

## Appendix XI-1

November 2018

### Appendix XI: IR Spectroscopy

These notes are intended to supplement what you have learned in earlier courses and the oral advice given by your instructor in this course.

An IR spectrum is typically run over the range  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . The whole range of the spectrum may not be useful for several reasons. The main reason to consider is that the lower energy limit is where the materials used for holding the sample start absorbing. Thus, although the whole range is always recorded, we often narrow the range in processing.

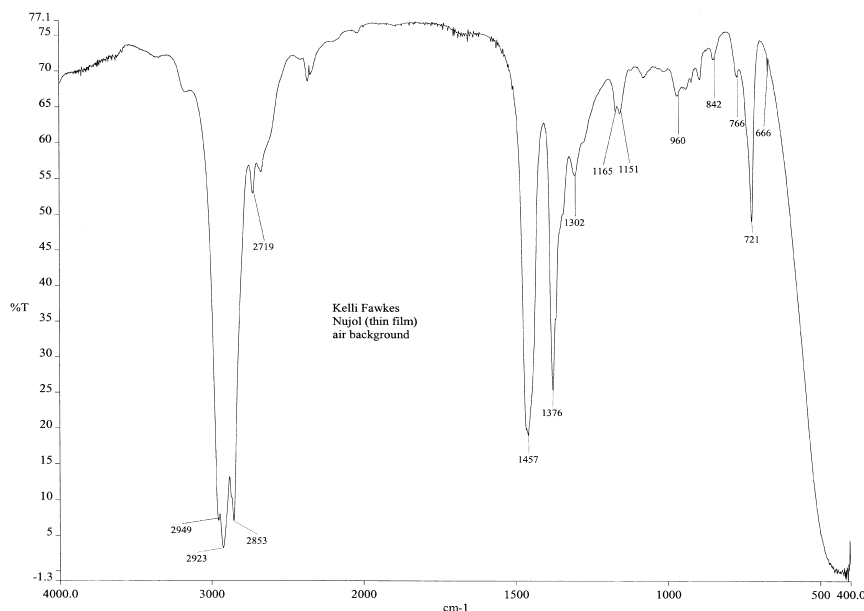
#### ATR

The simplest method of recording a spectrum is therefore to avoid having any sample container. An Attenuated Total Reflectance spectrometer has a diamond crystal window upon which a solid or liquid sample can be held down using a hand-cranked pressure device that squeezes the sample to the surface of the diamond. This works well for (organic) samples that are easily cleaned from the surface afterwards - making mostly inorganic samples unwelcome!

#### NaCl - Nujol mulls and neat liquids

The most common materials used to hold samples are large crystals of sodium chloride. These crystals are cut and polished so that they are transparent to the eye (ie in the visible range) and do not have any absorbing bands until  $\sim 600\text{ cm}^{-1}$ . Below that point, sodium chloride is unusable.

As you might imagine, sodium chloride (table salt) will dissolve in water. Its surface will also fog very quickly in atmospheric moisture, so the polished plates are kept in a desiccator. Remember to keep them away from the sinks when you are using them.



**Figure 1: Nujol with no sample as a thin film between NaCl plates.**

## Appendix XI-2

**Solid samples** are prepared by grinding the solid in a mortar and pestle until finely powdered. Two or three drops of an oil (Nujol is the proprietary name) are added to make a paste, which is then smeared on to one disk. A second disk is applied to make a sandwich and the combination is placed in the infrared beam. Of course, the Nujol also contributes to the spectrum so this must be allowed for in the interpretation of the results.

Samples that are **neat liquids** can be run directly, by sandwiching one or two drops of liquid between two clean NaCl plates.

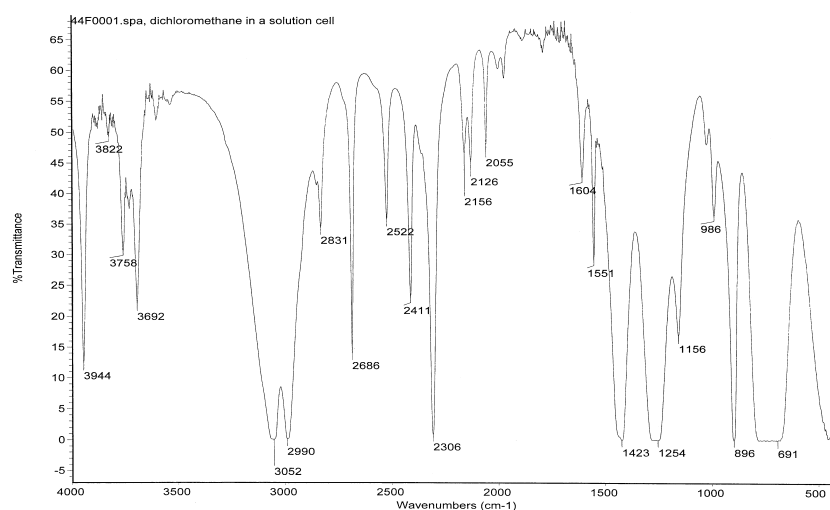
### KBr disks

Potassium bromide is also used, but rarely as a polished disk. It is usually used to form a matrix with the sample compound by grinding the mixture to a powder and then compressing a small sample in a hydraulic press. The idea is that the pressure causes the sample to briefly heat up and then fuse, to give a clear disk that is held inside the barrel of the press. The barrel is then placed in the infrared beam to record the spectrum.

Although the technique can take a while to perfect, it does give good spectra down to  $400\text{ cm}^{-1}$ , where the KBr starts to absorb.

### Solution cells

For samples that will dissolve in non-aqueous solvents, solution cells may be used. These are created by making a hollow sandwich of two NaCl plates with a Teflon ring between them. Two holes are drilled into one plate so that liquid can be squirted into the cavity. Again, the absorbing ability of NaCl limits the range to above  $600\text{ cm}^{-1}$ . The solvent can also be a problem, as it will generate its own spectrum. Although we try to compensate by running a background of just the solvent without the sample present, it is very difficult to have a perfect cancellation. There are many more solvent molecules than of solute, so it is difficult to avoid some solvent peaks. Consequently, the technique tends to be used in the  $2500$  to  $1550\text{ cm}^{-1}$  range, where most solvents are peak-free. This is ideal for monitoring metal carbonyl complexes. Other small windows might be used but for very specific systems of comparison.



**Figure 2: Dichloromethane in a solution cell with NaCl windows.**

### Appendix XI-3

The choice of solvent is worth a comment. Typically, non-polar solvents tend to encourage sharper peaks for the sample. Polar solvents will loosely associate with the polar bonds and this broadens the bands. On the other hand, polar solvents tend to dissolve the sample better, so the choice of solvent may become a balance of solubility vs sharpness of peaks.

#### **CsI**

Occasionally, low energy bands need to be observed in the  $400 - 200 \text{ cm}^{-1}$  range. In this case, caesium iodide crystals must be used for the appropriate transparency, even though they are quite soft and easily damaged. Similarly, the windows of the instrument need to be transparent, so many spectrometers do not go below  $400 \text{ cm}^{-1}$ .