

## Molecular Vibrations and Harmonic Motion.

For normal motions of a molecule (away from extremes such as disassociation) the harmonic approximation works well to describe vibrational motions. This is the same type of motion as found in a pendulum, a mass vibrating on a spring, or in rotational motion with constant angular velocity.

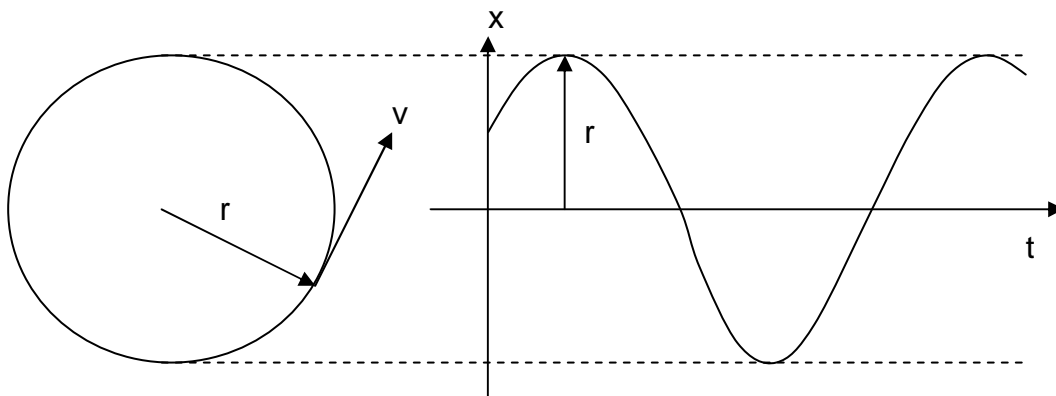


Figure 1.

For rotational motion, at constant angular velocity, the x direction projection of a point on the rotating circle will draw a plot of a cosine function shifted by a phase angle  $\phi$ . This is shown in Figure 1.

$$\text{Angular Velocity} = \omega = \frac{v}{r} = 2\pi\nu$$

(1.1)

where:  $v = \text{linear velocity}$

$r = \text{radius}$

$\nu = \text{frequency of rotation}$

Now consider a mass,  $m$ , hanging from a spring, with spring constant  $k$ , which is attached to a fixed wall (or infinite mass). This is depicted in Figure 2. The mass is given a vertical push and as the mass oscillates a roll of paper is moving past it with constant velocity and the mass marks the paper. The path traced on the paper is the same as the above path for the x projection of the rotating point.

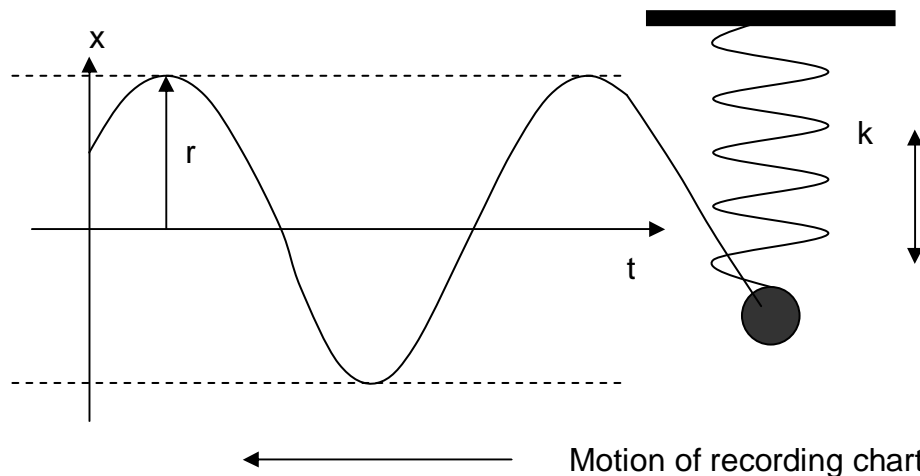
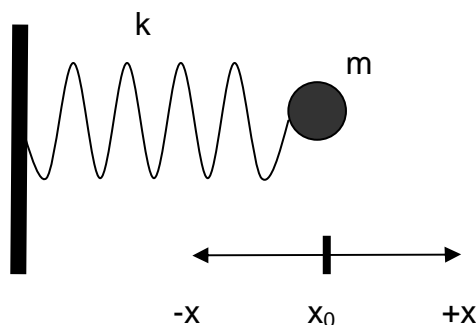


Figure 2.

Lets look at the spring and mass in more detail. Figure 3 shows the system and labels the displacements from equilibrium as  $-x$  and  $+x$  and the equilibrium position is at  $x_0$ . To expand or compress the spring stores energy and takes an application of force.

Figure 3.



Or,

$$(1.2) \quad F = -\frac{dV}{dx} = -kx$$

which gives the potential as:

$$(1.3) \quad V = \frac{1}{2}kx^2 \text{ or } \frac{1}{2}k(x_0 - x)^2, \text{ if } x_0 \neq 0$$

$V$  is the potential energy of the harmonic oscillator, or the stored energy in the spring at a given time.

From the definition of force,  $F = ma$ , one gets the relationship:

$$F = ma = m \frac{d^2x}{dt^2} = -kx$$

(1.4)

or,

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x$$

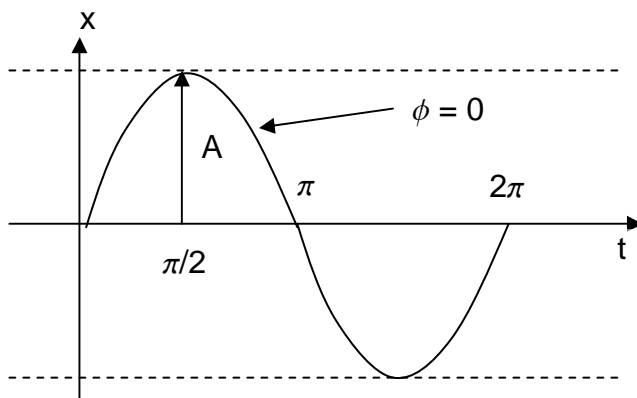
This differential equation has solutions of the form:

$$(1.5) \quad x = A \sin(\omega_0 t + \phi), \text{ where } \omega_0 = \left(\frac{k}{m}\right)^{\frac{1}{2}}$$

and  $A$  is the maximum amplitude that the mass reaches, or  $A = |x_{\max} - x_0| = r$ .

Figure 4.

Plot of the solution to equation in 1.4 when the phase angle,  $\phi$ , is zero.



Another way to look at the problem is to plot the potential energy,  $V$ , versus the displacement of the mass from its equilibrium position.

Figure 5.

In this figure the mass would oscillate between  $+x_{\max}$  and  $-x_{\max}$ . The potential energy is at a maximum at  $+x_{\max}$  and  $-x_{\max}$ , and is zero at  $x_0$ .

In fact, conservation of energy gives us that the total energy,  $E$ , is the sum of the potential energy,  $V$ , and the kinetic energy,  $T$ , at any time. Therefore, at  $+x_{\max}$  and  $-x_{\max}$  the total energy,  $E = V$ , and at  $x_0$ ,  $E = T$ . This tells us that :

$$(1.6) \quad E = V(x_{\max}) + T(x_{\max}) = V(x_{\max}) \quad \text{since } T(x_{\max}) = 0$$

or

$$E = V(x_{\max}) = \frac{1}{2} k (x_{\max} - x_0)^2$$

However, at  $x_0$  the situation reverses and  $E = V(x_0) + T(x_0) = T(x_0)$  since  $V(x_0) = 0$  and the total energy is the kinetic energy which at  $x = x_0$  is:

$$E = V(x_0) + T(x_0) = T(x_0) \quad \text{since } V(x_0) = 0$$

$$(1.7) \quad \text{or}$$

$$E = T(x_0) = \frac{1}{2} m v^2$$

Therefore:

$$(1.8) \quad T_{\max} = V_{\max}$$

$$\text{or} \quad \frac{1}{2} m v^2 = \frac{1}{2} k (x_{\max} - x_0)^2$$

On the projected  $x$  vs.  $t$  plot, Figure 1., from the point on the circle one has:

$$(1.9) \quad x_{\max} - x_0 = r$$

which can be substituted into the above equation 1.8 to give:

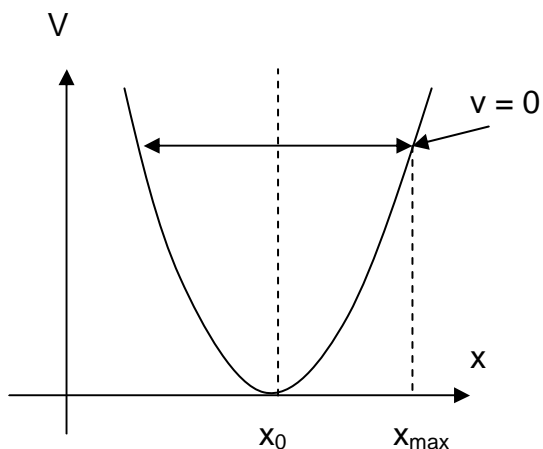
$$(1.10) \quad \frac{1}{2} m v^2 = \frac{1}{2} k r^2$$

which can be rearranged to:

$$(1.11) \quad v^2 = \frac{k}{m} r^2$$

which becomes on substitution of the relationship,  $\omega = v / r$ :

$$(1.12) \quad \omega = \sqrt{\frac{k}{m}} = 2\pi\nu$$



or, finally,

$$(1.13) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

Now, if the infinite mass of the wall is replaced by a finite mass  $M$ , which will be able to move, one can make the problem into the previous problem by substituting the reduced mass,  $\mu$ , for  $m$  in equation 1.13.

$$(1.14) \quad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M} \quad \text{or} \quad \mu = \frac{mM}{m+M}$$

giving:

$$(1.15) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

(The reduced mass comes from the new center of mass when the wall is replaced by  $M$ . for a finite  $M$  the center of mass is between  $m$  and  $M$  and the original mass  $m$  now acts like it is attached to an infinite wall positioned at the center of mass point.)

Consider the case where  $m = M$ .

$$(1.16) \quad \mu \xrightarrow{M \rightarrow m} \frac{m}{2} \quad \text{and} \quad \nu \xrightarrow{M \rightarrow m} \sqrt{\frac{2k}{m}}$$

And, to check, consider the case where  $M$  becomes infinite:

$$(1.17) \quad \mu = \frac{mM}{m+M} = m \left( \frac{M}{m+M} \right) \xrightarrow{M \rightarrow \infty} m \quad \text{and} \quad \nu \xrightarrow{M \rightarrow \infty} \sqrt{\frac{k}{m}}$$

Compare the reduced masses of  $\text{H}_2$ ,  $\text{HF}$  and  $\text{HCl}$

$$(1.18) \quad \begin{aligned} \mu_{\text{H}_2} &= \frac{1 \times 1}{1 + 1} = 0.500 \\ \mu_{\text{HF}} &= \frac{1 \times 19}{1 + 19} = 0.950 \\ \mu_{\text{HCl}} &= \frac{1 \times 35}{1 + 35} = 0.973 \end{aligned}$$

For  $\text{HF}$  and  $\text{HCl}$  the reduced mass and corresponding vibrational frequency are nearly that of a hydrogen atom attached to the infinite wall, while the  $\text{H}_2$  molecule has a vibration shifted by a factor of 2 from the infinite wall case.  $\text{HF}$  and  $\text{HCl}$  are examples of the local mode concept in that the vibration of the hydrogen atom is almost independent of the motion of the attached  $\text{F}$  or  $\text{Cl}$ . This approximation becomes even better when the hydrogen is attached to a large molecule.

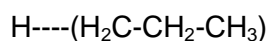
## Local Mode Concept

This idea is fundamental to how infrared spectroscopy is used by most chemists. Essentially it says that vibrations of functional groups act independently of each other and the molecule. This isn't entirely true, but at higher frequencies it is useful. At lower frequencies in the infrared the couplings between functional groups begin to be more apparent and the result is the "fingerprint" region that is much more sensitive to the couplings, and, hence, more nearly unique to the individual molecule.

A good example of the local mode concept is to consider a hydrocarbon, say, propane,



The hydrogen – carbon stretch of a  $-\text{CH}_3$  group looks a lot like hydrogen attached to an infinite mass vibration, or,

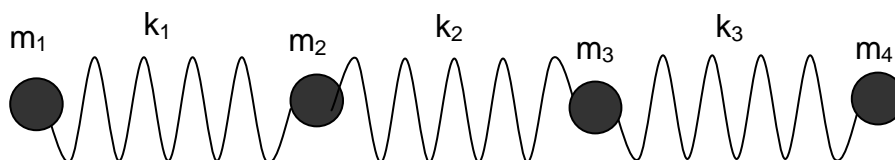


The CH stretch will act like an independent vibrational oscillator as long as the other motions of the molecule are significantly different in frequency (energy).

One way to visualize this is to consider a series of connected springs and masses as shown in Figure 6.

Figure 6.

A set of coupled springs and masses.



If  $m_1$  and  $k_1$  are small compared to  $k_2$ ,  $m_2$  then  $m_2$  won't move much compared to  $m_1$ .

## Quantization of the Harmonic Oscillator.

By only letting radiation be absorbed or emitted if a transition between levels occurs one quantizes the harmonic oscillator. Mathematically this corresponds to:

$$(1.19) \quad E_n = \left(n + \frac{1}{2}\right) h\nu, \quad n = 0, 1, 2, \dots$$

The one-half term comes from what we call the zero-point energy. Essentially, even at absolute zero, there will be some vibrational energy present in a molecule. Substituting in the for frequency,  $\nu$ , from Eqn. 1.15 gives:

$$(1.20) \quad E_n = \left(n + \frac{1}{2}\right) h \left( \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \right), \quad n = 0, 1, 2, \dots \text{ or,}$$

$$E_n = \left(n + \frac{1}{2}\right) h \sqrt{\frac{k}{\mu}}$$

However, the more significant result is related to the energy associated with transitions between energy levels, which is:

$$(1.21) \quad \Delta E_{nm} = h\nu(n - m), \quad \text{where } n \text{ and } m \text{ are integers } \geq 0.$$

Of special note is that the spacings between energy levels are equal (contrast to the Bohr atom levels).

