

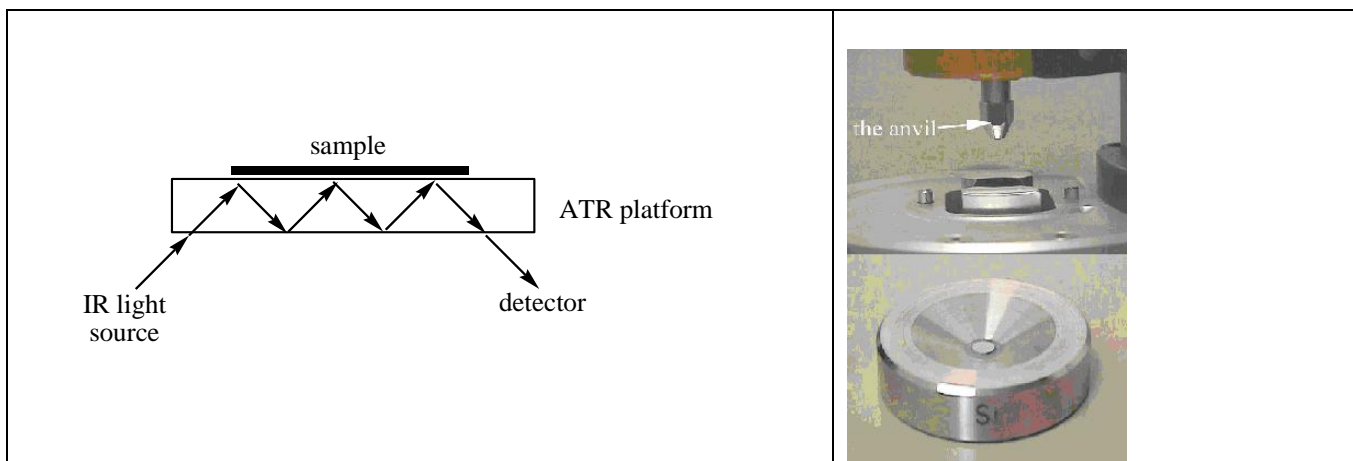
IR Unknowns Elemental Analyses

In this exercise, you will propose a structure for an unknown solid and an unknown liquid using IR and given information about their molecular weights and elemental analysis (use this to determine a molecular formula and degrees of unsaturation).

Obtain an IR of the solid unknown two ways: KBr pellet and ATR platform. Obtain an IR of the liquid sample two ways: run a neat IR on it using salt plates and the ATR platform. Propose possible structures using the elemental analysis and molecular weights.

Sample Preparation

A chemist can take an IR spectrum of a solid, a liquid or a gas. In addition, there are a number of sampling techniques available for taking an IR spectrum. In many instances the IR sample can be prepared in minutes (or less). However, the method by which an IR is taken can produce shifts in the wavenumbers (cm^{-1}) observed. The intermolecular forces of interaction will vary depending on whether the sample is a pure liquid (neat), mixed with ionic KBr, mixed with Nujol (and alkane oil), mixed with a solvent in a solution cell or gaseous. These differences in the intermolecular forces of interactions can produce differences in the stretching and bending vibrational wavenumbers. For this reason, it is essential that the method used to obtain the IR be reported along with the key wavenumbers in reporting IR data. A very convenient modern method places the sample, in any solid or liquid form, on an ATR platform (attenuated total reflectance) and bounces an IR beam through a sample.

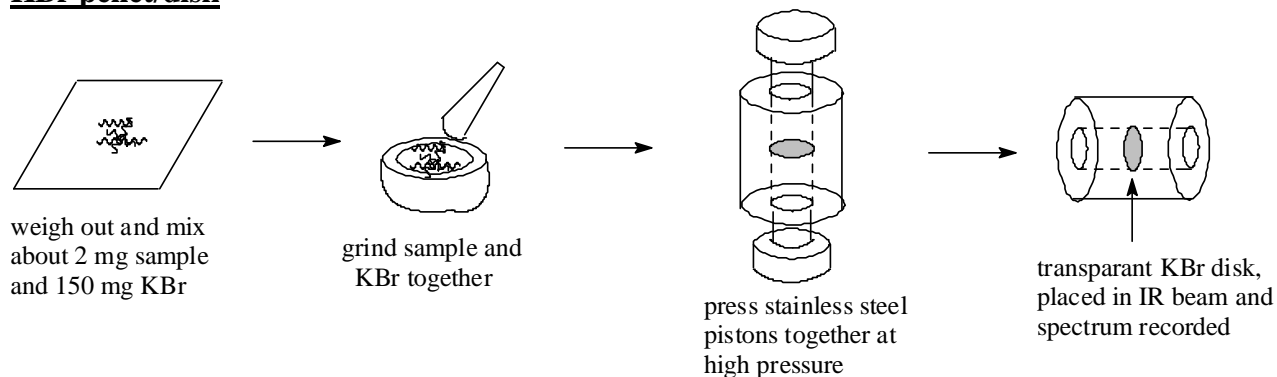


Solids

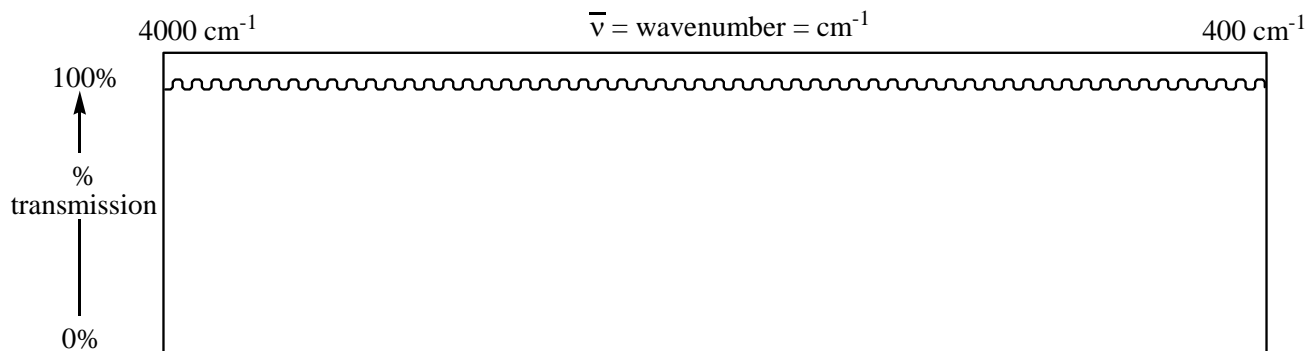
Solids are often ground up with the ionic salt, KBr. Usually 1-2 mg of sample is mixed with 150-200 mg of the KBr salt. It is always tempting to add more sample, but too much sample can make the pellet opaque. KBr is transparent throughout the entire IR region, as long as it remains dry. An open bottle of KBr is often stored in a hot oven ($\approx 140^\circ\text{C}$) to keep it dry. The solid sample and KBr are ground together with a mortar and pestle (at least a minute) or in a vibrating wiggle bug (stainless steel ball bearing in a small stainless steel container, rapidly vibrating for about a minute). The powdered mixture is then pressed between two small metal pistons with highly polished stainless steel faces in a stainless steel cylinder at enormous pressure ($\approx 25,000 \text{ lbs/in}^2$). At this pressure the solid material liquefies and flows to form a pellet that can appear as a thin transparent disk and can come out as clear as glass. This pellet is supported on holders and placed in the line of the IR beam and a spectrum taken. This is a desirable method for solids

since the entire IR region can be observed for relevant wavenumbers without any interfering alkane bands from waxy Nujol (see below).

KBr pellet/disk

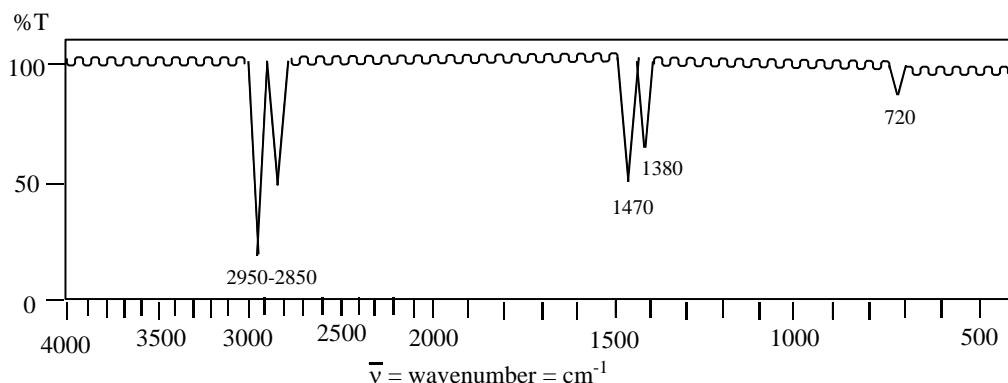


IR spectrum of KBr (no absorptions, if dry)



IR sample in Nujol

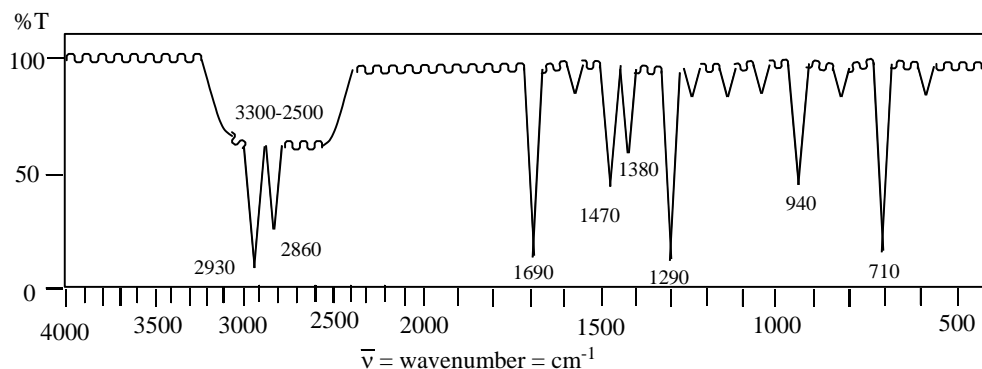
A common alternative approach with solids is to run a Nujol mull. Nujol is a liquid alkane-paraffin material. There are absorptions in the sp^3 C-H stretching region and sp^3 C-H bending region that will render this part of the IR spectrum meaningless. Also, the actual spectrum of the solid sample may appear weak in relation to the intense alkane C-H vibrations of Nujol. The oily mixture of Nujol and sample can be placed on highly polished NaCl salt plates and pressed together to make a thin film. NaCl, like KBr, does not absorb in the IR region. The sample is placed in the IR beam and the spectrum is recorded. A spectrum of Nujol alone is shown below. Also shown is a sample of benzoic acid mixed with Nujol. The nonuseful regions of this IR spectrum are the regions where Nujol absorbs. The IR spectrum using KBr shows just the benzoic acid.



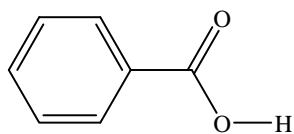
IR spectrum of Nujol (higher molecular weight alkane) shows typical alkane absorptions. Since these bands absorb in Nujol, they will not be useful in a spectrum of any unknown run in Nujol. All wave numbers have units of cm^{-1} in this book.

$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$
octadecane = Nujol

sp^3 C-H stretch 2850-2950 from symmetric and asymmetric CH_2 , CH_3 and CH stretch
 sp^3 C-H bend 1470 from CH_2 , CH_3 bend
 sp^3 C-H bend 1380 from CH_3
 sp^3 C-H rocking 720 from several consecutive CH_2 's

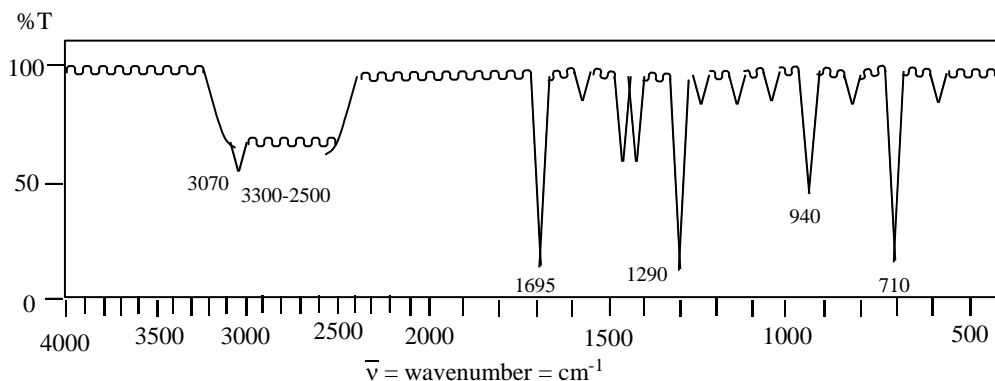


sp^3 C-H peaks are present because the sample is run in Nujol (an oily alkane hydrocarbon).

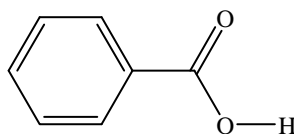


benzoic acid in Nujol mull

broad acid OH ~2500-3400
 sp^2 C-H ~3000-3100
 conjugated C=O ~1700
 acyl C-O ~1290
 monosubst. arom. sp^2 C-H bend 710 (typically = ~700 & ~750)



Without Nujol the sp^3 C-H bands are gone

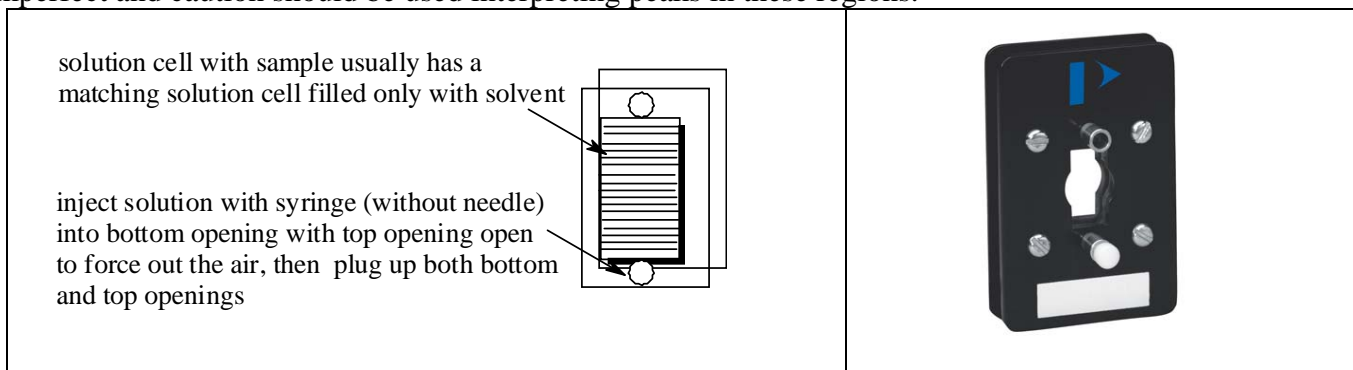


benzoic acid (KBr pellet)

broad acid OH ~2500-3400
 sp^2 C-H ~3000-3100 (pokes through just a little bit)
 conjugated C=O ~1700
 acyl C-O ~1290
 monosubst. arom. sp^2 C-H bend 710 (typically = ~700 & ~750)

Solution Cell

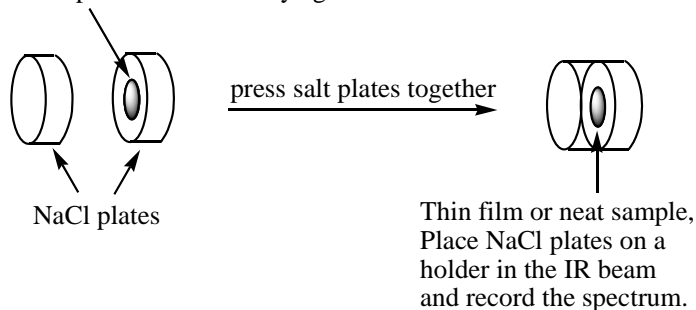
Additionally, a solid (or liquid) can be dissolved in a solvent that has minimal IR absorptions (such as CCl_4 or CHCl_3) and the mixture placed in a solution cell. On older double beam instruments, a second solution cell is filled with only the solvent. An IR beam is simultaneously passed through each cell and the two IR beams are mixed to subtract out the solvent. Alternatively, in an FT-IR instrument two different spectra are acquired (solvent + sample and solvent alone = background). The solvent spectrum is digitally subtracted from the solvent (background) + sample to produce an approximate spectrum of the sample, alone. This largely eliminates the effect of the solvent. However, if the solvent has regions of intense absorption, then the subtraction is often imperfect and caution should be used interpreting peaks in these regions.



Neat Liquid Salt Plate

One of the easiest methods of all involves placing a small drop of a liquid sample between two highly polished NaCl salt plates and pressing them together to produce a thin liquid film of the sample. This approach is referred to as a neat sample or a thin film sample. As with KBr pellets, the NaCl plates do not absorb anywhere in the IR spectrum so the only wavenumbers recorded will be due to the liquid sample. As mentioned above, liquid samples can also be run in solution cells. This might be necessary if the sample is too volatile (because of a low boiling point) and evaporates before the spectrum is completed. If, instead, too much sample is put on the salt plates, even the medium size peaks will bottom out. If that happens, take the plates apart and wipe one clean and try again until a good spectrum is obtained.

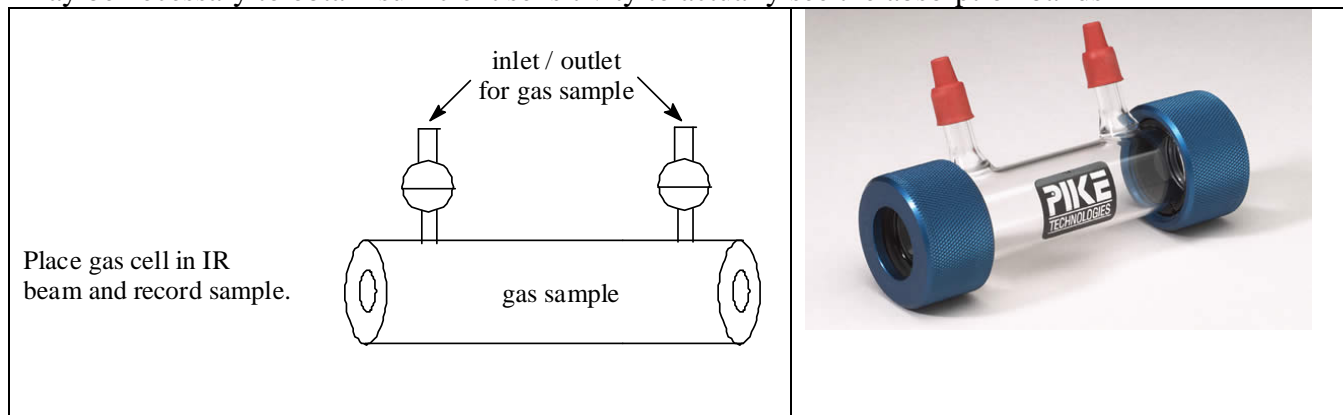
Neat sample - a small drop is placed between the plates and pressed together. If too much sample is used, the bands will be too intense. Take plates apart and wipe one clean and try again.



<http://www.organicchem.org/oc1web/exp/ir/irpro.html>

Gas Cell

Finally, vapor phase IR of gases can be obtained with special gas cells. Since the concentration of gases is so low, longer cells are used to allow more sample to be placed in the path of the IR beam. Even with the gas cell's longer path length, multiple passes of the IR beam may be necessary to obtain sufficient sensitivity to actually see the absorption bands



ART platform URL

<http://www.organicchem.org/oc1web/exp/ir/irpro.html>

KBr press URL

<http://www.organicchem.org/oc1web/exp/ir/irpro.html>

Solution cell URL

<http://www.google.co.uk/imgres?q=ir+solution+cell&hl=en&biw=1009&bih=550&tbn=isch&tbnid=o8vbfWL3gsKZgM:&imgrefurl=http://cnx.org/content/m43564/latest/&docid=iRiGDD0XJC8XLM&imgurl=http://cnx.org/content/m43564/latest/graphics5.jpg&w=267&h=360&ei=mE3UUb2mKrHtiQLWn4H4Cg&zoom=1&iact=hc&vpx=395&vpy=154&dur=2281&hovh=261&hovw=193&tx=105&ty=171&page=1&tbnh=162&tbnw=120&start=0&ndsp=16&ved=1t:429r:3s:0i:91>

gas cell URL

<http://www.kromatek.co.uk/products/Short-Path-Gas-Cells-%E2%80%93-For-Samples-with-Higher-Vapor-Phase-Concentration.html>