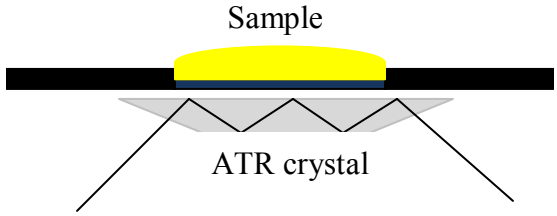
ATR protocol (JASCO FTIR-4100)

1. Introduction to ATR technique (Attenuated Total Reflectance)

While traditional IR spectrometers have been used to analyze solids, liquids and gases by means of transmitting the infrared beam directly through the sample, ATR uses the reflectance of the sample instead. An attenuated total reflection measures the change that occurs in a totally internally reflected infrared beam when the beam comes in contact with the sample. The infrared beam hits an optically dense crystal (*i.e.* diamond, zinc selenide or germanium) which then creates an evanescent wave that subsequently protrudes the sample (0.5-5 μm). The regions where sample absorbs energy, the evanescent wave will be altered, which will be detected.

It is important that the sample has good contact with the ATR crystal because the small extension of the evanescent wave beyond the crystal. This is accomplished by applying a moderate pressure to the sample during the measurement. Full and intimate contact of the sample onto the ATR crystal is essential to achieve high quality results. The refractive index of the crystal has to be significantly greater than the one of the sample.



While the analysis of samples by ATR is widely used, there are several factors that affect the quality of the final spectrum such as the refractive indices of the ATR crystal and the sample ($n_{crystal} > n_{sample}$), angle of incident IR beam, depth of penetration, wavelength of the IR beam, number of reflections, quality of the sample contact with ATR crystal, etc. The critical angle is given by

$$\Theta_c = \sin^{-1}\left(\frac{n_{sample}}{n_{crystal}}\right)$$

For instance, a diamond/ZnSe system possesses a refractive index of $n_{crystal}$ =2.4 and a critical angle of θ_c=38.7°. If the refractive index of the sample is higher than the refractive index of the crystal, derivative shaped absorbance bands are observed (see below) since the critical angle requirement was not met. The resulting spectrum is a mix of the ATR and external reflectance. The penetration depth is directly proportional to the wavelength of the incident beam, which means that photons with higher wavenumbers penetrate the sample less than photons with lower wavenumbers. Consequently, peaks on the left hand side often appear a little smaller than expected i.e. OH peaks, etc. It is important to correct this effect by applying the ATR correction to the raw spectrum.

General Pointers

i. The FTIR instruments and the software located in YH1096, YH1111 and YH6076 are identical. The type and size of the crystals (first floor is ZnSe (~$1200), sixth floor is a diamond crystal (~$5000!!)) used in the ATR setup and the way the pressure is applied to the sample are a little different.

ii. For 30BL, the first section of instruction period should consider any change to the micro-screw setting: 1.0 for powdery, 2.0 for smaller crystals and 3.0 for large crystals. Settings outside of this range will not improve the quality of the spectrum. Sample quantity (~10-20 mg) will be the most important and highly variable parameter.

iii. For 30CL, no press screw adjustment is needed. The applied pressure has to be adjusted to the quantity and nature of the sample: the thicker the sample is the higher pressure should be in order to have better reflectance. Generally 20 mg of sample are sufficient. The high pressure clamp should be turned to its slip-clutch limit to achieve maximum pressure. **In Chem 30CL, the pressure has to be released in order to be able to remove the clamp. If this is not done, the pin will hit the diamond crystal the next time it is placed on the sample and break it. You will receive a bill for the damaged crystal ($5000+) due to the fact that you handled grossly negligent!**

iv. The setup should be cleaned using *FisherBrand* moist-wipe (lint-free wipes). The used wipes can be rinsed with acetone and save them in a box labeled “used wipes”.

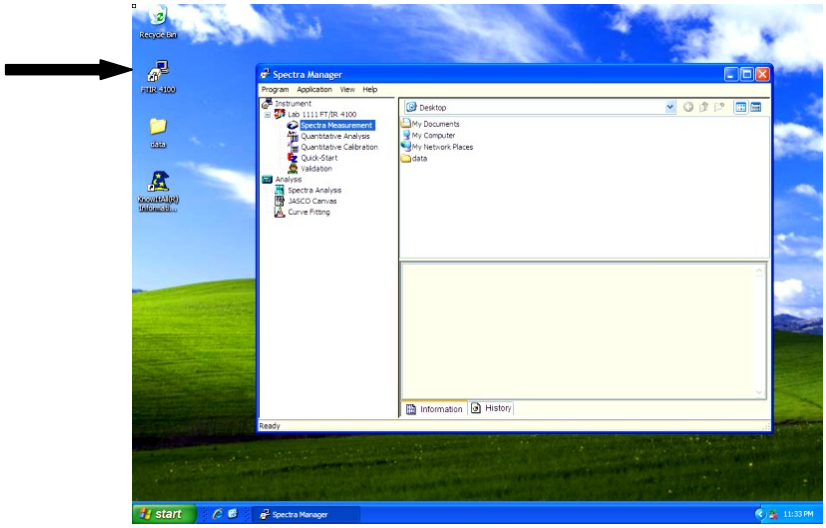
v. The ATR has to be cleaned after each measurement. Keep in mind the film left over is often more reflective than the samples applied due to better contact, which can lead to false spectra. If unsure about the quality of the cleaning, a new background spectrum should be acquired prior to applying the sample to the crystal.

FTIR initialization (only necessary if you are the first one to measure the sample or the program has to be restarted)

i. Turn on LCD monitor power (press any key on the keyboard usually). All programs/windows now open must be closed.

ii. Turn on FTIR (switch on top). Double-click "FTIR 4100" icon.

iii. Double-click "*Spectra Measurement*". This program manages several other programs, including for your purposes, "Spectra measurement" and "Spectra Analysis".



Cleaning the ATR module

i. **<u>Scratching the crystal surface must be avoided at all cost!!</u>** It is expected some residual sample will be left. The TA will remove most of the remaining residual film before and after each meeting.

ii. Much of the formed pellet can be dislodged with a wooden boiling stick. A metal spatula will be potentially too abrasive and damaging to the crystal. Students are not allowed to use them.

iii. With the remaining solid at the edges, apply some acetone, dab the top with a *FisherBrand* wipe, and repeat this 4-5 times.

iv. With acetone, moisten lint-free cloth provided by TA, and use this to scrub the general area in and around the crystal surface. It is not necessary to do this for more than a second or two. The solvent should not be applied in a way that the setup is soaked since it will leak into the optics as well.

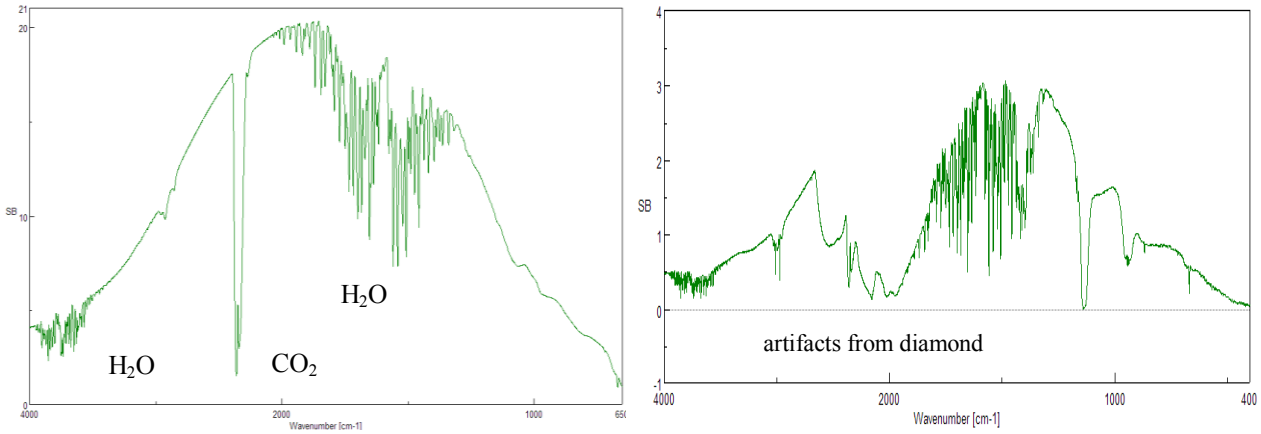
v. Remember to wipe the surface of the screw above.

vi. The next background scan will subtract any remaining residue.

Acquiring the background spectrum

i. Click "*B*" icon to acquire current background spectrum. The information window (see below) will pop-up. For the background spectrum, skip this by clicking "OK". This will initiate the Spectra measurement program to acquire scans for background spectrum. This data will be sent automatically to the "Spectra Analysis" program.

ii. The background spectrum should look like the ones below which only contains the CO_2 and the water peaks for the FTIR setup in the 1st floor (left side below). The right hand side shows the background spectrum for a diamond ATR setup, which shows additional peaks mainly in 1800-2300 cm^{-1} range and at 1140 cm^{-1} which are due to the diamond crystal.

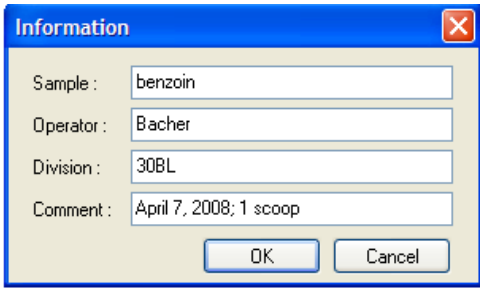


Sample setup on the ATR module

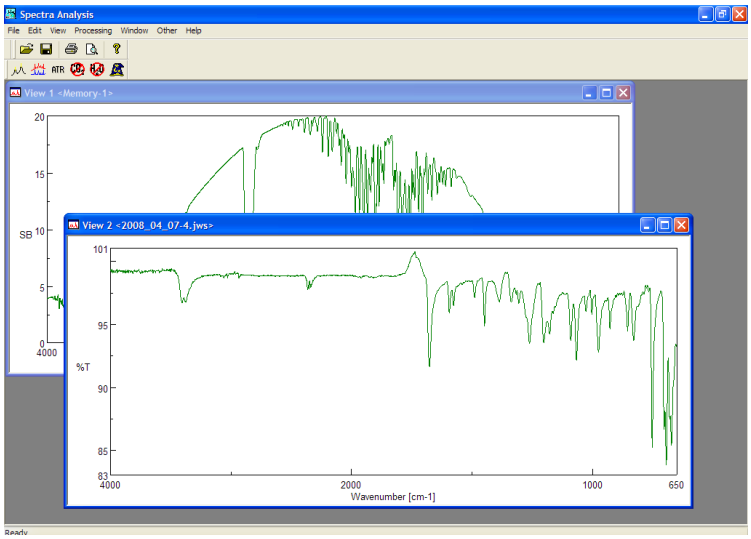
i. Apply one drop or a small micro-spatula portion (15-20 mg) to fill the dwell 60-80% full (in Chem 30BL). Make sure not to scratch the crystal with the spatula.

ii. Apply the press to the sample. The screw setting should usually not be changed.

iii. In the "Spectra measurement" program click "*S*". Enter your name and the name of your sample in the "Information" popup window.



iv. Clicking *OK* will initiate data acquisition, Fourier transformation of the data, and transfer of the data to a new "View" window in the "Spectra Analysis" program.



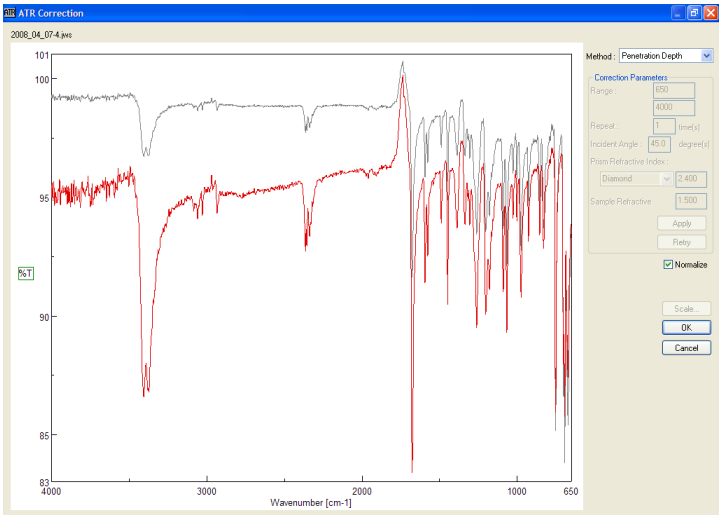
v. If the signal is not appearing well enough above the noise, apply 5-10 mg more and try pressing the sample again.

vi. A low amount of sample also gives rise to artifacts in the FTIR spectrum (~1100 (as strong peak) and 1740 cm^{-1} (often as inverted peak)).

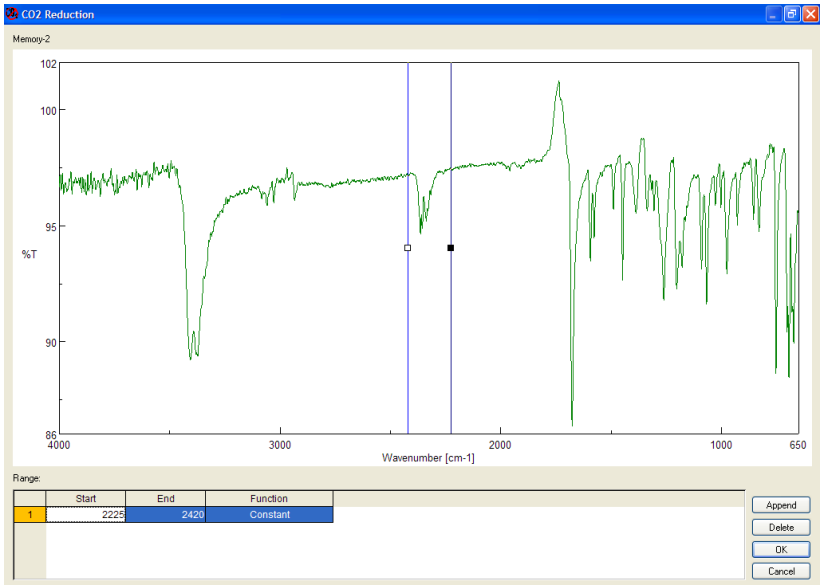
Data Processing

Here are the buttons that are going to be used for the data processing:

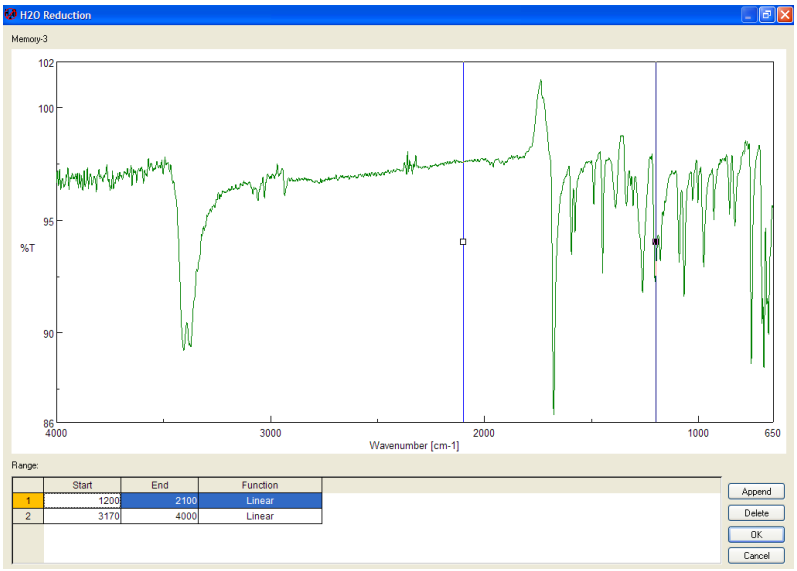
i. In Spectra Analysis, click the "*ATR*" button (3rd button), click *OK*, and a 2nd "View" window pops up. Note that the peaks on the left side increased in size.



ii. Click the "CO_2" button (4th button), click *OK*, and a 3rd "View" window pops up. Note that the peaks in the CO_2 window disappeared.

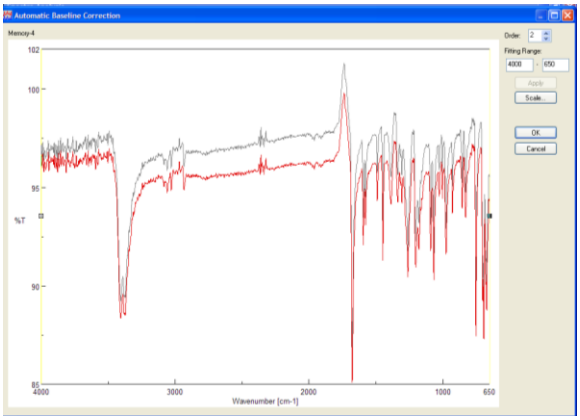


iii. Click the "H_2O" button (5th button), click *OK*, and a 4th "View" window pops up.

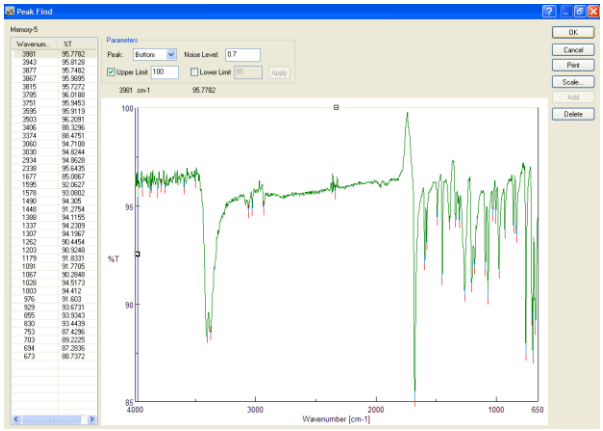


Note: This step might have to be performed twice in order to remove the water peaks from both ranges.

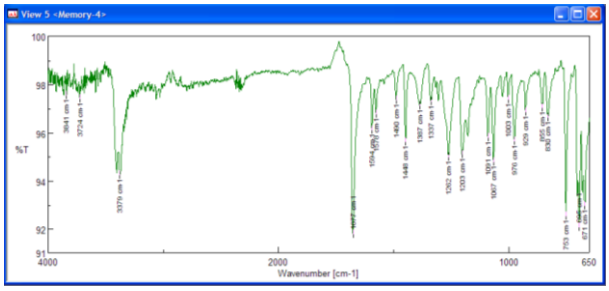
iv. Click "Automatic Baseline Correction"  . Click *OK*, and a 5th "View" window pops up.



v. Click the "Peak Find" icon  . The noise level can be adjusted by either choosing the upper and lower limit numerically or by dragging the appropriate horizontal lines in place. Click "Apply." Additional peaks can be added by dragging the vertical line to the peak and then clicking the "Add" button. Click *OK*, and a 6th "View" window pops up. (*Do not print from this screen!*)



vi. Click the "print" icon. The attached printer will print the spectrum with the user name, entered sample information and the numbers right at the peaks.



vii. Close all "View" windows, clicking "no" when prompted to save the data.

e. General remarks

Independent from the technique that is used, the IR spectra should be obtained in the range from 500-4000 cm^{-1} (for organic compounds). The background should be checked first before the spectrum of the compound is acquired. The new generation of FTIR spectrometer allows processing the data electronically, which usually leads to an improved quality of a spectrum using background correction techniques.

The laboratory course uses IR plates made from AgCl. Keep in mind that these plates are very expensive (~$150). The compound should not react with them (strong oxidizing or reducing reagent?). If you check them out from the TA (in exchange for your ID card), it is your responsibility to return them in proper condition (**clean and complete!**). They are cleaned with **dry acetone** and **Kim wipes**, and <u>not</u> with water, alcohol and the brown or white paper towels! (*Why?*) AgCl plates have to be stored a closed box, protected from light, because they are light sensitive.

The IR samples should be prepared at the workbench, and not at or on top of the IR instrument. We encountered problems in past, because students spilled chemicals inside the instrument, which caused 'wrong' spectra and serious damage to the instrument, which cost $$$$.