Overview of Molecular Spectroscopy

In an earlier lecture, we discussed photoelectron spectroscopy as a means of measuring the electronic energy levels of a system. The purpose of spectroscopy, in general, is to probe allowed energies, which could be electronic energy levels, or energy levels of the nuclei. Recall that, in the Born-Oppenheimer approximation, we separate the electronic and nuclear Schrödinger equations and determine energy levels separately:

\[
\hat{H}_{elec}(R)\psi_{\alpha}(x,R) = \varepsilon_{\alpha}^{(elec)}(R)\psi_{\alpha}^{(elec)}(x,R) \]
\[
\hat{K}_n + V_{nn}(R) + \varepsilon_{\alpha}^{(elec)}(R) \psi_{\beta}^{(nucl)}(R) = E_{\beta} \psi_{\beta}^{(nucl)}(R)
\]

where \(\\alpha\) and \(\beta\) are the complete sets of quantum numbers for the electronic and nuclear subsystems, respectively. Thus, we determine the electronic energy levels at fixed nuclear configurations and then on each Born-Oppenheimer electronic surface \(\varepsilon_{\alpha}^{(elec)}(R)\), we determine nuclear energy levels \(E_{\beta}\). Pictorially, we can represent the nuclear energy levels we obtain on several of the electronic surfaces of bonding orbitals as shown in the figure below:

**Figure:** Bound energy levels on the Born-Oppenheimer surfaces or bonding orbitals.

Note that the surfaces of non-bonding orbitals have no bound levels. The basic idea is that subjecting a system to electromagnetic radiation of some frequency \(\nu\) induces transitions among the various energy levels. If the absorption of a photon of frequency \(\nu\) causes a transition from an initial energy level \(E_i\) to a final energy level \(E_f\), then the energy difference \(E_f - E_i\) is related to \(\nu\) via

\[
h\nu = E_f - E_i
\]

We have already seen that X- or UV radiation is needed to induce transitions among electronic energy levels. However,
on each electronic energy surface, we have a large manifold of nuclear energy levels characterized by different types of
motion. Bond vibrations are generally the highest frequency and have the largest spacing between energy levels. Bending
motion is also a high-frequency vibration. Rotational motion or motion of dihedral angles about single bonds is much lower
frequency. Consequently, between vibrational energy levels, there might be many rotational energy levels. Finally, nuclear
spins couple to the magnetic field component of the external radiation, and this causes a very small energy splitting, so
between rotational levels, there will be nuclear spin states. The table below shows the frequency of the external radiation
and the type of transition induced by it:

<table>
<thead>
<tr>
<th>(\textbf{Radiation})</th>
<th>(\textbf{Frequency})</th>
<th>(\textbf{Transition})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio waves</td>
<td>(10^7 - 10^9)</td>
<td>Nuclear spin</td>
</tr>
<tr>
<td>Microwave, Far IR</td>
<td>(10^9 - 10^{12})</td>
<td>Rotational</td>
</tr>
<tr>
<td>Near IR</td>
<td>(10^{12} - 10^{14})</td>
<td>Vibrational</td>
</tr>
<tr>
<td>Visible, UV</td>
<td>(10^{14} - 10^{17})</td>
<td>Valence electrons</td>
</tr>
<tr>
<td>X-ray</td>
<td>(10^{17} - 10^{19})</td>
<td>Core electrons</td>
</tr>
</tbody>
</table>

In order to generate a spectrum, sweep through a range of frequencies and record the frequencies at which radiation
is absorbed as well as the intensity of the absorption. This gives us a graph of absorption intensity \(\alpha (\nu)\) (also
denoted \(I(\nu)\)) at frequency \(\nu\). Generally, we are interested in a limited range of frequencies, e.g. the entire IR
spectrum, which gives us information about rotational and vibrational transitions only, thereby characterizing motions in
the nuclear subsystem.

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**Rotational and vibrational energy levels in molecules: Microwave and infrared spectroscopy**

**Rotational levels**

Recall in problem set # 4, we considered the energy levels and wave functions of a particle of mass \(m\) constrained to
move on a ring of radius \(R\) in the \((xy)\) plane. The energy levels are given by

\[
E_n = \frac{(\hbar)^2}{2mR^2}n^2 \quad n=0,1,2,...
\]

The wave functions are given by

\[
\psi_n(\theta) = \frac{1}{\sqrt{2\pi}}e^{in\theta}
\]

where \(\theta\) is the angle made by the position vector of the particle and the positive \(x\) axis. If we now consider
a diatomic molecule with nuclear masses \(m_1\) and \(m_2\) and equilibrium bond length \(R_e\) rotating in the \((xy)\)
plane, as shown in the figure below:
The origin is placed at the molecule’s center of mass

\[ R = \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \]

(In the figure, \( m_2 > m_1 \).) The energy levels of the molecule rotating in the plane wave exactly the same as those of a particle on a ring, namely

\[ E_n = \frac{\hbar^2}{2I} n^2 \]

Here \( I \) denotes the moment of inertia of the molecule, given by

\[ I = \mu R_e^2 \]

and \( \mu \) is the reduced mass of the molecule

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

If the molecule rotates in three dimensions, then we need two angles \( \theta \) and \( \phi \) to characterize it. We will take these to be the angles in the spherical polar coordinate system (\( \theta \) is the polar angle and \( \phi \) is the azimuthal angle). The energy levels are given by

\[ E_n = \frac{\hbar^2}{2I} n(n+1) \quad n=0,1,2,... \]

In order to avoid confusion between \( n \), the radial quantum number for the hydrogen atom, we use a different letter for the rotational energy levels. We use the symbol \( J \) and write the rotational levels as

\[ E_J = \frac{\hbar^2}{2I} J(J+1) \quad J=0,1,2,... \]
The rotational wave functions are exactly the same as the angular part of the hydrogen-atom wave functions, namely the spherical harmonics \( Y_{Jm}(\theta, \phi) \). Here, the quantum number \( m \) characterizes the z-component of the molecule's angular momentum and takes on the values \( m = -J, ..., J \). Hence, each rotational energy level has a degeneracy \( \ deg(E_J) = (2J+1) \).

Now, if the molecule absorbs a photon of frequency \( \nu \), the molecule can undergo a transition between rotational energy levels. What is the energy difference between the energy level with \( J+1 \) and the energy level with \( J \)? This is given by

\[
\Delta E_{(J+1),J} = \frac{\hbar^2}{2I}(J+1)(J+2) - \frac{\hbar^2}{2I}J(J+1) \\
= \frac{\hbar^2}{2I}[J^2 + 3J + 2 - J^2 - J] \\
= \frac{\hbar^2}{2I}(2J+2) \\
= \frac{\hbar^2}{I}(J+1)
\]

Therefore, the frequencies at which transitions can occur are given by

\[
\nu = \frac{\hbar^2}{2\pi I} \frac{J+1}{\hbar} \\
= \frac{\hbar}{2\pi I} \frac{J+1}{\hbar} \\
= \frac{\hbar}{2\pi I} \frac{J+1}{\hbar} \\
\equiv 2B(J+1)
\]

where the rotational constant \( B \) is given by

\[
B = \frac{\hbar}{4\pi I}
\]

Example

The molecule \( \text{NaH} \) is found to undergo a rotational transition from \( J=0 \) to \( J=1 \) when it absorbs a photon of frequency \( 2.94 \times 10^{11} \text{ Hz} \). What is the equilibrium bond length of the molecule?

SOLUTION

We use \( J=0 \) in the formula for the transition frequency

\[
\nu = 2B = \frac{\hbar}{2\pi I} = \frac{\hbar}{2\pi \mu R_e^2}
\]

Solving for \( R_e \) gives

\[
R_e = \sqrt{\frac{\hbar}{2\pi \mu \nu}}
\]

The reduced mass is given by

\[
\mu = \frac{m_{Na}m_H}{m_{Na}+m_H} = \frac{22.989 \times 1.0078}{22.989 + 1.0078} = 0.9655
\]

where \( \mu \) is in atomic mass units or relative units. In order to convert to kilograms, we need the conversion factor \( 1 \text{ au} = 1.66 \times 10^{-27} \text{ kg} \). Multiplying this by \( 0.9655 \) gives a reduced mass of \( 1.603 \times 10^{-27} \text{ kg} \). Substituting in for \( R_e \) gives

\[
R_e = \sqrt{\frac{1.055 \times 10^{-34}}{2\pi \cdot 0.9655 \times 1.603 \times 10^{-27} \times 2.94 \times 10^{11}}} \approx 1.899 \times 10^{-10} \text{ m} = 1.89 \text{ \AA}
\]
The Quantum Harmonic Oscillator

As we will see in the next section, the classical forces in chemical bonds can be described to a good approximation as spring-like or Hooke's law type forces. This is true provided the energy is not too high. Of course, at very high energy, the bond reaches its dissociation limit, and the forces deviate considerably from Hooke's law. It is for this reason that it is useful to consider the quantum mechanics of a harmonic oscillator.

We will start in one dimension. Note that this is a gross simplification of a real chemical bond, which exists in three dimensions, but some important insights can be gained from the one-dimensional case. The Hooke’s law force is

\[ F(x) = -k(x-x_0) \]

where \( k \) is the spring constant. This force is derived from a potential energy

\[ V(x) = \frac{1}{2}k(x-x_0)^2 \]

Let us define the origin of coordinates such that \( x_0 = 0 \). Then the potential energy

\[ V(x) = \frac{1}{2}kx^2 \]

If a particle of mass \( m \) is subject to the Hooke’s law force, then its classical energy is

\[ \frac{p^2}{2m} + \frac{1}{2}kx^2 = E \]

Thus, we can set up the Schrödinger equation using the prescription from the last lecture. The result is

\[ \left[ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right] \psi(x) = E\psi(x) \]

In this case, the Hamiltonian is

\[ \hat{H} = -\frac{\hbar^2}{2m}\frac{d}{dx^2} + \frac{1}{2}kx^2 \]

Since \( x \) now ranges over the entire real line \( x \in (-\infty, \infty) \), the boundary conditions on \( \psi(x) \) are conditions at \( x = \pm \infty \). At \( x = \pm \infty \), the potential energy becomes infinite. Therefore, it must follow that as \( x \rightarrow \pm \infty \), \( \psi(x) \rightarrow 0 \). Hence, we can state the boundary conditions as \( \psi(\pm \infty) = 0 \).

Solving this differential equation is not an easy task, so we will not attempt to do it. Here, we simply quote the allowed energies and some of the wave functions. The allowed energies are characterized by a single integer \( n \), which can be \( 0, 1, 2, \ldots \) and take the form

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \nu \]

where \( \nu \) is the frequency of the oscillator

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \]

Defining the parameter

\[ \alpha = \frac{\sqrt{km}}{\hbar} = \frac{m\omega}{\hbar} = \frac{4\pi^2m\nu}{\hbar} \]

the first few wave functions are

\[ \psi_0(x) = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2 / 2} \]
\[ \psi_1(x) = \left( \frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\alpha x^2 / 2} \]
\[ \psi_2(x) = \left( \frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2 / 2} \]
\[ \psi_3(x) = \left( \frac{\alpha^3}{9\pi} \right)^{1/4} (2\alpha x^3 - 3x) e^{-\alpha x^2 / 2} \]

You should verify that these are in fact solutions of the Schrödinger equation by substituting them back into the equation.
with their corresponding energies. The figure below shows these wave functions, their associated allowed energies and the corresponding probability densities

$$\langle p_n(x) = |\psi_n(x)|^2 \rangle$$

**Figure:** Wave functions, allowed energies, and corresponding probability densities for the harmonic oscillator.

Note that since $x \in (-\infty, \infty)$, the normalization condition is

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1$$

Despite this, because the potential energy rises very steeply, the wave functions decay very rapidly as $|x|$ increases from 0 unless $n$ is very large.

**Bond vibrations**

Chemical bond, if stretched too far, will break. A typical potential energy curve for a chemical bond as a function of $|R|$, the separation between the two nuclei in the bond is given in the figure below:
The small blue curve is an approximate harmonic oscillator curve fit to the true potential energy curve at low energies. If the energy of the bond is not too high, then the potential energy curve is well approximated by a harmonic oscillator curve (shown in blue in the figure). The true curve is given by a function of the form
\[ V(R) = D_e \left(1 - e^{-a(R-R_e)} \right)^2 \]
where \(D_e\) is the dissociation energy. This curve is well approximated by a simpler harmonic oscillator function at low energy
\[ V(R) = \frac{1}{2} k (R-R_e)^2 \]
Thus, as long as the energy is not too high, the energy levels are those of a harmonic oscillator
\[ E_n = (n+1) \hbar \nu_0 \quad n=0,1,2,... \]
where \(\hbar \nu_0\) is the intrinsic frequency
\[ \hbar \nu_0 = \frac{\sqrt{k}}{\mu} \]
where \(\mu\) is the reduced mass.

The energy change in a transition from energy level \(n\) to level \((n+1)\) is
\[
\begin{align*}
\Delta E_{(n+1),n} &= (n+1+1) \hbar \nu_0 - (n+1) \hbar \nu_0 \\&= (n+2-n-1) \hbar \nu_0 \\&= \hbar \nu_0 \end{align*}
\]
Hence, the frequency at which transitions occur is

\[
\begin{align*}
\Delta E_{(n+1),n} &= h\nu_0 \\
h\nu &= \Delta E_{(n+1),n} = h\nu_0 \\
\nu &= \nu_0
\end{align*}
\]

Example

In \(\text{NaH}\), a photon of wavelength \(8.53 \times 10^{-6} \text{ m}\) can induce a vibrational transition from the \(n=0\) to the \(n=1\) level. What is the force constant \(k\) of the \(\text{NaH}\) bond?

**SOLUTION**

First, find the frequency \(\nu\) of the photon:

\[\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{8.53 \times 10^{-6} \text{ m}} = 3.515 \times 10^{13} \text{ Hz}\]

Now, since \(\nu = \nu_0\), the intrinsic frequency is also \(3.515 \times 10^{13} \text{ Hz}\). Since \(\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}\),

\[k = 4\pi \nu_0^2 \mu\]

Plugging in

\[k = 4\pi \left(3.515 \times 10^{13} \text{ Hz}\right)^2 \text{ (1.603} \times 10^{-27} \text{ kg}) = 78.2 \text{ N/m}\]

We noted in the last lecture that the frequency plotted on the x-axis of a spectrum is almost always in units known as wavenumbers \((\text{cm}^{-1})\), which is the inverse of the wavelength. The conversion from \(\text{Hz}\) to wavenumbers proceeds via the relation

\[\nu = \frac{c}{\lambda}; \frac{\nu}{c} = \frac{1}{\lambda}\]

This means that the conversion from \(\text{Hz}\) to \(\text{cm}^{-1}\) requires that we divide the frequency by \(2.998 \times 10^{10} \text{ cm/s}\):

\[\nu \text{ (in \ cm}^{-1}) = \frac{\nu \text{ (in \ Hz)}}{2.998 \times 10^{10} \text{ cm/s}}\]

Hence, the frequency in the example above \(3.515 \times 10^{13} \text{ Hz}\) is

\[\frac{3.515 \times 10^{13} \text{ Hz}}{2.998 \times 10^{10} \text{ cm/s}} = 1170 \text{ cm}^{-1}\]

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**Two and three-dimensional harmonic oscillators**

In more than one dimension, there are several different types of Hooke's law forces that can arise. Consider a diatomic molecule \(AB\) separated by a distance \(r\) with an equilibrium bond length \(R_{\text{eq}}\). If we consider the bond between them to be approximately harmonic, then there is a **Hooke's law** force between them of the form

\[F = -k(r-R_{\text{eq}})\]

which arises from a potential energy

\[V = \frac{1}{2}k(r-r_{\text{eq}})^2\]

Note, however, that if the diatomic exists in two dimensions, then \(r=r|\text{A}-\text{B}|\), where \(r|\text{A}-\text{B}|\) is the relative vector \(r=r_{\text{A}}-r_{\text{B}}=|x,y|\) and \(r=\sqrt{x^2+y^2}\). The Hooke's law potential is no longer a sum of terms involving only \(|x|\) and only \(|y|\). This is also true in three dimensions where \(|r=(x,y,z)|\) and \(|r=\sqrt{x^2+y^2+z^2}|\). This is a somewhat complicated
For now, let us take $R_{eq}=0$ as an approximation. Then, in two dimensions, the Hooke's law potential becomes a harmonic potential in $x$ and a harmonic potential in $y$:

$$V(x,y)=\frac{1}{2}k(x^2 + y^2)$$

and the classical energy

$$\frac{p_x^2}{2\mu} + \frac{p_y^2}{2\mu} + \frac{1}{2}k(x^2 + y^2) = E$$

where $\mu$ is known as the reduced mass of the diatomic

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Now we see that the classical energy is a sum of terms involving motion and forces in the $x$ direction and motion and forces in the $y$ direction:

$$E = \varepsilon_x + \varepsilon_y$$

$$\varepsilon_x = \frac{p_x^2}{2\mu} + \frac{1}{2}kx^2$$

$$\varepsilon_y = \frac{p_y^2}{2\mu} + \frac{1}{2}ky^2$$

As with the particle in a two-dimensional box, we will need two independent integers $n_x$ and $n_y$ to satisfy the boundary conditions along the $x$ and $y$ directions, and the allowed values of $\varepsilon_x$ and $\varepsilon_y$ become

$$\varepsilon_{n_x} = \left(n_x + \frac{1}{2}\right)\hbar\nu$$

$$\varepsilon_{n_y} = \left(n_y + \frac{1}{2}\right)\hbar\nu$$

so that the allowed values of the total energy are

$$E_{n_x ,n_y} = (n_x + n_y + 1)\hbar\nu$$

Also, as with the particle in a two-dimensional box, the wave functions are products of harmonic oscillator wave functions in the $x$ and $y$ directions. Some examples are

$$\psi_{00}(x,y) = \left(\frac{\alpha}{\pi}\right)^{1/2}e^{-\alpha (x^2 + y^2)/2}$$

$$\psi_{10}(x,y) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4}\left(\frac{\alpha}{\pi}\right)^{1/4}xe^{-\alpha (x^2 + y^2)/2}$$

$$\psi_{11}(x,y) = \left(\frac{4\alpha^3}{\pi}\right)^{1/2}xye^{-\alpha (x^2 + y^2)/2}$$

The figure below shows 6 such wave functions, $\psi_{00}(x,y)$, $\psi_{10}(x,y)$, $\psi_{20}(x,y)$, $\psi_{03}(x,y)$, $\psi_{11}(x,y)$, $\psi_{21}(x,y)$:
Wave functions for a two-dimensional harmonic oscillator. All of this generalizes straightforwardly to three dimensions, again assuming $R_{eq}=0$. In this case

$$V(x,y,z) = \frac{1}{2}k(x^2 + y^2 + z^2)$$

the classical energy is

$$\frac{p_x^2}{2\mu} + \frac{p_y^2}{2\mu} + \frac{p_z^2}{2\mu} + \frac{1}{2}k(x^2 + y^2 + z^2) = E$$

which is a sum of three terms $\varepsilon_x + \varepsilon_y + \varepsilon_z$, and we need three integers $n_x$, $n_y$, and $n_z$. The allowed values of these three energies will be

$$\varepsilon_{n_x} = \left(n_x + \frac{1}{2}\right)h\nu \quad \varepsilon_{n_y} = \left(n_y + \frac{1}{2}\right)h\nu \quad \varepsilon_{n_z} = \left(n_z + \frac{1}{2}\right)h\nu$$

and the allowed values of the total energy will be

$$E_{n_x n_y n_z} = \left(n_x + n_y + n_z + \frac{3}{2}\right)h\nu$$

Similarly, the wave functions will be products of one-dimensional harmonic oscillator functions in the $x$, $y$, and $z$ directions. Thus, the ground state would be

$$\psi_{000}(x,y,z) = \left(\frac{\alpha}{\pi}\right)^{3/4}e^{-\alpha (x^2 + y^2 + z^2)/2}$$

and other wave functions can be constructed in a similar manner.

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