

# Molecular Vibrations

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## Introduction

The familiar mass on a spring system and a spring between two masses are scenarios often used to describe harmonic motion. These same concepts can be used to describe molecular vibrations as well. To do this, each atom is treated as a mass, and their bond is considered the spring. This relationship is significant because equations that can be used to depict the masses connected by a spring can also give the frequencies for molecular vibrations.

There are three main situations that involve a mass with a spring. There is a mass connected to a non-mobile object with a spring, two equal masses connected with a spring, and two unequal masses connected by a spring. These can each model a different type of molecule. A mass connected to a non-mobile object with a spring is representative of a relatively small atom with an atom of much greater magnitude, such as HCl. Two equal masses connected with a spring is useful for describing a diatomic molecule, such as H<sub>2</sub> or O<sub>2</sub>. Moreover, a molecule with atoms of different masses, such as CO, can be illustrated by two unequal masses on a spring. The latter two of these models will be used most often in describing molecular vibrations because a molecule consisting of a small atom and an atom of much greater mass, shown by the first case, can be modeled by two unequal masses on a spring, where one mass is much greater than the other. These will then be utilized to find the frequencies of H<sub>2</sub> and H<sub>2</sub>O molecular vibrations.

## Background

### Mass on a Spring

The first, and most simple of these scenarios, is the mass connected to a non-mobile object with a spring. The force of the spring is proportional to the spring constant ( $k$ ) and the displacement of the object ( $x$ )

$$(1) F = -kx,$$

which is the negative change in spring potential energy with respect to time,

$$(2) \quad F = -\frac{dU}{dx},$$

and the spring potential energy is

$$(3) \quad U = \frac{1}{2}kx^2.$$

The displacement of the mass is

$$(4) \quad x = A\cos\omega t = A\cos\frac{2\pi t}{T}$$

where

$$(5) \quad \omega = 2\pi f$$

and  $\omega$  is the angular frequency of the harmonic motion,  $T$  is the period, and  $f$  is the linear frequency. Given by Newton's Second Law,

$$(6) \quad F = ma, \text{ where } a = \frac{d^2x}{dt^2} = \ddot{x}$$

Therefore,  $-kx = m\ddot{x}$ . Using Eq. (6) and the displacement shown in Eq. (4),

$$(7) \quad \ddot{x} = -\omega^2 x \text{ and } \omega = \sqrt{\frac{k}{m}}$$

can be determined. Equation (7) states that the natural frequency of this mass is dependent on the spring constant and the magnitude of the mass. Due to the limitations of this model, two equal masses connected by a spring, and two unequal masses connected by a spring, will have the more focus in this report than this case.

## Two Equal Masses Connected by a Spring

To begin demonstrating the molecular vibrations of a diatomic molecule, two equal masses connected by a spring is most useful. For sake of this application, the equal masses will be referred to as atom 1 and atom 2, both of which are of the element. The spring potential in this case is

$$(8) \quad U(x_1, x_2) = \frac{1}{2}k(x_1 - x_2)^2$$

where  $x_1$  and  $x_2$  are the displacements of atoms 1 and 2, respectively. Since this potential energy in Eq. (78) is dependent on two variables, partial derivatives must be taken to find the force of the spring on each atom, such that

$$(9) \quad F_1 = -\frac{\partial}{\partial x_1} U(x_1, x_2) = -k(x_1 - x_2)$$

and

$$(10) \quad F_2 = -\frac{\partial}{\partial x_2} U(x_1, x_2) = k(x_1 - x_2).$$

A dynamic matrix (D) is found by

$$(11) \quad D = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} \\ \frac{\partial^2 U}{\partial x_1 \partial x_2} & \frac{\partial^2 U}{\partial x_2^2} \end{pmatrix}.$$

The force on one atom if an atom is moved is expressed by the second derivative of the potential energy. The dynamic matrix is used to find the eigenvalues ( $\lambda$ ) and eigenvectors (Y) such that

$$(12) \quad \mathbf{D}\mathbf{Y} = \lambda\mathbf{Y}$$

where  $\lambda$  is a scalar. Eigenvalues are related to the model by

$$(13) \quad \lambda = m\omega^2,$$

providing the information needed to find the natural frequency of the atoms' harmonic motion. In the case of two equal masses,

$$(14) \quad D = \begin{pmatrix} k & -k \\ -k & k \end{pmatrix}$$

and there are two eigenvalues:  $\lambda = 0, 2k$ , found using differential equations. If  $\lambda = 0$ , then  $\omega = 0$  so there is no vibration, but a translation instead. However, if  $\lambda = 2k$ , then there is a vibration with natural frequency

$$(15) \quad \omega = \sqrt{\frac{2k}{m}}$$

Since real life motion is in three dimensions, the motions of a molecule are also in three dimensions. There are three possible motions of a diatomic molecule: translation, rotation, and vibration. Translation occurs when both atoms' motion is in the same direction in the same plane, while rotation occurs when atoms have motion in two different planes. In order for a vibration to occur, the atoms must have opposing motion in the same plane. In a diatomic molecule there will be three translations, two rotations, and one vibration.

## Two Unequal Masses Connected by a Spring

Although it is much simpler to discuss the motions of a diatomic molecule, most molecules found in the world consist of two different atoms, such as CO or LiH. This is demonstrated by two unequal masses on a spring. Using the background from above, the dynamic matrix is also used to find the eigenvalues and eigenvectors in this system. In this instance,

$$(16) \quad D = \begin{pmatrix} \frac{k}{m_1} & \frac{-k}{\sqrt{m_1 m_2}} \\ \frac{-k}{\sqrt{m_1 m_2}} & \frac{k}{m_2} \end{pmatrix}$$

and

$$(17) \quad \lambda = \omega^2$$

It can be determined that

$$(18) \quad \lambda = k \frac{m_1 + m_2}{m_1 m_2}$$

and

$$(19) \quad \omega = \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

Due to this, it is proven that the natural frequencies of the vibrations are dependent on the masses of each atom. If the mass of atom 1 is much greater than the mass of atom 2,

$$(20) \quad \lim_{m_1 \rightarrow \infty} \omega = \sqrt{\frac{k}{m_2}},$$

which is the same frequency of a mass connected to a non-mobile object on a spring. In addition, if the mass of atom 1 is equal to the mass of atom 2, then Eq. (15) will be the result. By modeling each molecule as consisting of two atoms with different masses, the natural frequencies of molecular vibrations can be determined of all three cases discussed thus far.

## Applications

### Modeling H<sub>2</sub> Vibrations

It is now time to use this background to determine the angular frequency of the molecular vibrations of an H<sub>2</sub> molecule; since H<sub>2</sub> is a diatomic molecule, Eq. (15) will be utilized to do this. The value for k must be solved using

$$(21) \quad k = \frac{\partial^2 V}{\partial r^2},$$

where V is the potential energy of a molecule, and the mass of a hydrogen atom is  $m_H = 1.67 \times 10^{-24}$  g. The potential energy of a diatomic molecule is given by the Morse potential energy function,

$$(22) \quad V(r) = D_e(1 - e^{-a(r-r_e)})^2,$$

where  $D_e$  is the depth of the potential at equilibrium, r is the distance between the atoms,  $r_e$  is the equilibrium bond distance, and a is a constant. Evaluating  $\frac{\partial^2 V}{\partial r^2}$  at  $r = r_e$ ,

$$(23) \quad k = 2D_e a^2$$

For an H<sub>2</sub> molecule,  $D_e = 7.605 \times 10^{-12}$  erg,  $a = 1.93 \times 10^8 \text{ cm}^{-1}$ , and  $r_e = 7.414 \times 10^{-9}$  cm. Therefore,  $k = 5.67 \times 10^5$  dyne/cm. Using Eq. (15), the angular frequency is determined as  $\omega = 8.24 \times 10^{14} \text{ s}^{-1}$ . Then, by using Eq. (14), the linear frequency of the vibration is found to be  $f = 1.31 \times 10^{14} \text{ s}^{-1} = 4386 \text{ cm}^{-1}$ . In Fig. 1 below, the motions and vibration of the H<sub>2</sub> molecule is represented.

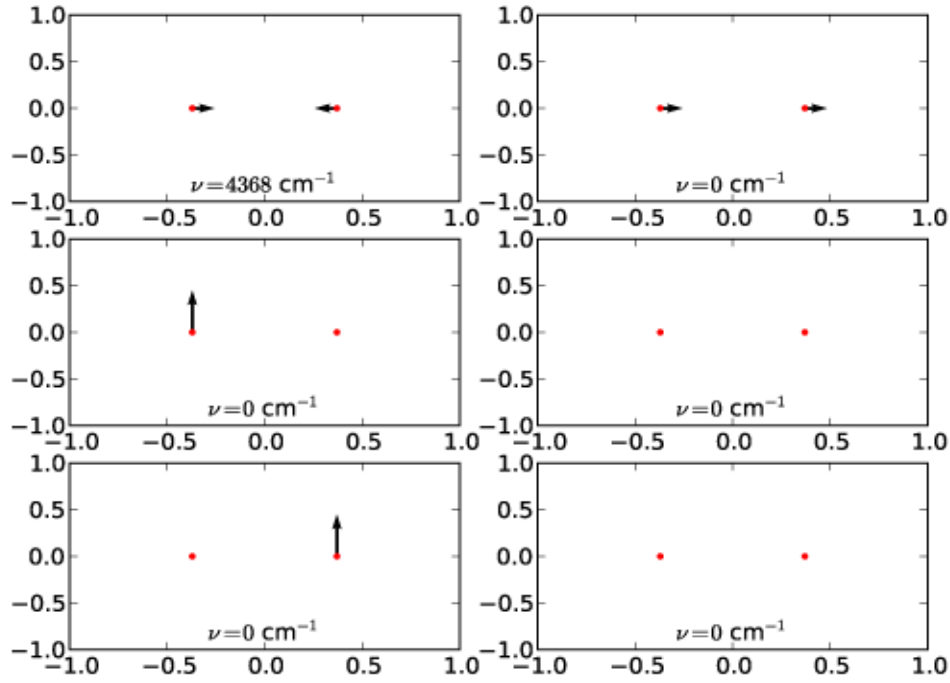


Fig. 1 Demonstrating the three dimensional motion of  $H_2$  molecule and displayed potentials with the one vibration shown in the upper left graph.

## Modeling $H_2O$ Vibrations

Water is arguably the most used molecule in daily life. Unlike  $H_2$ ,  $H_2O$  contains atoms of different masses. Due to this, there are more variables that contribute to the potential energy of the molecule, which must be reflected in calculating the potential energy. The number of vibrations is also different from  $H_2$  due to the added oxygen. There are three vibrations, three translations, and three rotations. To find the frequencies of the vibrations, the Born-Oppenheimer potential is expanded as a power series which will be used to the fourth term in this case [1].

$$(24) \quad V = \frac{1}{2}k_1(\Delta r_1^2 + \Delta r_2^2) + k_2(\Delta r_1 + \Delta r_2) + k_3(\Delta r_1 + \Delta r_2)r_e\Delta\theta + \frac{1}{2}k_4(r_e\Delta\theta^2)$$

For  $\text{H}_2\text{O}$ ,  $\Delta r_1$  and  $\Delta r_2$  are the change in bond length from equilibrium for the hydrogen to oxygen bonds and  $r_e \Delta \theta$  is the change in bond angle from its  $104.52^\circ$  at equilibrium. In this scenario,  $k_1 = 84.5 \times 10^4$ ,  $k_2 = -1.0 \times 10^4$ ,  $k_3 = 2.28 \times 10^4$ ,  $k_4 = 7.607 \times 10^4$  all in dynes/cm<sup>2</sup>. By inputting these values in Eq. (24), we obtain three frequencies,  $f_1 = 3970 \text{ cm}^{-1}$ ,  $f_2 = 3850 \text{ cm}^{-1}$ ,  $f_3 = 1651 \text{ cm}^{-1}$ . Figure 2 displays the frequencies as well as the motions of the  $\text{H}_2\text{O}$  molecule below.

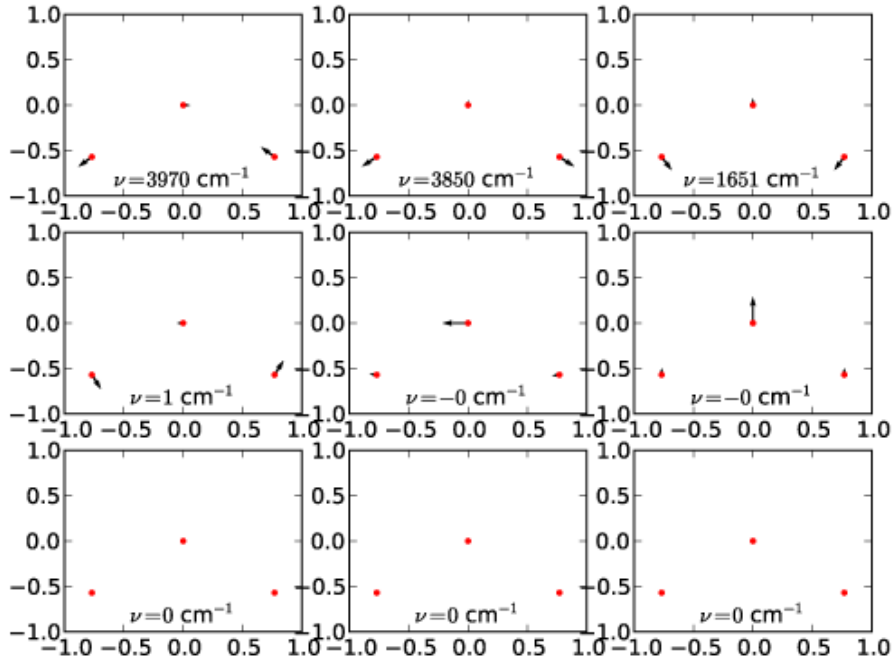


Fig. 2 There are 3 vibrational modes shown in the top row of graphs with displayed potential energies. Asymmetrical stretching is displayed in the upper left graph, symmetrical stretching in the top middle graph, and bending in the upper right graph.

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## **REFERENCES**

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