Advanced infrared spectroscopy I:
The fingerprint region

Characteristic absorptions of alkanes

$C_{10}H_{22}$ decane; neat liquid, salt plates

Characteristic absorptions of alkenes

The intensity of an IR band varies with the change in dipole moment when the bond is stretched. A C=C bond is less polar than a C=O or an N=O bond. The C=C stretch is therefore much weaker in the infrared. It may even be absent in a symmetrical alkene.

Non-symmetrical C=C
C=C str expected

Symmetrical C=C
No C=C str

Almost symmetrical C=C
Very weak C=C str

NB: A carbonyl group is permanently polarised, and stretching the bond will increase the polarity.
Characteristic absorptions of alkenes

Not all vibrations give rise to strong IR bands. Sometimes the C=C stretch can be rather small and difficult to see.

cyclohexene; neat liquid, salt plates

Characteristic fingerprint absorptions of alkenes

C–H str alkene ~2900 cm\(^{-1}\)
C–H str aliphatic ~3100 cm\(^{-1}\)
C=C str 1640 – 1680 cm\(^{-1}\)

1-hexene; neat liquid

It is, in principle, possible to deduce the substitution pattern on a double bond from the fingerprint region of the IR spectrum. Typical out-of-plane (oop) vibrations of substituted alkenes are listed underneath. Note that information about the substitution pattern of a C=C double bond is often easier to obtain or to confirm by \(^1\)H NMR.

Monoalkenes: 2 strong bands one near 990 cm\(^{-1}\) and the other near 910 cm\(^{-1}\).

Cis-1,2-disub\(^2\) alkenes: 1 strong band near 700 cm\(^{-1}\).

Trans-1,2-disub\(^2\) alkenes: 1 strong band near 790 cm\(^{-1}\).

1,1-Disub\(^1\) alkenes: 1 strong band near 890 cm\(^{-1}\).

Trisub\(^1\) alkenes: 1 medium intensity band near 815 cm\(^{-1}\).

Tetrasub\(^1\) alkenes: no =CH bending vibrations!!!

In-plane (ip) scissoring vibrations occur at ~1415 cm\(^{-1}\) for:

\[ R \quad R \quad H \quad R \quad H \]

Characteristic absorptions of alkenes

2 bands 910 + 990 cm\(^{-1}\) terminal alkene

H\(_3\)C\(\equiv\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\) cis-2-heptene; neat liquid

near 700 cm\(^{-1}\) cis alkene
Characteristic fingerprint absorptions of alkenes

- C–H str alkene
- weak C=C str

trans-2-hexene; neat liquid

near 970 cm$^{-1}$

trans alkene

C–H str aromatic

Combination + overtone bands

C=C str aromatic

2 or 3 bands between 1600 and 1450 cm$^{-1}$

Characteristics of IR spectra for aromatic compounds:

$\text{=C-H str}$ absorption to the left of 3000 cm$^{-1}$

C=C str absorption often 2 pairs of bands between ~1600 and 1450 cm$^{-1}$; sometimes only 2–3 bands are observable weak overtone / combination bands occur in the range 1667–2000 cm$^{-1}$ at positions characteristic of substitution patterns — these can be diagnostically useful but are beyond the scope of this course

$\text{=C-H str}$ absorptions occur in the range 900–690 cm$^{-1}$ — these are due to OOP bending and can be diagnostically useful since the bands occur at positions characteristic of substituent patterns as follows:

- **Monosub** aromatic: 2 strong bands one near 690 cm$^{-1}$ and the other near 750 cm$^{-1}$.
- **o-Disub** aromatic: 1 strong band near 750 cm$^{-1}$.
- **m-Disub** aromatic: 2 strong bands one near 780 cm$^{-1}$ and the other near 690 cm$^{-1}$; a 3rd medium intensity band may be seen near 880 cm$^{-1}$.
- **p-Disub** aromatic: 1 strong band in the range 850–800 cm$^{-1}$.

- 900 cm$^{-1}$
- 800 cm$^{-1}$
- 700 cm$^{-1}$

Characteristics of IR spectra for aromatic compounds:

- **Me**
- toluene; neat liquid

weak overtone/combination bands

1667–2000 cm$^{-1}$

weak overtone / combination bands

1667–2000 cm$^{-1}$

690 + 750 cm$^{-1}$

mono-substituted
Characteristic absorptions of aromatics

**ortho-chlorotoluene**; neat liquid

- **750 cm\(^{-1}\)**

**meta-chlorotoluene**; neat liquid

- **690 + 780 + 880 cm\(^{-1}\)**

**para-chlorotoluene**; neat liquid

- **800 cm\(^{-1}\)**

**styrene**; neat liquid

- \(\equiv\text{CH oop}\) alkene
- \(\equiv\text{CH oop}\) aromatic
Characteristic absorptions of ethers

- **Dibutyl ether; neat liquid**
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
  - \text{asym C-O str} ~1100 cm$^{-1}$

- **Anisole; neat liquid**
  - $\text{Ar-O-CH}_3$
  - \text{Ar-O-R show 2 C-O stretches}
  - \text{sym C-O-C str} ~1250 cm$^{-1}$
  - \text{asym C-O-C str} ~1250 cm$^{-1}$
  - (IR inactive in symmetrical dialkyl ethers)

Characteristic absorptions of esters

- **Ethyl butanoate; neat liquid**
  - $\text{CH}_3\text{COOEt}$
  - \text{C-O str} 1000 – 1250 cm$^{-1}$

- **Normal ester**
  - \text{C=O str} ~1735 cm$^{-1}$

Characteristic absorptions of nitro compounds

- **Nitrobenzene; neat liquid**
  - $\text{NO}_2$
  - Two $\text{N}=\text{O str}$ 1600 – 1500 cm$^{-1}$ and 1390 – 1300 cm$^{-1}$