Normal Modes of Vibration

The atoms in molecules are constantly moving. The distance between any pair of atoms and bond angles is constantly changing with time, although the average bond length and bond angles are well defined and remain the same for long periods of time. At room temperature, this motion is mostly small amplitude oscillations, so called molecular vibration. Chemical reactions occur on a much longer time scale than vibration (many orders of magnitude). Each degree of freedom of the molecule has on average an energy of $k_B T$ where k_B is the Boltsmann constant and T is the temperature. It is important to understand vibrational motion of molecules for many reasons. Vibrational motion is an important source and sink of kinetic energy in chemical reactions. Also, by using infrared spectroscopy which probes the vibrational motion, one can learn about molecular structure and the chemical composition of unknown samples. Sharp peaks in the IR absorption can be associated with particular molecules, or fragments of molecules. Each peak corresponds to a 'vibrational mode' of the molecule. In most cases the vibrational modes can be well approximated by so-called 'normal modes' of vibration.

Vibration of a diatomic molecule

In a diatomic molecule, the vibrational motion corresponds to oscillations in the bond length. The interaction potential function may, for example, be approximated by a Morse potential

$$V(r) \; = \; D \; \left(e^{-2\alpha(r - r_b)} - 2e^{-\alpha(r - r_b)} \right)$$

This form of the potential function often gives a good representation of the potential energy of covalently bonded atoms. Under typical conditions - reasonably strong bonds and room temperature - the deviations of the bond length from its optimal value is small, on the order of 0.1 or less. For such small displacements of the atoms, the potential energy can often be well described by a harmonic oscillator approximation. The appropriate harmonic approximation can be found by Taylor expansion the potential function about the minimum energy. Let x denote the deviation, $x = r - r_0$, from the optimal distance between the atoms. The Taylor expansion about $x = 0$ is

$$V(x) \; = \; V(0) \; + \; x V'(0) \; + \; \frac{x^2}{2} V''(0) \; + \; h.o.t.$$

Since $V(x)$ has a minimum at $x = 0$, $V'(0) = 0$. Neglecting the higher order terms, we

have

$$V(x) - V(0) \;=\; \frac{1}{2}\,V''(0)\,x^2 \;=\; \frac{1}{2}\,k\,x^2$$

Here, k denotes the so called spring constant (the harmonic oscillator potential function is applicable to a spring with stiffness given by the spring constant). The force acting on the harmonic oscillator is

$$F(x) \;=\; -\frac{d}{dx}V(x) \;=\; -kx$$

The classical trajectory of a harmonic oscillator can be obtained from the equation of motion (Newton's second law)

$$F(x) \;=\; m\ddot{x}(t)$$

$$-kx(t) \;=\; m\ddot{x}(t)$$

$$\ddot{x}(t) \;=\; -(k/m)\,x(t)$$

The notation $\ddot{x}(t)$ means second derivative of x with respect to t. This differential equation has the general solution

$$x(t) \;=\; A sin(\omega t) \;+\; B cos(\omega t)$$

where $\omega = \sqrt{k/m}$. A and B are constants that need to be evaluated from the initial conditions. Another way to write the general solution is

$$x(t) \;=\; C sin(\omega t + \phi)$$

The deviation of the bond length from the optimal value varies in a sinusoidal way in time with frequency, ω.

Quantum mechanically, the harmonic oscillator has bound state energy levels spaced apart by $\Delta E = \hbar\omega$. The vibrational motion can be excited by the absorption of a quantum of light, a photon, with energy $\Delta E = h\nu = \hbar\omega$. The selection rule for vibrational excitations in the harmonic approximation is $\Delta\nu = \pm 1$, i.e. the system can only be excited by absorption of a photon to the next higher level, or de-excited by emission of a photon to the next lower level. Within the harmonic approximation, the absorption spectrum therefore has just one peak This frequency typically corresponds to the infrared radiation.

Polyatomic molecules

For larger molecules, the trajectory of an atom is in general not a simple sinusoidal function corresponding to one frequency. Also, even if the molecule is initially distorted in such a way that only one of the bonds is stretched, all the bond lengths will eventually be changing with time. Special modes, so-called normal modes, can under some

circumstances be defined so that if only one mode is excited initially, then the other modes will not be excited. In that sense the simplicity of the diatomic is recovered in molecules with many atoms.

A simple system which illustrates this is a linear triatomic molecule where the atoms can only move along a line (a one-dimensional system). Even if only atom A is displaced initially, the motion of atom A, $x_A(t)$, is not just a sinusoidal function corresponding to a single frequency. After a while, the B-C bond starts vibrating also. The vibrational motion of the three atoms is coupled together.
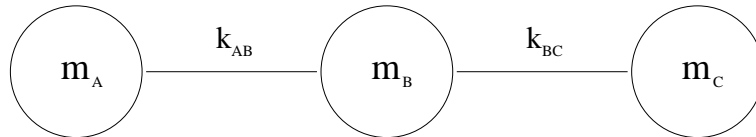

Figure 1: *A simple model of a molecule. The three atoms A, B, and C, with mass m_A, m_B og m_C, are confined to move along a line. The chemical bonds can be approximated by springs with spring constants k_{AB} and k_{BC}.*

The classical equation of motion (Newton's second law) can be solved exactly for polyatomic molecules if the interaction potential is approximated as a quadratic function (a multidimensional harmonic oscillator). The solutions are called 'normal modes' and they give the characteristic frequencies which are the dominant features in typical absorption spectra of polyatomic molecules. Let $x_A(t)$ be the displacement of atom A at time t from the optimal, lowest potential energy position of the atom, and similarly for $x_B(t)$ and $x_C(t)$. Analogous to the case of a diatomic molecule, a Taylor expansion of the potential energy about the optimal configuration of the atoms gives

$$V(x_A, x_B, x_C) = \frac{k_{AB}}{2}(x_B - x_A)^2 + \frac{k_{BC}}{2}(x_C - x_B)^2 \tag{1}$$

if third order and higher terms are neglected. This is the harmonic approximation to the full potential energy surface. The spring constants k_{AB} and k_{BC} are directly related to the second derivative of the potential energy with respect to the distance between atoms.

The equation of motion for each one of the atoms is

$$F_i = m_i \ddot{x}_i \tag{2}$$

where i is A, B or C. Using the fact that the force is the negative derivative of the potential energy, the three equations can be written as

$$-\frac{\partial V}{\partial x_i} = m_i \ddot{x}_i \tag{3}$$

where the partial derivative, $\frac{\partial V}{\partial x_i}$, denotes differentiation with respect to x_i while the other variables are kept fixed. In the case of the linear, triatomic molecule the force on each atom is

$$\begin{cases} \frac{\partial V}{\partial x_A} &= -k_{AB}(x_B - x_A) \\[2mm] \frac{\partial V}{\partial x_B} &= k_{AB}(x_B - x_A) - k_{BC}(x_C - x_B) \\[2mm] \frac{\partial V}{\partial x_C} &= k_{BC}(x_C - x_B). \end{cases} \tag{4}$$

Inserting this form of the force into the equations of motion, and dividing by the mass of the atom gives

$$\begin{cases} \frac{k_{AB}}{m_A}(x_B - x_A) &= \ddot{x}_A \\[2mm] -\frac{k_{AB}}{m_B}(x_B - x_A) + \frac{k_{BC}}{m_B}(x_C - x_B) &= \ddot{x}_B \\[2mm] -\frac{k_{BC}}{m_C}(x_C - x_B) &= \ddot{x}_C. \end{cases} \tag{5}$$

The problem is to solve this set of three, coupled differential equations. One can attempt to find a solution where all the atoms oscillate with the same frequency, i.e.

$$\begin{cases} \ddot{x}_A &= -\omega^2 x_A \\[2mm] \ddot{x}_B &= -\omega^2 x_B \\[2mm] \ddot{x}_C &= -\omega^2 x_C. \end{cases} \tag{6}$$

Here, ω is some frequency which has the same value in all three equations. To test if this will work, this form for $\Delta \ddot{x}_A$ can be inserted into the equation of motion to give (after switching left and right hand sides of each equation)

$$\begin{cases} -\frac{k_{AB}}{m_A} x_A + \frac{k_{AB}}{m_A} x_B &= -\omega^2 x_A \\[2mm] \frac{k_{AB}}{m_B} x_A - \left(\frac{k_{AB}}{m_B} + \frac{k_{BC}}{m_B} \right) x_B + \frac{k_{BC}}{m_B} x_C &= -\omega^2 x_B \\[2mm] \frac{k_{BC}}{m_C} x_B - \frac{k_{BC}}{m_C} x_C &= -\omega^2 x_C. \end{cases} \tag{7}$$

This set of linear equations can be written in a matrix form as

$$\begin{bmatrix} -\frac{k_{AB}}{m_A} & \frac{k_{AB}}{m_A} & 0 \\ \frac{k_{AB}}{m_B} & -\frac{k_{AB}}{m_B} - \frac{k_{BC}}{m_B} & \frac{k_{BC}}{m_B} \\ 0 & \frac{k_{BC}}{m_C} & -\frac{k_{BC}}{m_C} \end{bmatrix} \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} = -\omega^2 \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} \tag{8}$$

This is a matrix eigenvalue problem. The task is to determine the eigenvalue $-\omega^2$ and corresponding eigenvector. As will be discussed below, three different eigenvalues $-\omega_i^2$ and eigenvectors $\mathbf{v}_i$ can be found in this case. A non-trivial solution exists only when the determinant of the matrix

$$\begin{bmatrix} -\frac{k_{AB}}{m_A} + \omega^2 & \frac{k_{AB}}{m_A} & 0 \\ \frac{k_{AB}}{m_B} & -\frac{k_{AB}}{m_B} - \frac{k_{BC}}{m_B} + \omega^2 & \frac{k_{BC}}{m_B} \\ 0 & \frac{k_{BC}}{m_C} & -\frac{k_{BC}}{m_C} + \omega^2 \end{bmatrix} \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} \tag{9}$$

is zero. This gives a third order polynomial equation for ω^2 which has three roots.

A special case: A molecule of the type $A - A - A$

The calculation is simplified greatly if the mass of all three atoms is taken to be the same, i.e. $m_A = m_B = m_C \equiv m$, and the two spring constants are taken to be the same, i.e. $k_{AB} = k_{BC} \equiv k$. Then the eigenvalue problem becomes

$$\begin{bmatrix} -\frac{k}{m} & \frac{k}{m} & 0 \\ \frac{k}{m} & -\frac{k}{m} - \frac{k}{m} & \frac{k}{m} \\ 0 & \frac{k}{m} & -\frac{k}{m} \end{bmatrix} \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} = -\omega^2 \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}. \tag{10}$$

After dividing through by $\frac{k}{m}$ and defining $\lambda \equiv -m\omega^2/k$ this becomes

$$\begin{bmatrix} -1 & 1 & 0 \\ 1 & -2 & 1 \\ 0 & 1 & -1 \end{bmatrix} \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} = \lambda \begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix} \tag{11}$$

which is easy to solve by hand. The determinant is the third order polynomial

$$\begin{aligned} p(\lambda) &= (-1 - \lambda)(-2 - \lambda)(-1 - \lambda) - (-1 - \lambda) - (-1 - \lambda) \\ &= -\lambda(\lambda + 1)(\lambda + 3) \end{aligned} \tag{12}$$

which has roots at $\lambda_1 = 0, \lambda_2 = -1$, and $\lambda_3 = -3$. By inserting the eigenvalues into the eigenvalue equation one can find the corresponding eigenvectors. They are

$$\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}, \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ -2 \\ 1 \end{bmatrix}.$$

Note that the length of the eigenvectors is arbitrary, all they say is what the relative displacements of the atoms are, not how much they get displaced. The interpretation of the three solutions are as follows:

- The first solution corresponds to zero frequency and all three atoms are displaced in the same way $x_A = x_B = x_C$. This is simply uniform translation.
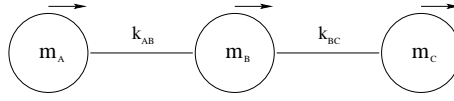
- The second solution corresponds to frequency $\omega_2 = \sqrt{k/m}$. The eigenvector shows that atom B does not move at all, while A and C move equally much but in opposite direction. This is the so-called symmetric stretch.
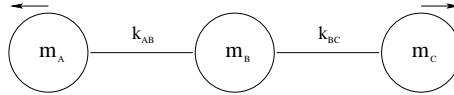
- The third solution corresponds to $\omega_3 = \sqrt{3k/m}$ a higher frequency than the symmetric stretch. The eigenvector shows that while atoms A and B are displaced equally much in the same direction, atom B is displaced twice as much in the opposite direction. This is the so-called asymmetric stretch.
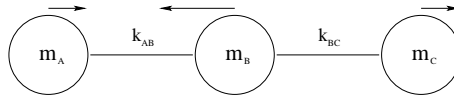
A general solution for the dynamics of the three atoms is a linear combination of these three normal mode solutions. But, the three normal modes are independent, i.e. there is no energy flow from one mode to another. If the molecule is vibrating in such a way that only one mode is active, then the molecule will continue to move according to that one normal mode. The others never come into play. Recall, that the central approximation here is that the interaction potential is harmonic. For more realistic anharmonic interaction potentials, such as the Morse potential, the independent normal modes are only approximate solutions, but typically they represent the dominant feature in the absorption spectrum.

Spectroscopy

In absorption spectroscopy, the molecule absorbs energy from the oscillating electric and magnetic field in the electromagnetic wave only if the frequency matches that of the vibrational oscillations (such matching of frequencies is called resonance). The energy of the absorbed photon is

$$E_i = h\nu_i = \frac{h\omega_i}{2\pi} = \frac{h\sqrt{\frac{k}{m}}}{2\pi}. \tag{13}$$

A polyatomic molecule has more than one normal mode of vibration. Each normal mode has a different frequency and there is, in principle, an absorption peak for each one of the modes. No peak is observed, however, if the normal mode displacements do not lead to a change in the dipole moment of the molecule.

where $h = 6,626 \times 10^{-34}$ J·s, is Planck's constant and $\nu_i = \omega_i/2\pi$ is the frequency.

More complex situations

When the mass of the atoms is not the same, for example CO_2, the solution of the eigenvalue problem is a little more complicated, but the normal modes are still a symmetric stretch and an antisymmetric stretch. Also, when the spring constant for the two bonds is not the same, as in OCS, the calculation is much more tedious and the solutions do not have any symmetry (or antisymmetry). These problems can, however, easily be solved using Mathematica and similar tools.

References

P.W. Atkins: *Molecular Quantum Mechanics,* chapters 11.5-11.8.

C.N. Banwell: *Fundamentals of Molecular Spectroscopy,* chapters 3.1 og 3.5.