INFRARED SPECTROSCOPY

or

VIBRATIONAL SPECTROSCOPY

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Functional group transformations can be easily followed by IR spectroscopy.
Infrared spectroscopy deals with transitions within the vibrational levels of a molecule.

<table>
<thead>
<tr>
<th></th>
<th>microwave</th>
<th>FAR IR</th>
<th>MID IR</th>
<th>NEAR IR</th>
<th>visible</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ / m</td>
<td>3 x 10^{-4}</td>
<td>3 x 10^{-5}</td>
<td>3 x 10^{-6}</td>
<td>7.8 x 10^{-7}</td>
<td></td>
</tr>
<tr>
<td>$\bar{\nu}$ / cm^{-1}</td>
<td>33</td>
<td>330</td>
<td>3300</td>
<td>12800</td>
<td></td>
</tr>
<tr>
<td>$\nu$ / Hz</td>
<td>1 x 10^{12}</td>
<td>1 x 10^{13}</td>
<td>1 x 10^{14}</td>
<td>3.8 x 10^{14}</td>
<td></td>
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<tr>
<td>energy / J</td>
<td>6.6 x 10^{-22}</td>
<td>6.6 x 10^{-21}</td>
<td>6.6 x 10^{-20}</td>
<td>6.6 x 10^{-19}</td>
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</tbody>
</table>

The region of 4000 – 400 cm^{-1} is of interest to organic chemists as most vibrational transitions of organic functional groups occur in this region.
Use of infrared spectrum

Every type of bond in a molecule has a unique natural vibrational frequency

Therefore the IR spectrum of every molecule is unique as much as the fingerprint of human beings.

By comparing IR spectra of two samples one can establish whether or not they are identical samples. If their IR spectra exactly match (coincide peak to peak) then they are likely to be same substance.
Use of infrared spectrum

Absorption due to vibrational transitions of each bond type is different and they are confined to a small portion of the IR region.

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>O-H</th>
<th>N-H</th>
<th>C-H</th>
<th>C≡C</th>
<th>C≡N</th>
<th>X≡C≡Y (C, O, N, S)</th>
<th>Rich information in metal carbonyls (Organo metallics)</th>
<th>Various types of C=O</th>
<th>C=C</th>
<th>C=N</th>
<th>N=O</th>
<th>C-Cl</th>
<th>C-O</th>
<th>C-N</th>
<th>C-C</th>
<th>Finger print region</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000-2500</td>
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<tr>
<td>2500-2000</td>
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<tr>
<td>2000-1800</td>
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<tr>
<td>1800-1650</td>
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<td>1650-1550</td>
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<tr>
<td>1550-650</td>
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</tbody>
</table>

This allows identification of functional groups in organic molecules because each functional group has a vibrational frequency which appear in a narrow region of the IR region.

Table shows approximate regions where various common type of functional group’s stretching vibrations occur
For a non-linear molecule containing \( n \) atoms the number of vibrational degrees of freedom is \((3n-6)\)

For example water molecule has 3 degrees of vibrational freedom corresponding to two stretching mode and one bending mode of vibration. These are called fundamental modes or normal modes of vibration and they occur without change of center of gravity of the molecule.
For a linear molecule containing $n$ atoms the number of vibrational degrees of freedom is $(3n-5)$

For example CO$_2$ molecule has 4 degrees of vibrational freedom corresponding to two Stretching mode and two bending modes of vibration.

- C-O symmetrical stretching
- C-O asymmetrical stretching
- C-O scissoring bending
- C-O scissoring bending

$+$ and - indicate movement perpendicular to plane of page

Note that both scissoring vibrations are equivalent
The vibrational frequencies can be calculated as it relates to bond strength and masses of atoms attached that undergo vibration (Hooke’s law)

\[ \overline{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \]

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

\( K \) = force constant, bond order or bond strength and \( \mu \) is reduced mass

From the above equation it is apparent that

stronger the bond higher the vibrational frequency

higher the masses of atoms lower the vibrational frequency
Stronger the bond, higher the vibrational frequency

Higher the masses of atoms, lower the vibrational frequency

\[ \nu = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \]

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

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>( \nu_{C=C} ) (cm(^{-1}))</th>
<th>( \nu_{C-H} ) (cm(^{-1}))</th>
<th>( \nu_{C-X} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡C</td>
<td>2150</td>
<td>3300</td>
<td>3000</td>
</tr>
<tr>
<td>C≡C</td>
<td>1650</td>
<td>3100</td>
<td>1200</td>
</tr>
<tr>
<td>C–C</td>
<td>1200</td>
<td>2900</td>
<td>600</td>
</tr>
<tr>
<td>C≡C–H</td>
<td>3300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡C–H</td>
<td>3100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–C–H</td>
<td>2900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–H</td>
<td></td>
<td>3000</td>
<td>1200</td>
</tr>
<tr>
<td>C–C</td>
<td></td>
<td>1100</td>
<td>750</td>
</tr>
<tr>
<td>C–O</td>
<td></td>
<td>1100</td>
<td>600</td>
</tr>
<tr>
<td>C–Cl</td>
<td></td>
<td>750</td>
<td>500</td>
</tr>
<tr>
<td>C–Br</td>
<td></td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>C–I</td>
<td></td>
<td>500</td>
<td></td>
</tr>
</tbody>
</table>

C–H stretching, C–H bending. Force constant for bending is smaller than stretching.
Selection rules for Infrared transitions

For a particular vibration to be infrared active there must be a change in the dipole moment of the molecule during the vibration.

In other words transition dipole moment must not be zero.

Homonuclear diatomic molecules are inactive in the infrared spectrum. They do not have a dipole moment to start with and during the vibration also the dipole moment is zero. eg: H₂, O₂, N₂ etc.

Heteronuclear diatomic molecule such as CO, NO are active in IR

Symmetrical polyatomic molecules such as CO₂, the symmetric stretching vibration is infrared inactive where as the asymmetric stretching vibration is IR active

\[ \Delta \nu = \pm 1, \text{ transition can take place between Adjacent vibrational levels, 0 to 1, 1 to 2 etc.} \]
IR spectrum shows bands rather than line spectrum due to coupling of various rotational transitions within a given vibrational transition.

IR spectrum is generally complex and contains many bands in addition to the ones corresponding to fundamental vibrational transitions.

**Overtones:** Bands corresponding to integral multiple of fundamental vibration. They are due to transition from ground state to higher vibrational states. They are very weak bands. An absorption band at 1050 cm$^{-1}$ may well have an accompanying band at 2100 (2ν) and 3150 (3ν) cm$^{-1}$.

**Combination bands:** Two vibrational frequencies in a molecule couple to give a new frequency within the molecule. This band is a sum of the two interacting bands.

**Difference bands:** Similar to combination bands. The observed frequency is the difference between the two interacting frequencies.

**Fermi resonance:** When a fundamental vibration couples with overtone or combination Band, the coupled vibration is called a Fermi resonance.
Types of infrared spectrometers

Dispersive type spectrometer

IR source → Sample compartment → Chopper → Monochromator

R → S → IR D
Fourier Transform infrared spectrometer

Interferogram is like a time domain spectrum

On Fourier transformation it gives the frequency domain spectrum
Calibration of IR spectrum

A thin film of polystyrene is used as a standard for calibration

Peaks at 1603 and 3062 cm\(^{-1}\) are used to calibrate the spectrum
Sampling techniques for IR spectroscopy

Gas sample – in sample tube of 10 cm length fitted with IR transparent windows
  KBr, NaCl, CsF, AgF, ZnSe
Liquids – as thin film formed between NaCl plates
Solid – as a KBr Pellet or as a Nujol mull
Nujol is a viscous mineral oil (hydrocarbon) in which the solid is finely suspended

Solution – in a suitable solvent such as CCl₄ or CHCl₃ in a cell consisting of NaCl windows. Usually the solvent spectrum is subtracted from the actual sample spectrum.
What to look for in an infrared spectrum?
Position of bands – characteristic infrared frequencies

Intensity of bands – strong, medium, weak

Shape of bands – fine structure, sharp, broad, very broad

First effort – quick glance to determine the presence or absence of some important functional groups – unambiguously C=O, OH, NH, C=C, CΞC, CΞN and NO₂

What one should not do with an IR spectrum

Interpretation of every band/peak in the spectrum
THANK YOU