FTIR: Fourier Transform Infrared Spectroscopy/Spectrometry

Allows all IR wavelengths to fall on the sample simultaneously. An interferometer causes + and – interference to occur at sequential wavelengths as a moving mirror changes the path length of the light beam. The detector’s initial direct output is a seemingly “jumbled” set of electronic signals, but after applying a Fourier transform on the output a “normal” spectrum results.

Ideal Case:
Harmonic Oscillators/Oscillation
Typical IR Spectrum

% Transmittance

0 100

C-H

C=O

Functional group region

Fingerprint region

Wavenumbers / cm^{-1}
Hooke’s Law for a vibrating spring: \( F = -kx \)

- \( F \) = restoring force
- \( x \) = displacement
- \( k \) = spring (or force) constant

For an oscillator, vibrating with frequency \( \nu \): 
\[
E_{total} \propto h\nu
\]

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

Wave-number, typically in cm\(^{-1}\), “reciprocal centimeters”

\( E_{total} = K.E. + P.E. \)
Harmonic Oscillator

Newtonian Mechanics:

Hooke's law: \( F = -kx \), \( F = -dV/dx \), \( V = \text{P.E.} \)
\( V = \frac{1}{2} k \cdot x^2 \), \( k = d^2V/dx^2 \)

Newton's 2\textsuperscript{nd} Law of Motion: \( F = m \cdot a = m \cdot d^2x/dt^2 \)

\[-k \cdot x = F = m \cdot d^2x/dt^2\]

\[m \cdot x'' + k \cdot x = 0, \text{ O.D.E. = Ordinary Differential Equation}\]

Solution: \( x(t) = A \cdot \cos(2\pi \nu t) \);
\[\nu = (2\pi)^{-1} \left( \frac{k}{\mu} \right)^{1/2}\]
\[\mu \equiv \text{reduced mass} \equiv \frac{m_1 \cdot m_2}{m_1 + m_2}\]

Quantum Mechanics (Schrödinger Wave Equation):

\( E_\nu = (\nu + \frac{1}{2})h\nu \), \( \nu \equiv \text{vibrational quantum number} = 0, 1, 2, \ldots \)

Note: ZPE (Zero-Point Energy) = \( \frac{1}{2} h \nu \)

Selection Rules: Allowed Transitions: \( \Delta \nu = \pm 1 \)

Intensity (I) of an absorption band \( \propto \frac{d\mu_{\text{dipole}}}{dx} \)
For diatomic molecule:

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

\( \mu \equiv \text{reduced mass} \equiv \frac{m_1 m_2}{m_1 + m_2} \)

Note how \( \bar{\nu} \) depends on \( k \) and \( \mu \).

<table>
<thead>
<tr>
<th></th>
<th>C≡C</th>
<th>C=C</th>
<th>C–C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2150</td>
<td>1650</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>C–H</th>
<th>C–C</th>
<th>C–O</th>
<th>C–Cl</th>
<th>C–Br</th>
<th>C–I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3000</td>
<td>1200</td>
<td>1100</td>
<td>800</td>
<td>550</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
</tr>
</tbody>
</table>

(continued)
Bending motions are easier than stretching motions:

<table>
<thead>
<tr>
<th>C–H stretch</th>
<th>–C–H bending</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000 cm(^{-1})</td>
<td>1340 cm(^{-1})</td>
</tr>
</tbody>
</table>

Hybridization Effects:

<table>
<thead>
<tr>
<th>(\equiv C–H) sp</th>
<th>=C–H sp(^2)</th>
<th>–C–H sp(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3300 cm(^{-1})</td>
<td>3100 cm(^{-1})</td>
<td>2900 cm(^{-1})</td>
</tr>
</tbody>
</table>

Resonance Effects:

Normal ketone: C=O stretch

| 1715 cm\(^{-1}\) |

Ketone conjugated with a double bond:

| 1680 cm\(^{-1}\) |

\(O\)

\(R\) \(C\) \(=\) \(CH\) \(CH\) \(CH\) \(+\) \(CH\) \(O\) \(-\) \(C\)
Normal (or Fundamental) Modes of Vibration

Recall for a Linear Molecule: $3N - 5$

**CO$_2$**

- **Symmetric stretch:** $v_1 = 1340$ cm$^{-1}$
- **Asymmetric stretch:** $v_3 = 2349$ cm$^{-1}$
- **In-plane bending:** $v_{2a} = 667$ cm$^{-1}$
- **Out-of-plane bending:** $v_{2b} = 667$ cm$^{-1}$
Recall for a Non-Linear Molecule: 3N – 6 Modes of Vibration

\( \text{H}_2\text{O} \)

Symmetric “stretch”: \( v_1 = 3657 \, \text{cm}^{-1} \)

Asymmetric “stretch”: \( v_3 = 3756 \, \text{cm}^{-1} \)

“Bending”: \( v_2 = 1595 \, \text{cm}^{-1} \)
**H₂O**

- Symmetrical stretching ($v_s$ OH)
  - $3652 \text{ cm}^{-1}$

- Asymmetrical stretching ($v_{as}$ OH)
  - $3756 \text{ cm}^{-1}$

- Scissoring ($\delta_s$ OH)
  - $1596 \text{ cm}^{-1}$

**CO₂**

1. Symmetrical stretching ($v_s$ CO₂)
   - $2350 \text{ cm}^{-1}$

2. Asymmetrical stretching ($v_{as}$ CO₂)
   - $1340 \text{ cm}^{-1}$

3. Scissoring (bending) ($\delta_s$ CO₂)
   - $665 \text{ cm}^{-1}$

4. Scissoring (bending) ($\delta_s$ CO₂)
   - $665 \text{ cm}^{-1}$
Selection Rules (Symmetry Restrictions) in IR Spectroscopy:

Only certain fundamental modes of vibration will be “IR-active”, that is, will absorb IR radiation and thus will appear as a band in the IR vibrational spectrum:

Only those modes whose dipole moment changes during a vibrational mode will be IR active.

Go back and check out CO$_2$ and H$_2$O. What about homonuclear and heteronuclear diatomic molecules?

Animation of Modes of Vibration:
http://www.chem.purdue.edu/gchelp/vibs/index.html

Requires Chime software plug-in: and
Types of Vibrations

Stretching vibrations

Symmetric
Asymmetric

Bending vibrations

In-plane rocking
In-plane scissoring
Out-of-plane wagging
Out-of-plane twisting

http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/irspec1.htm
CH₂

Symmetrical stretching ($v_s \text{ CH}_2$)
~2853 cm⁻¹

Asymmetrical stretching ($v_{as} \text{ CH}_2$)
~2926 cm⁻¹

In-plane bending or scissoring ($\delta_s \text{ CH}_2$)
~1465 cm⁻¹

Out-of-plane bending or wagging ($\omega \text{ CH}_2$)
1350-1150 cm⁻¹

Out-of-plane bending or twisting ($\tau \text{ CH}_2$)
1350-1150 cm⁻¹

In-plane bending or rocking ($\rho \text{ CH}_2$)
~720 cm⁻¹
Vibrational Coupling

In addition to the vibrations mentioned above, interaction between vibrations can occur (*coupling*) if the vibrating bonds are joined to a single, central atom.

Vibrational coupling is influenced by a number of factors:

- Strong coupling of stretching vibrations occurs when there is a common atom between the two vibrating bonds.
- Coupling of bending vibrations occurs when there is a common bond between vibrating groups.
- Coupling between a stretching vibration and a bending vibration occurs if the stretching bond is one side of an angle varied by bending vibration.
- Coupling is greatest when the coupled groups have approximately equal energies.
- No coupling is seen between groups separated by two or more bonds.
Overtone & Combination Bands: *Water vapor as an example*

<table>
<thead>
<tr>
<th>v / cm$^{-1}$</th>
<th>Intensity</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1595.0</td>
<td>Very strong</td>
<td>$v_2$, Fundamental</td>
</tr>
<tr>
<td>3151.4</td>
<td>Medium</td>
<td>$2v_2$, Overtone</td>
</tr>
<tr>
<td>3651.7</td>
<td>Strong</td>
<td>$v_1$, Fundamental</td>
</tr>
<tr>
<td>3755.8</td>
<td>Very strong</td>
<td>$v_3$, Fundamental</td>
</tr>
<tr>
<td>5332.0</td>
<td>Medium</td>
<td>$v_2 + v_3$, Combination</td>
</tr>
<tr>
<td>6874</td>
<td>Weak</td>
<td>$2v_2 + v_3$, Combination</td>
</tr>
</tbody>
</table>
Box 3.1  Vibrational Frequencies of Some Common Bonds

![Diagram showing vibrational frequencies of various bonds in cm⁻¹ range from 4000 to 500 cm⁻¹.

- C-H: 3100 cm⁻¹ and 2700 cm⁻¹
- O-H: 3600 cm⁻¹
- N-H: 3500 cm⁻¹, 3300 cm⁻¹, and 2260 cm⁻¹
- C=O: 1850 cm⁻¹ and 1600 cm⁻¹
- C=O: 1570 cm⁻¹
- Unsaturated out-of-plane bending: 670 cm⁻¹ and 1050 cm⁻¹]
### APPENDIX A  TRANSPARENT REGIONS OF SOLVENTS AND MULLING OILS

<table>
<thead>
<tr>
<th>Wavelength (CM⁻¹)</th>
<th>3600</th>
<th>3200</th>
<th>2800</th>
<th>2400</th>
<th>2000</th>
<th>1800</th>
<th>1600</th>
<th>1400</th>
<th>1200</th>
<th>1000</th>
<th>800</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvents&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylene dichloride</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>-</td>
<td></td>
<td></td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tetrachloroethylene</td>
<td></td>
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<td></td>
<td></td>
<td>-</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Methylene dibromide</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromoform</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mulling Oils&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nujol&lt;sup&gt;®&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexachlorobutadiene</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorolube&lt;sup&gt;®&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> The open regions are those in which the solvent transmits more than 25% of the incident light at 1 mm thickness.

<sup>b</sup> The open regions for mulling oils indicate transparency of thin films.
APPENDIX B  CHARACTERISTIC GROUP ABSORPTIONS

ALKANES

ALKENES

VINYL
TRANS
CIS
VINYLIDENE
TRISUBSTITUTED
TETRASUBSTITUTED
CONJUGATED
CUMULATED
CYCLIC

ALKYNES

MONOSUBSTITUTED
DISUBSTITUTED

MONONUCLEAR AROMATICS

BENZENE
MONOSUBSTITUTED
1,2-DISUBSTITUTED
1,3-DISUBSTITUTED
1,4-DISUBSTITUTED
1,2,4-TRISUBSTITUTED
1,2,3-TRISUBSTITUTED
1,3,5-TRISUBSTITUTED

ALCOHOLS AND PHENOLS

FREE OH
INTRAMOLECULAR BONDED (WEAK)
INTRAMOLECULAR BONDED (STRONG)
INTERMOLECULAR BONDED

SATURATED TERT.
HIGHLY SYMMETRICAL SEC.
SATURATED SEC.
\( \alpha \)- UNSATURATED OR CYCLIC TERT.
\( \alpha \)- UNSATURATED SEC.
ALICYCLIC SEC. (5 OR 6-
MEMBERED RING)
SATURATED PRIMARY
\( \alpha \)- UNSATURATED TERT.
\( \alpha \)- UNSATURATED AND
\( \alpha \)- BRANCHED SEC.
DI-\( \alpha \)- UNSATURATES SEC.
ALICYCLIC SEC. (7 OR 8-
MEMBERED RING)
\( \alpha \)- BRANCHED AND/OR
\( \alpha \)- UNSATURATED PRIM.

\( ^{a} \) Absorptions are shown by heavy bars. \( s \) = strong, \( m \) = medium, \( w \) = weak, \( sh \) = sharp, \( br \) = broad. Two intensity designations over a single bar indicate that two peaks may be present.

\( ^{b} \) May be absent.

\( ^{c} \) Frequently a doublet.

\( ^{d} \) Ring bending bands.
ACETALS
“KETALS”
ETHERS
ALIPHATIC
AROMATIC (ARYL —O—CH₂)
VINYL
OXIRANE RING
PEROXIDES (ALKYL AND ARYL)
PEROXIDES (ACYL AND AROYL)
CARBONYL COMPOUNDS
KETONES
DIALKYL (—CH₂COCH₂—)
AROMATIC (CONJ)
ENOL OF 1,3-DIKETONE
α-HYDROXY ARYL KETONE
ALDEHYDES
ALKL
AROMATIC (CONJ)
CARBOXYLIC ACIDS
DIMER
CARBOXYLATE ION
ESTERS
FORMATES
ACETATES
OTHER UNCONJ ESTERS
CONJUGATED ESTERS
AROMATIC ESTERS

*Three bands, sometimes a fourth for ketals, and a fifth band for acetals.

b Conjugated aliphatic examples show C—O stretch at virtually the same position as aromatic structures.

C Conjugated examples show C—O stretch at lower wavenumbers (1710–1680 cm⁻¹). The O—H stretch (3300–2600 cm⁻¹) is very broad.
### APPENDIX C  ABSORPTIONS FOR ALKENES

#### TABLE C-1  Alkene Absorptions

<table>
<thead>
<tr>
<th>Structure</th>
<th>Vinyl</th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=C=C=R</td>
<td>1648 – 1638 cm⁻¹</td>
<td>1662 – 1626 cm⁻¹</td>
<td>1678 – 1668 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td>995 – 985 cm⁻¹</td>
<td>730 – 665 cm⁻¹</td>
<td>980 – 960 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td>915 – 905 cm⁻¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Vinyl
- cis: R=C=C=R
- trans: R=C=C=R

<table>
<thead>
<tr>
<th>Structure</th>
<th>Vinylidene</th>
<th>Trisubstituted</th>
<th>Tetrasubstituted</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=C=C=R</td>
<td>1658 – 1648 cm⁻¹</td>
<td>1675 – 1665 cm⁻¹</td>
<td>1675 – 1665 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td>895 – 885 cm⁻¹</td>
<td>840 – 790 cm⁻¹</td>
<td>very weak or absent.</td>
</tr>
</tbody>
</table>

- Vinylidene
- Trisubstituted
- Tetrasubstituted

---

$s$ = strong, $m$ = medium, $w$ = weak, $v$ = variable.

- This band also shows a strong overtone band.
- This band occurs near 1000 cm⁻¹ in conjugated trans-trans systems such as the esters of sorbic acid.

#### TABLE C-2  C=C Stretching Frequencies in Cyclic and Acyclic Systems (cm⁻¹)

<table>
<thead>
<tr>
<th>Ring or Chain</th>
<th>cis</th>
<th>trans</th>
<th>cis</th>
<th>cis</th>
<th>cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chain cis</td>
<td>1661</td>
<td>1676</td>
<td>1681</td>
<td>1672</td>
<td>1661</td>
</tr>
<tr>
<td>Chain trans</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three-membered ring</td>
<td>1641</td>
<td>1680</td>
<td></td>
<td>1685</td>
<td>1678</td>
</tr>
<tr>
<td>Four-membered ring</td>
<td>1566</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Five-membered ring</td>
<td>1611</td>
<td>1658</td>
<td>1686</td>
<td>1657</td>
<td></td>
</tr>
<tr>
<td>Six-membered ring</td>
<td>1649</td>
<td>1678</td>
<td>1685</td>
<td>1651</td>
<td></td>
</tr>
<tr>
<td>Seven-membered ring</td>
<td>1651</td>
<td>1673</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eight-membered ring</td>
<td>1653</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

- All rings have cis double bonds.
## APPENDIX D  ABSORPTIONS FOR PHOSPHORUS COMPOUNDS

### TABLE D-1  \( P=O \) and \( P-O \) Stretching Vibrations

<table>
<thead>
<tr>
<th>Group</th>
<th>Position cm(^{-1})</th>
<th>( \nu_{P-O} ) Bands(^a) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P=O ) stretch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphine oxides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aliphatic</td>
<td>( \sim 1150 )</td>
<td></td>
</tr>
<tr>
<td>Aromatic</td>
<td>( \sim 1190 )</td>
<td></td>
</tr>
<tr>
<td>Phosphate esters(^b)</td>
<td>1299–1250</td>
<td></td>
</tr>
<tr>
<td>( P-OH )</td>
<td>1040–910 (s)</td>
<td></td>
</tr>
<tr>
<td>( P-O-P )</td>
<td>1000–870 (s)</td>
<td>( \sim 700 ) w</td>
</tr>
<tr>
<td>( P-O-C ) (aliph)</td>
<td>1050–970 (s)(^c)</td>
<td>( 830–740 ) (s)(^d)</td>
</tr>
<tr>
<td>( P-O-C ) (arom)</td>
<td>1260–1160 (s)</td>
<td>( 994–855 ) (s)</td>
</tr>
</tbody>
</table>

\(^a\) s = strong; w = weak

\(^b\) The increase in \( P=O \) stretching frequency of the ester, relative to the oxides, results from the electronegativity of the attached alkoxy groups.

\(^c\) May be a doublet.

\(^d\) May be absent.
### TABLE E-1 γ-CH and Ring Bending (β-Ring) Bands of Pyridines<sup>a</sup>

<table>
<thead>
<tr>
<th>Substitution</th>
<th>Number of Adjacent H Atoms</th>
<th>γ-CH (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>β-Ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-</td>
<td>4</td>
<td>781–740</td>
<td>752–746</td>
</tr>
<tr>
<td>3-</td>
<td>3</td>
<td>810–789</td>
<td>715–712</td>
</tr>
<tr>
<td>4-</td>
<td>2</td>
<td>820–794</td>
<td>775–709</td>
</tr>
</tbody>
</table>

<sup>a</sup> The γ and β notations are explained in the text (Section 3.6.30.4) and in the book by Katritzky (1963).

### TABLE E-2 Characteristic γ-CH or β-Ring Bands of Furans, Thiophenes, and Pyrroles

<table>
<thead>
<tr>
<th>Ring</th>
<th>Position of Substitution</th>
<th>Phase</th>
<th>γ-CH or β-Ring Modes&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Furan</td>
<td>2-</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>~925</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>Liquid</td>
<td>960–915</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>Solid</td>
<td>955–906</td>
</tr>
<tr>
<td></td>
<td>3-</td>
<td>Liquid</td>
<td>885–870</td>
</tr>
<tr>
<td>Thiophene</td>
<td>2-</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>~925</td>
</tr>
<tr>
<td></td>
<td>3-</td>
<td>Liquid</td>
<td>885–870</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>2-Acyl</td>
<td>Solid</td>
<td>774–740</td>
</tr>
</tbody>
</table>

<sup>a</sup> The γ and β notations are explained in the text (Section 3.6.30.4) and in the book by Katritzky (1963).
*Free OH, medium and sharp; bonded OH, strong and broad