectrum correspond to different kinds of bond vibrations (e.g. a broad peak before 3000 cm-1 is indicative of O-H stretching). One way to determine which bonds vibrate at which frequencies on the IR spectrum is to use isotopic substitution. Replacing one of the atoms participating in the bond with its isotope shifts the frequency of the bond vibration in a predictable way. For example, if the hydrogen in the O-H group of an alcohol is substituted with its isotope, deuterium (D), the stretching frequency of this O-D bond will be shifted with respect to the original O-H bond.

The reason why these shifts occur has to do with the fact that chemical bonds act like springs. A spring oscillates in a harmonic motion as the spring is displaced from its equilibrium position. Therefore, a simple harmonic oscillator that obeys Hooke’s Law can model a bond between two atoms:

From Hooke’s Law, an equation can be derived for the energy difference for a harmonic oscillator:

$$ΔE=\left(\frac{h}{2π}\right)\left(\frac{k}{μ}\right)^{\frac{1}{2}}$$

Where, *h* is Planck’s constant

*k* is the stretching force constant

 μ is the reduced mass for the pair of atoms:

$$μ=\frac{m\_{A}m\_{B}}{m\_{A}+m\_{B}} (1)$$

and mA and mB are the masses of the two atoms.

For our purposes, the equation for $ΔE$ can be simplified to the following:

$$ΔE=\frac{1}{\sqrt{μ}} (2)$$

Where $ΔE$ is calculated for a pair of atoms (e.g. O-H) and the same pair with one of the atoms substituted with an isotope (e.g. O-D). Then, the theoretical vibrational frequency of the isotope-substituted group is proportional to the ratio of the energy differences between the two groups:

$$v\_{S}=\frac{ΔE\_{S}}{ΔE\_{U}}\*v\_{U} (3)$$

Where, $v\_{U}$ is the frequency of vibration of the unsubstituted group

$ΔE\_{U}$ is the energy difference for the unsubstituted group

$ΔE\_{S}$ is the energy difference for the isotope-substituted group

As the energy differences for harmonic oscillators is heavily reliant on the masses of the atoms, changing this mass even slightly with an isotopic substitution will result in a notable shift in the IR frequency. In this lab, you will be comparing the vibrational frequency of the O-H bond in methanol (MeOH) to same stretch in deuterated methanol (MeOD), in which the H of the alcohol is substituted with deuterium.

**Procedure**

This experiment will involve the use of liquid phase FT-IR. Always use gloves when handling salt plates and only clean plates with hexanes or heptane. Spectra will be recorded for CH3OH and CH3OD. Place a few drops of the protiated methanol onto one salt plate and sandwich the other plate on top. Twist the plates in a circular motion to spread out the liquid evenly, forming a thin layer. Always run a background spectrum first before inserting your sample. Make sure there are no bubbles before running the spectrum of your sample. Repeat this procedure for the CH3OD. Always wear gloves when handling the salt plates and avoid contact with water. Rinse the plates with hexanes or heptane between experiments.

**Data Analysis**

Note the position of the O-H stretching on the IR spectra of the regular methanol. Then, based on the frequency of the O-H stretch, calculate the theoretical frequency for the O-D stretch using equations 1-3 and compare that to the frequency of the O-D stretch you observed on the IR spectrum of the deuterated methanol.