Learning Objectives

- Understand how the quantum harmonic oscillator model can be used to interpret the infrared spectra of diatomic molecules
- Understand the origin of the transition moment integral and selection rules and how they are related

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups. IR spectroscopy is one of the most common and widely used spectroscopic techniques. Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

IR Spectroscopy

Transitions between vibrational energy levels can be induced about by absorption or emission of radiation. To understand this, knowledge of both the initial and final eigenstates is needed. The energy of the \((v^{\text{th}})\) eigenstate of a harmonic oscillator can be written as

\[
E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{(5.5.16)}
\]

where \(h\) is Planck's constant and \(v\) is the vibrational quantum number and ranges from 0, 1, 2, 3, ..., \(\infty\). Equation (5.5.16) is often rewritten as

\[
E_v = \left(v + \frac{1}{2}\right) h \nu_m \quad \text{(5.5.17)}
\]

where \(\nu_m\) is the vibrational frequency of the vibration.

Transitions in vibrational energy levels can be brought about by absorption of radiation, provided the energy of the radiation \((h\nu_{\text{photon}})\) exactly matches the difference in energy \((\Delta E_{vv'})\) between the vibrational quantum state \(v\) to quantum state \(v'\). This can be expressed as

\[
\begin{align}
\Delta E_{vv'} &= E_{v'} - E_v \\
&= \left(v' + \frac{1}{2}\right) h \nu_m - \left(v + \frac{1}{2}\right) h \nu_m \\
&= \left(v' - v\right) h \nu_m
\end{align}
\quad \text{(5.5.18)}
\]

Let's consider only transitions between adjacent eigenstates so

\[
|v' - v| = |\pm 1|
\]
which is positive if an IR photon is absorbed and negative if it is emitted. For the absorption of a IR photon, Equation \ref{5.5.18} simplifies to

\[
\begin{align}
\hbar \nu_{\text{photon}} &= \hbar \nu_m \\
&= \frac{\hbar}{2\pi} \sqrt{\frac{k}{\mu}} \label{5.5.19}
\end{align}
\]

The frequency of radiation \(\nu_{\text{photon}}\) that will bring about this change is \textit{identical} to the classical vibrational frequency of the bond \(\nu\) and can be expressed as

The Wavenumber unit

The cm\(^{-1}\) is the wavenumber scale and it can also be defined as 1/wavelength in cm. A linear wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process:

\[
\begin{align}
\bar{\nu}(\text{cm}^{-1}) &= \frac{1}{\lambda(\mu m)} \times 10^4 \left(\frac{\mu m}{cm}\right) \\
&= \frac{v(\text{Hz})}{c(\text{cm/s})} \label{5.5.28}
\end{align}
\]

Equation \ref{5.5.18} can be modified so that the radiation can be expressed in wavenumbers

\[
\widetilde{\nu}_m = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \label{5.5.23}
\]

where \(c\) is the velocity of light (cm s\(^{-1}\)) and \(\widetilde{\nu}\) is the wavenumber of an absorption maximum (cm\(^{-1}\))

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm\(^{-1}\)). The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 µm. Conventionally the IR region is subdivided into three regions (Table \ref{PageIndex{1}}): near IR, mid IR and far IR. Most of the IR used originates from the mid IR region.

Table \ref{PageIndex{1}}: Regions of the IR Spectrum

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength</th>
<th>Wavenumbers ((\widetilde{\nu})), cm(^{-1})</th>
<th>Frequencies (v), HZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near</td>
<td>0.78 -2.5</td>
<td>12800 - 4000</td>
<td>(3.8 \times 10^{14} - 1.2 \times 10^{14})</td>
</tr>
<tr>
<td>Middle</td>
<td>2.5 - 50</td>
<td>4000 - 200</td>
<td>(3.8 \times 10^{14} - 1.2 \times 10^{14})</td>
</tr>
<tr>
<td>Far</td>
<td>50 -100</td>
<td>200 -10</td>
<td>(3.8 \times 10^{14} - 1.2 \times 10^{14})</td>
</tr>
<tr>
<td>Most Used</td>
<td>2.5 -15</td>
<td>4000 -670</td>
<td>(3.8 \times 10^{14} - 1.2 \times 10^{14})</td>
</tr>
</tbody>
</table>
Example \(\PageIndex{1}\)

The force constants for typical diatomic molecules are in the range between 400 to 2000 \(N \cdot m^{-1}\)).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
<th>CO</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force constant, (k) (N.m(^{-1}))</td>
<td>970</td>
<td>480</td>
<td>410</td>
<td>320</td>
<td>1860</td>
<td>1530</td>
</tr>
</tbody>
</table>

For the diatomic molecules listed above, calculate the following:

a. angular frequency \(\text{rad} \cdot s^{-1}\))

b. natural frequency (Hz)

c. period (s)

d. separation between energy levels

e. wavelength \(\lambda\) of the electromagnetic radiation absorbed in the transition \(v=0 \rightarrow v=1\).

Solution

For \(\text{HCl}\):

a. angular frequency \(\omega = 5.45 \times 10^{14} \text{rad} \cdot s^{-1}\))

b. natural frequency: \(\nu = \frac{\omega}{2\pi} = 8.68 \times 10^{13}\) Hz

c. period (s): \(T = \frac{1}{\nu} = 1.15 \times 10^{-14}\) s

d. separation between energy levels: \(\Delta E = E_{v=1} - E_{v=0} = \hbar \omega = 5.75 \times 10^{-21} \text{J}\)

e. wavelength \(\lambda\) of the electromagnetic radiation absorbed in the transition \(v=0 \rightarrow v=1\): \(\lambda = \frac{3.46 \times 10^{-5}}{\nu} = \text{m}\)

The electromagnetic radiation released (and absorbed) for vibrations is primarily in the infrared (IR) part of the spectrum.

Calculating the above properties for the other molecules remains as an exercise.

Selection Rules for IR Transitions

Photons can be absorbed or emitted, and the harmonic oscillator can go from one vibrational energy state to another. Which transitions between vibrational states are allowed? For IR absorption to occur two conditions must be met:

1. There must be a change in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation wave. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.

2. If the frequency of the radiation \(\nu_{\text{photon}}\) matches the natural frequency of the vibration \(\nu_{m}\), the IR photon can be absorbed and the amplitude of the vibration increases.
Furthermore, there are selection rules that describe whether particular transitions is allow. These results from evaluating the following transition moment integral that expresses the probability of a transition from the \((v)\) to the \((v')\) eigenstates:

\[
\begin{align}
\mu_T &= \langle \psi_{v'} | \hat{\mu} (x) | \psi_{v} \rangle \\
&= \int_{-\infty}^{\infty} \psi_{v'}^*(x) \hat{\mu} (x) \psi_v (x) \, dx \label{5.5.29}
\end{align}
\]

To evaluate this integral we need to express the dipole moment operator, \(\langle \hat{\mu} \rangle\), in terms of the magnitude of the vibration \(\langle x \rangle\). The dipole moment operator is defined as

\[
\hat{\mu} = \sum_{\text{electrons}} e \vec{r} + \sum_{\text{nuclei}} q \vec{R} \label{5.5.30}
\]

where the two sums are over all the electrons and nuclei and involve the particle charge (\((-e)\) or \((q)\)) multiplying the position vector (\((\vec{r})\) or \((\vec{R})\), respectively). We can obtain this dipole moment operator in terms of the magnitude of the displacement coordinate, \(\langle x \rangle\), in a simple way by using a Taylor series expansion for the dipole moment .

\[
\mu (x) = \mu_{x=0} + \left( \frac{d \mu (x)}{dx} \right)_{x=0} x + \left( \frac{d^2 \mu (x)}{dx^2} \right)_{x=0} x^2 + \cdots \label{5.5.31}
\]

Retaining only the first two terms and substituting into Equation \(\ref{5.5.29}\) produces

\[
\mu_T = \mu_{x=0} \int_{-\infty}^{\infty} \psi_{v'} (x) \psi_v (x) \, dx + \left( \frac{d \mu (x)}{dx} \right)_{x=0} \int_{-\infty}^{\infty} x \psi_{v'}^*(x) \psi_v (x) \, dx \label{5.5.32}
\]

where

\[
\mu_{x=0} = 0
\]

is the dipole moment of the molecule when the nuclei are at their equilibrium positions, and

\[
\left( \frac{d \mu (x)}{dx} \right)_{x=0}
\]

is the linear change in the dipole moment due to the displacement of the nuclei in the normal mode. The derivative is the linear change because it multiplies \(\langle x \rangle\) and not a higher power of \(\langle x \rangle\) in Equation \(\ref{5.5.31}\). Both \(\mu(x)\) and

\[
\left( \frac{d \mu (x)}{dx} \right)_{x=0}
\]

are moved outside of the integral because they are constants that no longer depend on \(\langle x \rangle\) because they are evaluated at \(\langle x = 0 \rangle\).

The integral in the first term in Equation \(\ref{5.5.32}\) is 0 because any two harmonic oscillator wavefunctions are orthogonal. The integral in the second term of Equation \(\ref{5.5.32}\) is zero except when \(\langle v' = v \pm 1 \rangle\) as demonstrated in Exercise \(\PageIndex{1}\). Also note that the second term is zero if

\[
\int_{-\infty}^{\infty} \psi_{v'}^*(x) \psi_v (x) \, dx = 0 \label{5.5.33}
\]
Exercise \(\PageIndex{1}\))

Use one of the Hermite polynomial recursion relations to verify that the second integral in Equation \ref{5.5.32} is 0 unless \((v' = v \pm 1)\).

If we are to observe absorption of infrared radiation due to a vibrational transition in a molecule, the transition moment cannot be zero. This condition requires that the dipole moment derivative Equation \ref{5.5.33}) cannot be zero and that the vibrational quantum number change by one unit. The normal coordinate motion must cause the dipole moment of the molecule to change in order for a molecule to absorb infrared radiation. If the normal coordinate oscillation does not cause the dipole moment to change then \(\mu_T = 0\) and no infrared absorption is observed. So we can

\[
\underbrace{\Delta v = \pm 1}_{\text{For allowed transitions}} \label{5.5.34}\]

Consider oxygen and nitrogen molecules. Because they are symmetrical, their dipole moments are zero, \(\mu = 0\). Since the vibrational motion (only bond stretching for a diatomic molecule) preserves this symmetry, the change in the dipole moment due to the vibrational motion also is zero, \(\frac{d\mu(x)}{dx} = 0\). Consequently, oxygen and nitrogen do not absorb infrared radiation as a result of vibrational motion.

Exercise \(\PageIndex{2}\))

Explain why the molar absorptivity or molar extinction coefficients \(\epsilon\) in Beer's Law for the IR absorption of some vibrations are greater than others.

**Answer:**

Qualitatively, if the probability of transition is large, then the molar absorptivity is large. And similar if the transition were not allowed, then there will be no intensity and no observed peak in the spectrum. Transitions can be "partially allowed" as well, and these bands appear with a lower intensity than the full allowed transitions.

When looking at the Beer's Law

\[A = \epsilon c l\]  

where \(A\) is absorbance, \(\epsilon\) is the molar absorptivity, \(c\) is the molar concentration and \(l\) is the optical path length.

We are only looking at the change in the molar absorptivity as the IR absorptions of vibrations vary. To do this we have to look at the transition moment integral

\[
\mu_T = \langle \psi_{v',\uparrow} \rvert \hat{\mu}(x) \lvert \psi_v \rangle
\]

When the transition moment integral is zero, there is no transition as it is not allowed under the selection rules. This means that the IR is not absorbing any vibrations and therefore the molar absorptivity is zero, which means that absorbance according to Beer's Law is zero. As the transition moment integral increases, the molar absorptivity also increases and the overall absorbance increases.

The case \((v' = v + 1)\) corresponds to going from one vibrational state to a higher energy one by absorbing a photon with
energy \( h\nu \). The case \( \nu' = \nu - 1 \) corresponds to a transition that emits a photon with energy \( h\nu \). In the harmonic oscillator model infrared spectra are very simple; only the fundamental transitions, \( \Delta = \pm 1 \), are allowed. The associated transition energy is \( \hbar\omega \), according to Equation \( \ref{5.5.19} \). The transition energy is the change in energy of the oscillator as it moves from one vibrational state to another, and it equals the photon energy.

\[
\Delta E = E_{\text{final}} - E_{\text{initial}} = h\nu_{\text{photon}} = \hbar\omega_{\text{oscillator}} \label{5.5.35}
\]

In a perfect harmonic oscillator, the only possibilities are \( \Delta = \pm 1 \); all others are forbidden. This conclusion predicts that the vibrational absorption spectrum of a diatomic molecule consists of only one strong line since the energy levels are equally spaced in the harmonic oscillator model. If the levels were not equally spaced, then transitions from \( \nu = 0 \) to 1 and from \( \nu = 1 \) to 2, etc. would occur at different frequencies.

Only the fundamental transitions, \( \Delta = \pm 1 \), are observed in infrared spectra within harmonic oscillator model.

The actual spectrum is more complex, especially at high resolution. There is a fine structure due to the rotational states of the molecule. These states will be discussed in the next chapter. The spectrum is enriched further by the appearance of lines due to transitions corresponding to \( \Delta = \pm n \) where \( n > 1 \). These transitions are called overtone transitions and their appearance in spectra despite being forbidden in the harmonic oscillator model is due to the anharmonicity of molecular vibrations. Anharmonicity means the potential energy function is not strictly the harmonic potential. The first overtone, \( \Delta\nu = 2 \), generally appears at a frequency slightly less than twice that of the fundamental, i.e. the frequency due to the \( \Delta\nu = 1 \) transition.

Exercise \( \PageIndex{3} \)

Compute the approximate transition frequencies in wavenumber units for the first and second overtone transitions in HCl given that the fundamental is at 2,886 cm\(^{-1} \).

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")