

Chapter 17 Applications of Infrared Spectrometry

Problems: 2, 3, 4, 5, 7, 9, 11

Table 17-1 Applications of IR

IR can be used both qualitatively and quantitatively

Broken into 3 major regions

Near

Mid

Far

Mid ($670\text{-}4000\text{cm}^{-1}$) most widely used, can do absorption, reflection and emission

Near ($4000\text{-}14000\text{ cm}^{-1}$) good for certain species

water, CO_2 , S, low MW hydrocarbons, amine nitrogen

usually done by diffuse reflectance off of solid or liquid or transmission in gases

Far inorganic and metalorganic species.

Focus here is on mid IR

17A Mid infrared absorption

Major tool for structure of organics and biochemical

17A-1 Sample Handling

No good solvents exist that are transparent in IR, so can't simply dilute into solvent and measure like we did in the vis/UV

This makes sample handling probably the most difficult step

Gases

Low BP liquids and gases are pretty simple

A cylindrical cell with appropriate windows

cell from a few cm to 10m are available commercially

10 m cells actually aren't that long, have reflecting surfaces so light passes through sample multiple times

Solutions

Can prepare solutions, but few solvents are transparent over a wide range of λ 's, therefore need to pick solvent and IR region carefully

Solvents

Figure 17-1

Common organic solvents

As can see no single solvent clear in entire region

H_2O and alcohols not used

Absorb strongly

Attack alkali metal halides that are the usual cheap windows

of cells

In fact usually have to dry the above organic solvents because of this

Cells

Absorption bands are generally very strong, so cells have short pathlengths

.01 to 1 mm most common

Even then need sample concentrations only in .1 to 10% range

Can be either solid and fixed,

but most are variable and demountable Figure 17-2

Can actual path length of narrow cells can be determined using **interference fringes Figure 17-3**

Mount empty cell in light path

Get max and min pattern

Max come from light bouncing off one window back at first window, then bouncing back again when light traveling this back and forth path is in phase with light passing straight through, get the max

If b is that pathlength, then

$$2b = n\lambda; \quad n=2b/\lambda$$

If count the number of fringes between 2 frequencies get

$$\Delta N = \frac{2b}{\lambda_1} - \frac{2b}{\lambda_2} = 2b\bar{\nu}_1 - 2b\bar{\nu}_2;$$

$$b = \frac{\Delta N}{2(\bar{\nu}_1 - \bar{\nu}_2)}$$

So count up the number of fringes between 2 frequencies and divide by the difference in wavenumber

This is a useful technique and is also used to calibrate short pathlength cells in the UV as well. so lets try this calculation

My smallest CD cell has a nominal pathlength of 50 μ m

If I put it in the IR, and get 13 interference fringes between 3250 and 2090 cm^{-1} , what is the actual pathlength of the cell?

$$X=13/2(3250\text{cm}^{-1}-2090\text{cm}^{-1})$$

$= 13/2320 \text{ cm}^{-1}$
 $= .00560 \text{ cm}$
 $= .0560 \text{ mm}$
 $= 56 \mu\text{m}$

So the pathlength is off by $> 10\%$!

Interference fringes not normally seen in solvent filled cell because the refractive index is closer to refractive index of cell so don't get as much reflection

Can also see interference fringes if have just a film in the light path, and this can be used to determine the thickness of a plastic film

Liquids

When have small sample, or there is no good solvent, can run the pure liquid

Simple to do, just put a drop between two windows and squeeze together get pathlength $< 10 \mu\text{m}$ (.01 mm)

Pathlength isn't accurate enough for quantitative work

But great for qualitative characterization

Pure liquids may also contain a trace of water or alcohol, so may slowly fog the windows so they have to be repolished

Solids

give good IR spectra

make dispersion in solid or liquid matrix

Liquid - Mulls

Solid - Pelleting

Both are reasonable, but must grind particles to $< 1 \lambda$ (usually $< 2 \mu\text{m}$) in size

Mulls

Disperse solid in mineral oil (Nujol) or fluorinated hydrocarbon oil

2-5 mg of sample

1-2 drops Nujol

Grind

Put between 2 windows

Pelleting

KBr (and other alkali halide salts cold flow and glass like transition at RT and pressure

1 mg or less of fine ground powder
 100 mg KBr
 Either grind by hand or in a special mill

Put in special die apply 10,000 to 15,000 psi
 Sounds trick. actually just 2 polished screws and a wrench
Bring example to class

Best if done in vacuum to keep air out (can't do that here)
 May have some bonds at 3450 and 1640 from H₂O in sample or salt

Most libraries done with KBr, but that doesn't go <400 cm⁻¹
 Need CsI to get to 200 cm⁻¹

17A-2 Qualitative Analysis

Figure 17-4 Typical Spectra

Analysis a 2 step process

1. analyze 1200-3600 cm⁻¹

Called *group frequency region*

Identify probable functional groups in compound

2. Analyze details of 600-1200 cm⁻¹ with similar compounds

Called the *fingerprint region*

This will uniquely identify the compound

Group Frequencies

Can calculate what they should be from masses and force constants

Or can look up in table 17-2

Frequencies aren't exact because of other interactions

But are usually pretty close because interactions aren't that strong

More detailed chart Figure 17-5

(note date 1950 I think this chart has been in every IR text since that time)

Also note one or two of these are actually in fingerprint region

Going back to figure 17-4 identify as many bands as possible

C-H stretch 2900-3000 in all 4

1375 and 1450 are C-H bends

O-H stretch 3200 in alcohol

C-Cl stretch in chloride

Usually can't identify everybody, but it makes a good start on figuring out molecule

"Fingerprint" Region

Small structural differences make big changes in this region, so is unique 'fingerprint' of a molecule

Mostly due to single bond vibrations and oscillations

Since similar E have strong interactions with each other

Note big changes in this region for the two alkanes even though their structures are very similar

Some inorganic groups sulfate, nitrate, phosphate and nitrate also absorb in this region

Limitations of Correlation Charts

Unambiguous structure determination from IR alone nearly impossible

Lots of uncertainties

Always use whole spectrum, not just one region

Usually need to combine with NMR and mass spec

Collections of Spectra

Many catalogues of spectra available commercially

Computer interface with IR to match unknown

Sadtler collection 130,000 spectra

Lots of different match algorithms

17A-3 Qualitative Applications

a bit different from UV because of number of bands, and narrowness of band

Dispersive machines has worse accuracy and precision than standard UV FTIR is better, but still not as good

Need lots of attention to detail to make work

Deviations from Beer's Law

Usually narrow bands, so get instrumental deviations from Beer's law because aren't in region where all λ 's are equal

Therefore always make and used a calibration curve

Absorbance Measurements

In UV always used double beam with matched cells

FTIR doesn't have double beam

IR cells nearly impossible to match

1. Very short pathlengths, so hard to get 2 the same
2. Windows easily attacked by solvents so don't stay matched for long

Use two other methods

1. Cell-in/cell out

Take spectra of pure solvent with nothing in beam as reference

$$T_0 = P_0/P_r$$

Take spectra of sample with nothing in beam as reference

$$T_s = P_0/T_r$$

$$T = T_s/T_0 = P/P_0$$

2. Baseline method

Use a single sample and assume baseline is linear in region of peaks (see figure 17-7)

Typical Applications

Just about everything absorbs in IR, so is a nice general method
Lots of different bands to choose from, so can select one without outside interference

Examples

Analysis of aromatic mixture
Determination of air contaminants

17B Mid-Infrared Reflection Spectrometry

Useful way to deal with solids, also liquids films, food, fibers and others

17B-1 Types of Reflection

specular reflection
diffuse reflection
internal reflection
attenuated total reflection (ATR)

Specular Reflectance

Reflecting surface is a smooth polished surface
Angle of reflectance = angle of incidence
Some light is absorbed by reflecting material so measure of reflected light like a transmission measurement

Used for smooth solids or smoothly coated solids
Not as widely used as diffuse and total reflectance

17B-2 Diffuse Reflectance

Diffuse reflectance Infrared Fourier Transform Spectroscopy (Drifts)
Spectra from powdered sample with minimal preparation
Can only be done with FTIR because intensity of reflected light is so low

When light hits a finely divided powder reflects off each different plane in the powder

Different planes randomly oriented so light reflected in all directions
skip theory

Instrumentation

Drop adapter in cell compartment
Adapter diagramed in figure 17-9
Beam from IR is cut down (collimated) and focused on a sample container holding sample
Diffuse reflection over an arc is focused by curved mirrors onto detector

In an single beam instrument need 2 runs
1 with sample
1 with a good reflector like KCl

Comparison of Absorption and Reflection

Figure 17-10
Pure KBr vs 5% compound in KBr
Peak positions match
Peak intensities vary considerably
Fairly typical

17B-3 Attenuated Total Reflectance

Ours is single reflection ATR. Crystal mirrors underneath bound light up, prisms in bottom of crystal make the light hit sample at 45 incidence and reflection angle. We have two different crystals, ZnSe and Si. Can do powders, films, or liquids

Principles

As light passes from more dense to less dense medium get reflection

The larger the angle of incidence, the more reflection
Beyond some angle all light is reflected

In theory and in practice beams acts as if it penetrates a short distance into the less dense medium

Can penetrate up to several wavelengths
Depends on λ , and the two indices of refraction

Penetrating radiation is called *evanescent wave*

As some of the penetrating light is absorbed radiation is attenuated hence the name - *attenuated total reflectance*

Instrumentation

Again you drop a single adapter into your sample compartment

Figure 17-11

Sample is on both sides of a transparent crystalline material

High refractive index

Mixed TI Br/TI I

Germanium

ZnS

Get proper incident angle, get lots of reflections

Various cell angles can be chosen

Cell for liquids as well

Attenuated Total Reflectance Spectra

Again Similar but not identical to absorption spectra

Same peak positions but intensities vary

Lots of different samples can be used

17C Photoacoustic Infrared -skip

17D Near Infrared -skip

17E Far-Infrared Skip

17F Infrared Emission Skip