Emission
- Photoluminescence (PL)
- Raman Spectroscopy
- UV Photoelectron Spectroscopy

Reflection
- Optical Microscopy
- Ellipsometry
- Reflection Spectroscopy

Absorption
- Photoconductance (PC)
- Photoelectron Spectroscopy

Transmission
- Absorption Coefficient
- Infrared Spectroscopy

Fig. 10.1 Optical characterization techniques.
http://9-4fordham.wikispaces.com/Electro+Magnetic+Spectrum+and+light

### TABLE 16-1 IR Spectral Regions

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelengths (λ), µm</th>
<th>Wavenumbers (ν), cm⁻¹</th>
<th>Frequencies (ν), Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near</td>
<td>0.78 to 2.5</td>
<td>12800 to 4000</td>
<td>3.8 × 10ⁱ⁴ to 1.2 × 10¹⁴</td>
</tr>
<tr>
<td>Middle</td>
<td>2.5 to 50</td>
<td>4000 to 200</td>
<td>1.2 × 10¹⁴ to 6.0 × 10¹²</td>
</tr>
<tr>
<td>Far</td>
<td>50 to 1000</td>
<td>200 to 10</td>
<td>6.0 × 10¹² to 3.0 × 10¹¹</td>
</tr>
<tr>
<td>Most used</td>
<td>2.5 to 15</td>
<td>4000 to 670</td>
<td>1.2 × 10¹⁴ to 2.0 × 10¹³</td>
</tr>
</tbody>
</table>

(7800 ~ 2500Å)
• Near-IR (14000–4000 cm\(^{-1}\) or 0.8–2.5 μm): can excite overtone or harmonic vibrations.

• Mid-infrared (4000–400 cm\(^{-1}\) or 2.5–25 μm): may be used to study the fundamental vibrations and associated rotational-vibrational structure.

• Far-infrared (400–10 cm\(^{-1}\) or 25–1000 μm): may be used for rotational spectroscopy.
FIGURE 16-1 IR absorption spectrum of a thin polystyrene film. Note the scale change on the $x$-axis at 2000 cm$^{-1}$.

- Could be transmittance vs. wavelength, absorbance vs. wavenumber or wavelength.
THEORY OF INFRARED ABSORPTION SPECTROMETRY

- IR absorption, emission, and reflection spectra for molecular spices can be rationalized by assuming that all arise from various changes in energy brought about by transitions of molecules from one vibrational or rotational energy state to another.

Dipole Moment Changes During Vibrations and Rotations

- Infrared radiation is not energetic enough to bring about electronic transitions. Absorption of infrared radiation is thus confined largely to molecular species that have small energy differences between various vibrational and rotational states.
- In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion.
• The dipole moments is determined by the magnitude of the charge difference and the distance between the two centers of charge.

• **No net change in dipole moment** occurs during the vibration or rotation of homonuclear species such as O\textsubscript{2}, N\textsubscript{2}, or Cl\textsubscript{2} \Rightarrow such compounds cannot absorb in the infrared.

**Vibrational Transitions**

• Vibrational energy levels are quantized, and for most molecules the energy differences between quantum states correspond to the **mid-infrared region**.

**Rotational Transitions**

• The energy required to cause a change in rotational level is quite small and corresponds to radiation of \( \nu \leq 100 \text{ cm}^{-1} \) (\( \lambda > 100 \text{ \mu m} \)).

• Because rotational levels are quantized, absorption by gases in this **far-IR region** is characterized by discrete, well-defined lines.
• In liquids or solids, **intramolecular collisions** and interactions cause broadening of the lines into a continuum.

**Types of Molecular Vibrations**

• Vibrations fall into the basic categories of stretching and bending.
• A **stretching** vibration involves a continuous change in the interatomic distance along the axis of the bond between two atoms.
• **Bending** vibrations are characterized by a change in the angle between two bonds and are of four types: **scissoring, rocking, wagging,** and **twisting.**
FIGURE 16-2
Types of molecular vibrations. Note that + indicates motion from the page toward the reader and – indicates motion away from the reader.
Harmonic Oscillator Vibrational Frequency

The natural frequency of the oscillation is

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

\( \nu_m \) = natural frequency
\( m \) = mass of the attached body
\( k \) = force constant of the spring

• The equation may be modified to describe the behavior of a system consisting of two masses \( m_1 \) and \( m_2 \) connected by a spring.

• It is only necessary to substitute the reduced mass \( \mu \) for the single mass \( m \), where

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]
FIGURE 16-3 Potential-energy diagrams. (a) harmonic oscillator. (b) Curve 1, harmonic oscillator; curve 2, anharmonic motion.
⇒ Thus, the vibrational frequency for such a system is given by

\[ \nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{k(m_1 + m_2)}{m_1 + m_2}} \]

Quantum Treatment of Vibrations

\[ \Delta E = h\nu_m = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \]

\[ E_{\text{radiation}} = h\nu = \Delta E = h\nu_m = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \]
The radiation in wavenumbers

\[ C = \lambda \times \nu \quad \Rightarrow \quad \frac{1}{\nu} = \frac{1}{\lambda} = \frac{\nu}{C} \]

\[ \nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12} \sqrt{\frac{k}{\mu}} \]

\( \nu \): wavenumber of an absorption peak in cm\(^{-1}\)

\( k \): the force constant for the bond in newtons per meter (N/m)

\( C \): the velocity of light in cm/s

\( \mu \): the reduced mass has in kg.

\[ \Delta E = h \nu_m = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \]

\[ \nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

\( k \): in the range between \( 3 \times 10^2 \) and \( 8 \times 10^2 \) N/m for most single bonds, with \( 5 \times 10^2 \) serving as a reasonable average value.

Double and triple bonds are found by this same means to have force constants of about two and three times this value (\( 1 \times 10^3 \) and \( 1.5 \times 10^3 \), respectively).
Vibrational Modes

• In defining the motion of a molecule, we need to consider:
  1. Translational motion of the entire molecule (3)
  2. Rotational motion of the entire molecule (2 or 3)
  3. Individual vibrations of each atom

• A molecule containing N atoms is said to have 3N degrees of freedom.

Number of possible modes

• Translational motion of the entire molecule: three coordinates

• Rotational motion of the entire molecule: three coordinates

⇒ The remaining \((3N-6)\) degrees of freedom involve interatomic motion and hence represent the number of possible vibrations within the molecule. ⇒ Normal mode
Factors Influence the Normal Modes

- Rotation about center bond in **linear molecule** is indistinguishable. \( \Rightarrow \) Linear molecule: \( 3N - 5 \)

(1) the symmetry of the molecules is such that no change in dipole results from a particular vibration
(2) the energies of two or more vibrations are identical or nearly identical
(3) the absorption intensity is so low as to be undetectable by ordinary means
(4) the vibrational energy is in a wavelength region beyond the range of the instrument.
• Occasionally **more peaks** are found than are expected based upon the number of normal modes.

⇒ These transitions are **forbidden** by **harmonic** oscillator selection rules, but are observed in vibrational spectra of real systems due to **anharmonic couplings** of normal modes.

1. The occurrence of **overtone** peaks that occur at two or three times the frequency of a fundamental peak. \( v = 0 \) to \( v = 1 \): fundamental

⇒ Overtones occur when a vibrational mode is excited from \( v=0 \) to \( v=2 \) (the first overtone), or \( v=0 \) to \( v=3 \) (the second overtone).

2. **Combination bands** involve changes in vibrational quantum numbers of more than one normal mode.

⇒ Combination bands typically have **weak** spectral intensities, but can become quite intense in cases where the **anharmonicity** of the vibrational potential is large.

• There are two types of combination bands: **difference transition and sum transition**.
• Vibrational ground state: (000)
• Vibrational excited states: (100, 010, 001)
• Vibrational overtones levels: (200, 300, 020, 002,...)
• Combination levels: (110, 101, 210, ..)

• A sum transition (sum band), occurs when two or more fundamental vibrations are excited simultaneously.
  ⇒ Example: 000 → 101; 001 → 012 are sum transitions.
  ⇒ harmonic-forbidden, and thus typically low intensities.
• Difference bands occurs when an excited molecules absorbs IR, between excited states of two different vibrations. Difference bands are seldom observed in conventional vibrational spectra,

⇒ Example: 100 → 010 is a difference transition.

⇒ Since the initial state of a difference band is always an excited state, difference bands are necessarily "hot bands".

• A hot transition is a transition between two states of a single normal mode of vibration, neither of which is the overall ground state.

⇒ Transition with Δν = 1 starting from an excited level.

• In the harmonic approximation, the normal modes of a molecule are not coupled, and all vibrational quantum levels are equally spaced, so hot bands would not be distinguishable from fundamental transitions.

• For an anharmonic oscillator, energy levels aren't equidistant (ΔE decreases when quantum number v increases), hot band frequencies are lower than fundamental corresponding band.
Fermi resonance  (comparable in frequency)

• Fermi resonance can occur when the frequency of one of the ground vibrations in a molecule is close to the frequency of overtone of other oscillation of the same molecule and respective oscillations are mechanically coupled with each other.

• In order for Fermi Resonance to occur
  ⇒ it requires that

  1. the two vibrations must have the same symmetries (Mulliken symbols).
  2. The transitions (accidentally) have almost the same energy.

  ⇒ The two bands are usually a fundamental vibration and either an overtone or combination band.

  ⇒ Resulting in a shift in frequency and a change in intensity in the spectrum.

  ⇒ Two strong bands are observed, instead of the strong and weak bands.
Before Fermi resonance  After Fermi resonance
• Fermi resonance does not really lead to additional bands.

http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes/Combination_Bands,_Overtones_and_Fermi_Resonances
https://en.wikipedia.org/wiki/Fermi_resonance
Vibrational Coupling

• Coupling: interaction between vibrations when, for example,
  1. Stretching vibration: there is a common atom between the two vibrating bonds
  2. Bending vibration: there is a common bond between vibrating groups

• The energy of a vibration, and thus the wavelength of its absorption peak, may be influenced by other vibrators in the molecule.
• Let us consider the infrared spectrum of carbon dioxide.
• **If no coupling occurred between the two C=O bonds,** an absorption peak would be expected at the same wavenumber as the peak for the C=O stretching vibration in an aliphatic ketone (about 1700 cm\(^{-1}\)).
• Experimentally, carbon dioxide exhibits two absorption peaks, the one at 2330 cm\(^{-1}\) and the other at 667 cm\(^{-1}\).

Carbon dioxide is a linear molecule and thus has \(3 \times 3 - 5 = 4\) normal modes.

• Two stretching vibrations are possible. The symmetric vibration causes no change in dipole. Thus, the symmetric vibration is infrared inactive.
- The asymmetric vibration produce a change in dipole moments, so absorption at 2330 cm\(^{-1}\) results.
- The remaining two vibrational modes of carbon dioxide involve **scissoring**. The two bending vibrations are the resolved components at 90° to one another of the bending motion in all possible planes around the bond axis.
- The two vibrations are identical in energy and thus produce a single peak at 667 cm\(^{-1}\).

\[\text{Stretching} \quad \text{Bending} \quad \text{Scissoring vibrations} \quad \text{asymmetric stretching}\]

\[2330 \text{ cm}^{-1} \quad 667 \text{ cm}^{-1}\]
H$_2$O molecule

- Triatomic molecule such as water, sulfur dioxide (SO$_2$), or nitrogen dioxide (NO$_2$) have $3 \times 3 - 6 = 3$ vibrational modes.

- The central atom is not in line with the other two, a symmetric stretching vibration will produce a change in dipole and will thus be responsible for infrared absorption.

- Stretching peaks at 3650 and 3760 cm$^{-1}$ appear in the infrared spectrum for the symmetric and asymmetric vibrations of the water molecule.

- There is only one component to the scissoring vibration for this nonlinear molecule.

$\Rightarrow$ For water, the bending vibration cause absorption at 1595 cm$^{-1}$.
Symmetric stretching

3650 cm\(^{-1}\)

Asymmetric stretching

3760 cm\(^{-1}\)

Scissoring

1595 cm\(^{-1}\)
### TABLE 4-8
Symmetry of molecular motions of water

<table>
<thead>
<tr>
<th>All motions</th>
<th>Translation ((x, y, z))</th>
<th>Rotation ((R_x, R_y, R_z))</th>
<th>Vibration (remaining modes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>(A_1)</td>
<td>(A_2)</td>
<td>2A&lt;sub&gt;1&lt;/sub&gt; = totally symmetric</td>
</tr>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>(B_1)</td>
<td>(B_1)</td>
<td>(B_1) = asymmetric</td>
</tr>
<tr>
<td>2B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(B_2)</td>
<td>(B_2)</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 4-9
Vibrational modes of water

<table>
<thead>
<tr>
<th>Symmetry Stretch/ Bend</th>
<th>Description</th>
<th>IR active</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt; Symmetric stretch</td>
<td>Change in dipole moment; more distance between positive H’s and negative O</td>
<td></td>
</tr>
<tr>
<td>B&lt;sub&gt;1&lt;/sub&gt; Asymmetric stretch</td>
<td>Change in dipole moment; change in distances between positive H’s and negative O</td>
<td></td>
</tr>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt; Symmetric bend</td>
<td>Change in dipole moment; angles of H–O vectors change</td>
<td></td>
</tr>
</tbody>
</table>
E: doubly degenerate, two orbitals have the same symmetry and the same level of energy.
As an example, we will consider a trigonal bipyramidal complex. The point group is $D_{3h}$, and the reducible and irreducible representations are as follows:

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$σ_h$</th>
<th>$2S_3$</th>
<th>$3σ_v$</th>
<th>Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Γ'$</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$A'_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$s$</td>
</tr>
<tr>
<td>$A'_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$d_{z^2}$</td>
</tr>
<tr>
<td>$A''_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$p_z$</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>$(p_x, p_y)$, $(d_{x^2-y^2}, d_{yz})$</td>
</tr>
</tbody>
</table>

These results show strong interaction with $d_{z^2}$ and somewhat weaker interaction with $d_{x^2-y^2}$ and $d_{yz}$ because their lobes are not directly aimed at the ligands. A partial energy level diagram is shown in Figure 8-25.

These results can be confirmed by the angular overlap method, described earlier in the chapter.

**Figure 8-25** Trigonal Bipyramidal Energy Levels.
$C_n$: rotations of $360°/n$.

$\sigma_h$ (horizontal): horizontal plane perpendicular to principal axis.

$\sigma_v$ (vertical): vertical plane parallel to principal axis.

INFRARED INSTRUMENTATION

• Two types of instruments for infrared absorption measurements are available from commercial sources:

1. **Dispersive** grating spectrometers that are used primarily for qualitative work.
   - Traditionally, dispersive instruments, available since the 1940s, were used to obtain infrared spectra.

2. Multiplex instruments, employing the **Fourier transform** that are suited to both qualitative and quantitative infrared measurements.
   - In recent decades, a very different method of obtaining an infrared spectrum has superseded the dispersive instrument.
   ⇒ **Fourier-transform infrared spectrometers** are now predominantly used and have improved the acquisition of infrared spectra dramatically.
1. Dispersive Infrared Spectrometers

- The dispersive element in dispersive instruments is contained within a monochromator.
- Dispersive infrared instruments are sometimes called grating or scanning spectrometers.
- A dispersive infrared instrument has a source and mirrors, similar to an FT-IR.
- The source energy is sent through both a sample and a reference path, through a chopper to moderate the energy reaching the detector, and directed to a diffraction grating, similar to a prism.

⇒ **Grating separates the wavelengths of light** in the spectral range and directs each wavelength individually through a slit to the detector.

⇒ **Each wavelength is measured one at a time**, with the slit monitoring the spectral bandwidth and the grating moving to select the wavelength being measured.
• The effect of the source is eliminated by making one measurement without the sample—the background measurement—and one with the sample.
⇒ The ratio of the two eliminates the background.
• It is common practice to reduce atmospheric H₂O and CO₂ absorption lines by purging the apparatus with dry nitrogen.
• The essential problem of the dispersive spectrometer lies with its monochromator.
• This contains narrow slits at the entrance and exit which limit the wavenumber range of the radiation reaching the detector to one resolution width.
• Samples for which a very quick measurement is needed cannot be studied with instruments of low sensitivity because they cannot scan at speed.
• However, these limitations may be overcome through the use of a Fourier-transform infrared spectrometer.
Fourier-transform infrared (FTIR) spectroscopy is based on the idea of the interference of radiation between two beams to yield an interferogram.

Interferogram is a signal produced as a function of the change of path length between the two beams.

The two domains of distance and frequency are interconvertible by the mathematical method of Fourier-transformation.

The basic components of an FTIR spectrometer are shown schematically in Figure 2.3.

The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by an analog-to-digital converter and transferred to the computer for Fourier-transformation.
Michelson Interferometers

Figure 2.4 Schematic of a Michelson interferometer. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.
Michelson Interferometers

- The most common interferometer used in FTIR spectrometry is a Michelson interferometer, which consists of two perpendicularly plane mirrors, one of which can travel in a direction perpendicular to the plane (Figure 2.4).
- A semi-reflecting film, the beam splitter, bisects the planes of these two mirrors.
- The beam splitter material has to be chosen according to the region to be examined.

⇒ **Materials** such as germanium or iron oxide are coated onto an ‘infrared-transparent’ substrate such as potassium bromide or cesium iodide to produce beam splitters for the **mid- or near-infrared regions**.

⇒ Thin organic films, such as poly(ethylene terephthalate), are used in the **far-infrared region**.
• Although the light from the source is incoherent, when it is split into two components by the beam splitter, the components are coherent and can produce interference phenomena when the beams are combined.

• The light intensity reaching the detector is **the sum of the two beams**.

• The two beams are **in phase when** \( L_1 = L_2 \).

• If \( M_1 \) is moved a distance \( x \), the retardation is \( \delta = 2x \) since the light has to travel an additional distance \( x \) to reach the mirror and the same distance to reach the beam splitter.

• For \( L_1 = L_2 \) the two beams reinforce each other because they are **in phase**, \( \delta = 0 \), and the detector output is a maximum.

• If \( M_1 \) is moved by \( x = \lambda/4 \), the retardation becomes \( \delta = 2x = \lambda/2 \). The two wave fronts reach the detector 180° out of phase, resulting in **destructive interference** or zero output.

  \( \Rightarrow \) If \( M_1 \) is moved by \( x = \lambda/2 \), \( \delta = \lambda \) and constructive interference results again.
Moving Mirrors

- The **moving mirror** is a crucial component of the interferometer.
- It has to be accurately aligned and must be capable of scanning two distances so that the path difference corresponds to a known value.
- The resolution for an FTIR instrument is limited by the **maximum path difference between the two beams**.
- The limiting resolution in wavenumbers (cm\(^{-1}\)) is the **reciprocal of the path length difference (cm)**.
  \[ \Rightarrow \text{For example, a path length difference of 10 cm is required to achieve a limiting resolution of 0.1 cm}^{-1}. \]
- Unfortunately, the precision of the optics and mirror movement mechanism become **more difficult to achieve at longer displacements of path lengths**.
- It is normal to incorporate a **laser monochromatic source** in the beam of the continuous source. The laser beam produces standard fringes which can ‘line-up’ successive scans accurately and can determine and control the displacement of the moving mirror at all times.
Sources

• Near-infrared: tungsten–halogen lamps
• Mid-infrared region: Globar (a silicon carbide rod) or Nernst (rare earth oxides) source
• Far-infrared region: a high-pressure mercury lamp

Detectors

• Near-infrared region: the detectors used are generally lead sulfide photoconductors.
• Mid-infrared region:
  (1) The normal detector for routine use is a pyroelectric device incorporating deuterium tryglycine sulfate (DTGS) in a temperature-resistant alkali halide window.
  (2) For more sensitive work, mercury cadmium telluride (MCT) can be used, but this has to be cooled to liquid nitrogen temp.
• Far-infrared region: germanium or indium–antimony detectors, operating at liquid helium temperatures.
Attenuated total reflectance (ATR) is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation.

ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample.
Interferometer

- The signal which exits the interferometer is the result of these two beams “interfering” with each other.
- The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it.
- The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position), which makes up the signal, has information about every infrared frequency which comes from the source.
- This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements.
- The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.
Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly.

A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the **Fourier transformation**. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

![Diagram](image)

*Time or distance*

\[ f(t) \rightarrow \text{decoding} \rightarrow f(\nu) \]
Fourier Transformation

- It transforms a mathematical function of time, $f(t)$, into a new function, sometimes denoted by $F$, whose argument is frequency with units of cycles or radians per second.

- The detector output—the interferogram—consists of a series of maxima and minima that can be described by the equation

\[ I(x) = B(f)[1 + \cos(2\pi xf)] \]

- When the source emits more than one frequency, the above equation is replaced by the integration

\[ I(x) = \int_0^f B(f)[1 + \cos(2\pi xf)] \, df \]
• Consider the source spectral distribution, \( B(f) = A \) for \( 0 \leq f \leq f_1 \) in the figure. The interferogram is obtained by eliminating the unmodulated term from Eq. (10.29):

\[
I(x) = B(f)[1 + \cos(2\pi xf)]
\]

\[
I(x) = \int_0^{f_1} A \cos(2\pi xf) \, df = Af_1 \frac{\sin(2\pi xf_1)}{2\pi xf_1}
\]

• The interferogram always retains its maximum at \( x = 0 \) where \( L_1 = L_2 \), because all wavelengths interfere constructively for that mirror position.
• For $x \neq 0$, waves interfere destructively and the interferogram amplitude decreases from its maximum as shown in the interferogram.

• The higher resolution spectral information is corresponding to larger mirror travel. 
  ⇒ There is a practical limit to the mirror displacement, represented by $x = L$. The best spectral resolution is $f = 1/L$. 
Another two interferograms

Relationship between light source spectrum and the signal output from interferometer

(a) Monochromatic light

(b) Dichroic light

(c) Continuous spectrum light

Time or distance

All intensities are standardized.
• What is measured in FTIR is the interferogram, containing not only the spectral information of the source, but also the transmittance characteristics of the sample.

• The interferogram is of little direct interest. It is the spectral response, calculated from the interferogram using the Fourier transformation, that is of interest.

\[ B(f) = \int_{-\omega}^{\omega} I(x) \cos(2\pi xf) \, dx \]

\[ I(x) = \int_{0}^{f} B(f)[1 + \cos(2\pi xf)] \, df \]

⇒ \( B(f) \) contains the spectral content of the source, the sample, and the ambient in the path of the measurement.

\( B(f) \): the source intensity modified by the sample.
Signal Averaging

• The main advantage of rapid-scanning instruments is the ability to increase the signal-to-noise ratio (SNR) by signal-averaging, leading to an increase of signal-to-noise proportional to the square root of the times of scan, as follows:

\[ \text{SNR} \propto n^{1/2} \]

• There are diminishing returns for signal-averaging in that it takes an increasingly longer time to achieve greater and greater improvement.

• The accumulation of a large number of repeat scans makes greater demands on the instrument if it is to exactly reproduce the conditions.
• Signal averaging: many times measurement

the signal part: will accumulate
the noise part: will be irregular and tend to cancel itself.

• The standard deviation of the mean of N measurements is smaller by a factor of N than the standard deviation of a single measurement.

• In practice, a number of complications and limitations.
Advantages

• FTIR instruments have several significant advantages over older dispersive instruments.

1. Multiplex advantage

⇒ Due to an improvement in the SNR per unit time, proportional to the square root of the number of resolution elements being monitored.

⇒ This results from the large number of resolution elements being monitored simultaneously.
Ex.

2 cm\(^{-1}\) resolution (800 - 8000 cm\(^{-1}\)) spectrum measured in 30 minutes on a dispersive spectrometer would be collected at equal S/N on an FT-IR spectrometer in 1 seconds, provided all other parameters are equal.

\[
\frac{(8000-800)}{2} = 3600 \quad \text{(\# of spectra elements)}
\]

\[
30 \text{ min} / 3600 = 0.5 \text{ sec/measurement}
\]

**FTIR**

\[
\sqrt{3600} = 60
\]

\[
\frac{S}{N} = \sqrt{n} \frac{S_x}{N_x}
\]

For measurement of \(N\) spectra:

- Sum \(N\) spectra
- Signal increases \(N\) times
- Noise increases \(\sqrt{N}\) times
- Effect of signal averaging from \(N\) spectra
- \(S/N\) increases \(\sqrt{N}\) times
2. Throughput advantage
⇒ Because FTIR spectrometry does not require the use of a slit or other restricting device, the total source output can be passed through the sample continuously. This results in a substantial gain in energy at the detector, hence translating to higher signals and improved SNRs.

3. Speed advantage
⇒ The mirror has the ability to move short distances quite rapidly, and this, together with the SNR improvements advantages, make it possible to obtain spectra on a millisecond timescale.
⇒ The precision of the scanning mirror position is known. By using a helium–neon laser as a reference, the mirror position is known with high precision.
Applications

Near-IR (13000–4000 cm$^{-1}$).

Mid-IR (4000–400 cm$^{-1}$)

Far-IR (< 400 cm$^{-1}$)

Many applications

Contrasted

Expanded: to emphasize features of interest.

Generally, there are less infrared bands

many bands

Figure 2.7 Absorbance spectrum of lactic acid. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.
• a choice of absorbance or transmittance as a measure of band intensity.
⇒ It almost comes down to personal preference which of the two modes to use.

• It is possible to analyze samples in the liquid, solid or gaseous forms.

Figure 2.8 Transmittance spectrum of lactic acid. From Stuart, B., Biological Applications of Infrared Spectroscopy, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.
Mid-IR (4000–400 cm\(^{-1}\)) Many applications

![Graph showing transmittance spectrum of lactic acid with peaks at different wavenumbers.

- **O–H**
- **C=O**
- **X–H stretching**
  - O–H, C–H and N–H
- **Double-bond**
  - C=C, C=N, C=O
- **Triple-bond**
  - C≡C, C≡N

**Fingerprint**

many vibrations are not so well behaved and may vary by hundreds of wavenumbers.

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*Figure 2.8* Transmittance spectrum of lactic acid. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.
Inorganic materials

• Transmittance spectroscopy is primarily used to detect certain impurities, e.g., oxygen and carbon in Si. **Interstitial** oxygen in silicon causes absorption at $\lambda = 9.05 \, \mu m$ (1105 cm$^{-1}$) at 300 K and at $8.87 \, \mu m$ (1227.6 cm$^{-1}$) at 77 K due to the antisymmetric vibration of the SiO$_2$ complex.
• **Substitutional** carbon has absorption peaks at $\lambda = 16.47 \, \mu m$ (607.2 cm$^{-1}$) at 300 K and at $\lambda = 16.46 \, \mu m$ (607.5 cm$^{-1}$) at 77 K due to a local vibrational mode.
• Nitrogen has shown an absorption peak at 963 cm$^{-1}$. 
• These absorption peaks are superimposed on phonon excitations of the silicon substrate and should be subtracted from the spectrum of a carbon- and oxygen-free reference sample.

Fig. 10.19  Transmission spectra for (a) Si wafer low in oxygen and carbon, (b) Si wafer with more oxygen and carbon, (c) difference between spectra in (a) and (b). Data after ref. 55. Reprinted from the Aug. 1983 edition of *Solid State Technology*. Copyright 1983 by Penn Well Publishing Company.
Researchers at the National Institute of Standards and Technology (NIST) and the University of Maryland have demonstrated that a new spectroscopy technique, which can simultaneously measure a material's topography and chemical composition with nanometer-scale spatial resolution. The spatial resolution of IR microscopy has been limited to tens of micrometers; the new approach reported by NIST improves the spatial resolution by a factor of about a thousand while retaining the high chemical specificity of IR spectroscopy. Photothermal induced resonance (PTIR) uses a tunable infrared laser and an atomic force microscope (AFM) to extract chemical information with nanometer-scale spatial resolution. Every material has a unique infrared spectrum that acts like a chemical fingerprint. Repeatedly scanning the sample at different wavelengths reveals the sample's underlying chemical composition with a resolution determined by the AFM tip size.
Nanoscale IR spectroscopy (AFM-IR) is a new technique that uses an AFM probe as an IR absorbance detector, enabling spatial resolution of better than 50 nm.

**Organo-metal trihalide perovskite (OTP) solar cells** are an area of research focus with potentially significant societal benefits.

Advantages: the high efficiency typical of inorganic semiconductors, low material cost, ease of fabrication and have seen unprecedented improvements in efficiency in recent years.

Project Leader: Dr. Andrea Centrone
Energy Research Group, NIST
Procedure

1. are there absorptions above 2700 cm\(^{-1}\)?
   --YES: very broad and intense?
   --YES: probably -OH
   --NO: go to #2
   --NO: go to #5

2. is there a weak absorption from 3000-3100 cm\(^{-1}\)?
   --YES: could be aromatic ring hydrogen or alkene hydrogen stretch
   --NO: go to #3

3. is there a sharp absorption from 2700-3000 cm\(^{-1}\)?
   --YES: could be simple alkane hydrogen stretch
   --NO: go to #4

4. is there a medium, sharp absorption from 3300-3500 cm\(^{-1}\)?
   --YES: NH (if singlet) or NH\(_2\) (if doublet) stretch
   --NO: go to #5
5. are there absorptions between 2000 and 1500 cm\(^{-1}\)?
   --YES: intense, from 1660-1770 cm\(^{-1}\)?
   --YES: probably C=O
   --NO: go to #6
   --NO: C=O, aromatic and secondary amine probably absent; go to #8

6. is there a sharp, medium absorption close to 1500 or 1600 cm\(^{-1}\)?
   --YES: could be aromatic or secondary amine
   --NO: go to #7

7. is there a sharp, medium absorption from 1640-1840 cm\(^{-1}\)?
   --YES: probably an alkene
   --NO: go to #8

8. are there absorptions between 1500-1100 cm\(^{-1}\)?
   --YES: intense between 1050-1300 cm\(^{-1}\)?
   --YES: could be C-C, C-O, or C-N stretches
   --NO: go to #11
   --NO: C-O, C-N, CH\(_2\), CH\(_3\) probably absent; go to #11
9. is there a medium, sharp absorption at 1375 cm\(^{-1}\)?
   --YES: could be -CH\(_3\)
   --NO: go to #10

10. is there a medium, sharp absorption at 1450 cm\(^{-1}\)?
    --YES: could be -CH\(_2\)- or -CH\(_3\)
    --NO: go to #11

11. are there strong absorptions below 900 cm\(^{-1}\)?
    --YES: sharp at 720 cm\(^{-1}\) could be -CH\(_2\)-
    --OTHERS: aromatic*, alkene or monochloro C-Cl possible