

## 5.2: Background

This absorption of infrared light energy causes functional groups in molecules to vibrate. This phenomenon serves as the basis of IR spectroscopy. At very small (molecular) scale the laws of physics work differently. In the macroscopic world, objects can have any value of energy on a spectrum. For example, imagine a ball placed on a hill (Figure 1). The higher on the hill the ball is placed the more potential energy that it can have. Because the ball can be placed anywhere on the hill, it can have any potential energy on a spectrum of potential energies. At the molecular scale, only certain energies are allowed. The energy levels are what scientists refer to as quantized in nature. Going back to our hill and ball analogy, the smooth side of the hill would be replaced with a set of steps. In such a case, not all values of potential energy are possible. Rather, the ball can only hold the values of potential energy corresponding to the height of each of the steps. The ability to only hold specific energy levels is referred to as quantization.

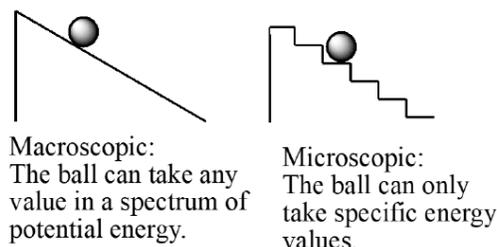


Figure 1. Potential energy in the macroscopic scale versus potential energy levels on the microscopic scale.

The same quantization of energy occurs within the vibrations of a molecule, meaning that only certain vibrational energies are allowed. The molecules can change the vibrational energy state that they are in by absorbing exactly the difference in energy between quantized energy levels. The energy required for this excitation depends strongly upon both the strength of the bond between atoms and the mass of atoms connected in the bond (Equation 5.2.1).<sup>6</sup> In this equation,  $\tilde{\nu}$  is the wavenumber of the absorption in  $\text{cm}^{-1}$  while  $c$  is the speed of light in a vacuum. The force constant of the bond (bond strength) is represented by  $f$ ; stronger bonds have a larger force constant. The reduced mass,  $m_{red}$ , is a measure of the masses of the atoms involved in the vibration. If you have a bond between a heavy atom or functional group and a much lighter one (e.g.  $\text{H} - \text{Cl}$ ) the lighter object moves much more than the heavier one, so the reduced mass is close in value to the lighter mass. If you have a bond vibration between two things of equal mass (i.e.  $\text{H}_3\text{C} - \text{CH}_3$ ) both sides of the bond share the vibration, so the reduced mass is about half of the mass of one side.

$$\tilde{\nu} = \frac{1}{2\pi c} \times \sqrt{\frac{f}{m_{red}}} \quad (5.2.1)$$

In the simplest analysis of a vibrational spectrum, each bond can vibrate independently and should have its own force constant and reduced mass. In reality, some vibrations are spread out throughout the entire molecule while others are more localized on one bond. Think about the suspension of a car driving over a pothole. If one tire drives over the pothole the whole car shakes, not just the front half of the car. Similarly, if a molecule is excited by light, it's probable that the vibration won't just be concentrated in one bond.

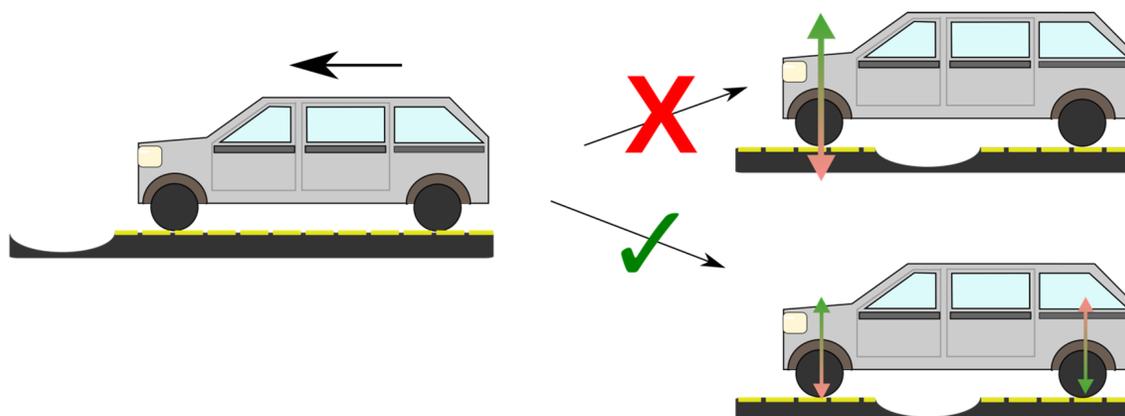


Figure 2. Normal modes in a car. Left: A car drives its front tires over a pothole. Right: Although only the front tires have passed over the bump, we see that the vibration does not stay in the front of the car. Rather, because the front and back tires are both attached to the body of the car, the vibration is delocalized to both front and rear tires. Similarly, many types of vibrations in molecules involve more than a single bond.

In this exercise, you will learn to use Orca to calculate the vibrational frequencies (in wavenumbers) and modes (how the atoms vibrate) of a small molecule, hexane. These data will then be used to help assign the resonances of an experimental IR spectrum of the same molecule. Moreover, you will use provided data to determine the effect of hybridization on bond strength and by extension vibrational frequency of a C – H bond.

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