Probing the Characteristic Vibrations of Benzoic Acid and Salicylic Acid with Infrared (IR) Spectroscopy. Qualitative Information from Infrared (IR) spectra

I. Theory Background

A. Spectroscopy

Molecular spectroscopy is a powerful tool used in determination of molecular structure and molecular energy levels. Rotational spectra give us information about the moments of inertia, interatomic distances, and angles. Vibrational spectra yield fundamental vibrational frequencies and force constants allowing determination of structural parameter. Electronic spectra allow determination of electronic energy levels and dissociation energies.

When a molecule undergoes a transition from energy state E_1 to another energy state E_2, energy is conserved by the emission or absorption of a photon. Hence, the terms emission spectroscopy (fluorescence) and absorption spectroscopy (uv-vis, infrared) indicate whether we measure emitted or absorbed photons. The frequency of the photon v is related to the separation between the energy levels of the two states by the relation,

$$hv = hc\tilde{v} = |E_1 - E_2| \quad (1)$$

where h is Plank constant and $\tilde{v} = \frac{1}{\lambda}$ is the transition energy in wavenumbers. The commonly used unit of wavenumber is cm^{-1}. The frequency of the photon in the absorption or emission process often indicates the kinds of molecular transitions involved. Electronic transitions take place when electrons in a molecule are excited from one energy level to a higher energy level. Vibrational transitions occur when a molecule absorbs or emits a quantum of energy, E, corresponding to the difference between quantized vibrational states of a molecule. Similarly, rotational transitions result from absorption or emission of a photon of energy matching the difference between the quantized rotational states of a molecule. The classification of the various regions of electromagnetic spectrum by the type of transition is possible because in general: electronic energy level differences are much greater than vibrational energy level differences, which are much greater that rotational energy level differences. Electronic transitions are in the visible and ultraviolet part of the spectrum; vibrational transitions are in the infrared, and rotational transitions are in the far infrared and microwave regions.

The IR spectroscopy is concerned primarily with the transitions between vibrational states. These transitions require photons with energy in the infrared range 14000 – 10 cm^{-1} (wavenumbers). The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared. The higher-energy near-IR, approximately 14000–4000 cm^{-1} (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 μm) has low energy and may be used for rotational spectroscopy.

B. Molecular vibrations

There is only one mode of vibration for a diatomic molecule, the bond stretch. In polyatomic molecules there are several modes of vibration because all the bond

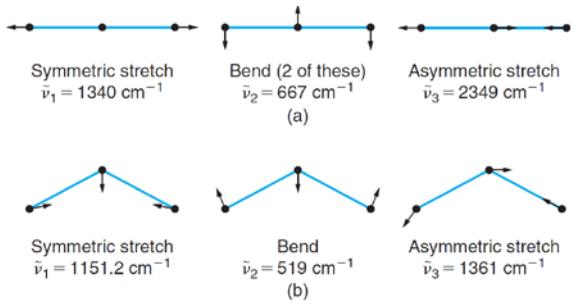

Figure 1. Vibrational Normal Modes. (a) Carbon dioxide. (b) Sulfur dioxide. (From Physical Chemistry by Robert G. Mortimer)

lengths and angles may change. However, each bond length or bond angle does not oscillate independently of the others. It turns out that there are collective motions of some or all of the nuclei that can oscillate independently, called **normal modes**. Each normal mode of vibration can also be characterized by a single **normal coordinate *Q*,** which varies periodically. A given normal coordinate is a measure of "amplitude" of a specific normal mode of vibration. Since normal modes of vibration can be excited independently of each other, normal coordinates are also independent in the sense that each one makes a separate contribution to the total vibrational potential and kinetic energy.

In a polyatomic molecule each atom has three degrees of freedom – it can move independently along each of the axes of a Cartesian coordinate system. For a molecule consisting of *N* atoms there are 3*N* degrees of motional freedom. Three of these represent translational motion in mutually perpendicular directions (the *x*-, *y*-, and *z*-axes) and three represent rotational motion about *x*-, *y*-, and *z*- axes. The remaining 3*N*-6 degrees of freedom give the number of ways the atoms in a nonlinear molecule can vibrate, *i.e.* the number of *normal modes of vibration*. For linear molecules there are 3*N*-5 vibrational degrees of freedom, *normal vibrations*, since a linear molecule has two rotational degrees of freedom. Figure 1 shows schematically the motion corresponding to the four normal modes of carbon dioxide (linear) and the three normal modes of sulfur dioxide (nonlinear), and shows the frequencies divided by the speed of light, given in cm^{-1} (wavenumbers).

In general, a normal mode is an independent, synchronous motion of atoms or groups of atoms that may be excited without leading to the excitation of any other normal mode and without involving translation or rotation of the molecule as a whole. In each normal vibration all atoms move in phase, i.e. the nuclei pass through the extremes of their motion simultaneously. The motions of the nuclei in a normal mode are such that the center of the mass does not move, and the molecule as a whole does not rotate. Each *normal mode of vibration* is associated with a characteristic frequency. Benzoic acid C_6H_5COOH, for example, with 15 atoms has 39 *normal vibrations* and 39 *fundamental frequencies* can be found spectroscopically. The *fundamental vibrations* occur when molecules absorb infrared radiation that promotes them to the first vibrationally excited state. The number of absorption bands observed in IR spectra can be sometimes greater than the number of *fundamental vibrations*. It can be increased by bands which are not fundamentals – overtones, combination bands and Fermi resonance bands. On excitation to the second or third excited states (or beyond), the first and second *overtone* vibrational frequencies, $2\nu_1$ and $3\nu_1$ respectively, are observed. An overtone is a multiple of a given fundamental frequency. Coupling of fundamental vibrations produces new vibrations at frequencies above or below those observed in the absence of coupling, for example, a *combination band* is a sum of two fundamental frequencies $\nu_1 + \nu_2$. *Fermi resonance*, due to interactions between fundamental vibrations and overtones, $\nu_1 + \nu_2$, is not uncommon in the infrared.

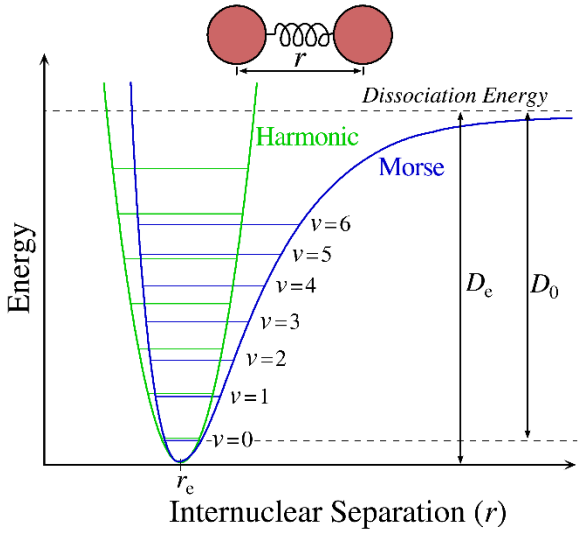

Figure 2. The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by ħω, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy De is larger than the true energy required for dissociation D0 due to the zero point energy of the lowest (v = 0) vibrational level.

The simplest model of vibrating molecule describes two atoms connected by a weightless spring which corresponds to a diatomic molecule with a chemical bond between the two atoms (Figure 2). In regions close to the equilibrium bond length r_e the potential energy of this model can be approximated by parabolic potential energy

$$V = \frac{1}{2}k(r - r_e)^2 \quad (2)$$

where k is the force constant of the bond, a measure of the strength of a bond. The potential energy V as a function of the internuclear distance r of the atoms from their equilibrium position r_e for a diatomic molecule is shown in Figure 2. In the harmonic oscillator approximation the potential energy function is parabolic in shape (green line in Figure 2). In the harmonic oscillator approximation the vibration of polyatomic molecules is that of normal modes, each acting like an independent harmonic oscillator.

Using harmonic potential energy to solve the Schrodinger equation (harmonic oscillator approximation) for the relative motion of two atoms of masses m_1 and m_2 we will obtain the evenly spaced quantized energy levels (vibrational energy levels)

$$E_\upsilon = h\nu\left(\upsilon + \frac{1}{2}\right) \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m_{\text{eff}}}} \quad (3)$$

where h is the Planck constant, υ is the vibrational quantum number (υ = 0, 1, 2, 3…), ν is the fundamental frequency of the particular mode, and m_{eff} is called reduced mass

$$\frac{1}{m_{\text{eff}}} = \frac{1}{m_1} + \frac{1}{m_2} \quad (4)$$

It follows from equation (3) that a harmonic oscillator has a zero point energy $E_0 = \frac{1}{2}h\nu$. The actual variation of the potential energy as a function of the displacement of atoms from their equilibrium position fits the parabolic function (harmonic approximation) only near the equilibrium internuclear distance (Figure 2). In practice the *anharmonic*, for example Mors potential function (blue line in Figure 2), more closely resembles the potential energy of vibrations in a molecule for all interatomic distances.

$$V = hcD_e\left(1 - e^{-\sqrt{\frac{\sqrt{m_{eff}}k}{2hcD_e}}(r - r_e)}\right)^2 \quad (5)$$

where D_e is the depth of the potential minimum. Near the well minimum the variation of V with displacement resembles a parabola, but unlike a parabola, Morse potential allows for dissociation at large displacements. If the Morse anharmonic potential is used to solve the Schrodinger equation the solution becomes more complex and the approximate solution for the vibrational energy levels is given by

$$E_\upsilon = h\nu\left(\upsilon + \frac{1}{2}\right) + h\nu\chi_e\left(\upsilon + \frac{1}{2}\right) \quad (6)$$

where χ_e is the anharmonicity constant. χ_e is dimensionless, typically 0.002 to 0.02.

The selection rule for a change in vibrational state brought about by absorption or emission is that the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. The molecule is not required to have a permanent dipole moment only that the change in the induced or permanent dipole moment, with respect to the change in the normal coordinate Q is greater than zero.

$$\left(\frac{\partial\mu}{\partial Q}\right) \neq 0 \quad (7)$$

More specifically the selection rule require that the vibrational quantum number can change by one $\Delta\nu = \pm 1$. Such vibration are called infrared active. Transition for which $\Delta\nu = +1$ corresponds to absorption and those for which $\Delta\nu = -1$ to emission. At room temperature almost all molecules will be in their vibrational ground states and, as dictated by the selection rule, the allowed transitions $0 \rightarrow 1$ will produce fundametal bands. The resulting spectrum will consist of single absorption line for each IR active normal mode. Vibrations which do not affects molecule's dipole moment are described as infrared inactive. These vibrations do not absorb radiation. An example of an infrared inactive vibration is stretching of a homonuclear diatomic molecule in which the dipole moment remains zero not matter how much the bond elongates.

C. Infrared Spectrum

Infrared spectra are usually recorded by measuring the transmittance (T) of the sample. The transmittance T of the solution is the fraction of incident radiation transmitted by the solution

$$T = \frac{P}{P_0} \quad (8)$$

Where P_0 is the radiant power of the incident beam and P the radiant power of the transmitted beam. The absorbance A of the beam is related to the transmittance through

$$A = -\log T = \log\frac{P_0}{P} \quad (9)$$

The absorption law, also known as Beer-Lambert law tells us quantitatively how the amount of attenuation depends on the concentration of the absorbing molecules and the path length over which the absorption occurs.

$$A = abc \quad (10)$$

Where, A is the absorbance, a is proportionality constant called absorptivity, c stands for the concentration in; and b is the thickness of the sample in cm. When the concentration is expressed in mol/dm^3 and b in cm, the proportionality constant, a, is called molar absorptivity and is given the symbol ϵ.

The frequencies of the absorption bands ν_s are proportional to the energy difference between the vibrational ground and excited states. The absorption bands due to the vibrational transitions are found in the wavelength region of $\lambda = 2.5 \ldots 1000$ μm which is equivalent to the wavenumber range $\tilde{\nu} = 4000 \ldots 10$ cm^{-1}.

Each absorption band is associated with a characteristic motion of atoms – normal mode of vibration. While the absorption frequency depends on the molecular vibrational frequency, the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule. This in turn depends on the change in the dipole moment that occurs as a result of molecular vibration. The electric field of the IR photon exerts forces in opposite directions on the opposite molecular charges. Thus changing the spacing between the positive (protons) and negative (electrons) charges and inducing a dipole moment to oscillate at the frequency of the photon. When the frequency of the photon matches the natural frequency of a particular normal mode of vibration. The transfer of energy from the IR photon to the molecule during the absorption process is possible if the vibration cause a change in the dipole moment of the molecule. The more the dipole moment changes during a vibration, the more easily the photon electric field can activate that vibration. It can be shown that the intensity of an infrared absorption band is proportional to the square of the change in the dipole moment, with respect to the change in the normal coordinate $\left(\frac{\partial \mu}{\partial Q}\right)^2$ of the molecular vibration, giving rise to the absorption band.

The frequencies of molecular vibrations depend on the masses of the atoms, their geometric arrangement, and the strength of their chemical bonds through the force constant, Eq. (3). Thus, they provide information on molecular structure, dynamics, and environment.

Two different approaches are used for the interpretation of vibrational spectroscopy and elucidation of molecular structure.

1. Use of group theory with mathematical calculations of the forms and frequencies of the molecular vibrations. The calculations are usually performed using a computer program such as Gaussian, GAMESS, NWCHEM, Orca or similar. Using various approximations to solve the Schrodinger equation these programs calculate harmonic vibrational frequencies.
2. Use of empirical characteristic frequencies for chemical functional groups.

In general, many identification problems are solved using the empirical approach. Certain functional groups show characteristic vibrations in which only the atoms in that particular group are displaced. Since these vibrations are mechanically independent from the rest of the molecule, these group vibrations will have a characteristic frequency, which remains relatively unchanged regardless of what molecule the group is in. The vibrational spectrum may be divided into typical regions as follows:

X–H stretch (str) highest frequencies (3700–2500 cm^{-1})

X≡Y stretch, and cumulated double bonds X=Y=Z asymmetric stretch (2500–2000 cm^{-1})

X=Y stretch (2000–1500 cm^{-1})

X–H deformation (def) (1500–1000 cm^{-1})

X–Y stretch (1300–600 cm cm^{-1})

The above represents vibrations as simple, uncoupled oscillators (with the exception of the cumulated double bonds). The actual vibrations of molecules are often more complex and typically involve coupled vibrations.

For many vibrational modes, only a few atoms have large displacements at the rest of the molecule is almost stationary. The frequency of such modes is nearly independent of the rest of the molecule. For example the stretching vibration of carbonyl group in aldehydes and ketones is almost always observed in the range 1650 – 1740 cm^{-1}. Such frequencies are characteristic of functional or structural group involved and are thus known as **group frequencies**. The presence of various group frequencies is of great importance in identifying the molecule. Extensive spectra/structure correlation tables have been developed to allow spectroscopists to assign vibrational bands in a given spectrum to the vibrational modes associated with a certain functional group. Not all bands are useful for identifying functional groups in the structure of organic molecules. In the region from ~400 to 1300 cm^{-1} vibrational frequencies are affected by the entire molecule so their frequencies varies from one molecule to the another containing particular functional group. The modes are useful for distinguishing one molecule from other containing similar functional groups and hence are often known as **fingerprint bands**. These bands find widespread use for identification purposes by comparison with library spectra.

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. A standard method of assigning vibrational spectra relies on correlating characteristic absorptions bands with certain functional groups. Over the years extensive spectral tables have been compiled with characteristic group frequencies. Characteristic group frequencies of some functional groups are listed in Table 2 and Table 3 at the end of this handout. An additional handout regarding interpretation of IR spectra is also provided on Blackboard Learn.

Material	*Wavenumber range (cm^{-1})*
NaCl	5000–625
KBr	5000–400
BaF_2	5000–870
CaF_2	5000–1100
KRS-5	5000–275
ZnSe	5000-550
Diamond	4500–2500; 1800–200

II. Sampling methods

Infrared spectroscopy can be used to investigate many different sample types either in bulk or in microscopic amounts over wide range of temperatures and physical states. Since quartz strongly absorbs in the near-IR region front-silvered or gold-coated reflective optics are employed. However, an IR transmitting material is often required for sample holders and other optics such as beamsplitter. Typical IR transmitting materials are listed in Table 1.

Table 1. IR Transmitting Materials.

A wide variety of sampling techniques exist that can be used to obtain the spectrum and the general criteria for suitable IR sample preparations include the following.

1. To obtain a good quality spectrum the sample should be uniformly thick and homogenously mixed without holes or voids. The most intense bands in the spectrum should be in the range of 5–15 % transmittance.
2. The highest point in the spectrum should lie between 95 and 100% of transmittance and the baseline should be relatively flat.
3. Water vapor and carbon dioxide bands should be minimized. This can be partially achieved by subtracting previously recorded background spectrum.

A. Gas Samples

Absorption spectra of gases can be measured in a variety of gas cells. The path length of gas cells can range from few centimeters to several meters. The gas cells are usually gas tight cylinders with IR transmitting windows on the ends and a means of introducing the gas into the cell.

B. Liquid Samples

Spectra of liquids can be measured in a demountable type cell or in a fixed thickness sealed cell. In the former a drop of liquid sample is sandwiched between the cell windows and clamped together in the cell holder. A thickness of about 0.01 mm is suitable for most pure liquids. The cell thickness is not reproducible even if reassembled with the same parts. A fixed thickness sealed cell is used for quantitative analysis where a reproducible thickness is needed for a series of samples. Sealed cell is also used for volatile samples. The cells are commercially available in many thicknesses ranging from 0.01 mm for pure liquids to a few millimeters for dilute solutions.

The sample concentration and path length should be selected to obtain the transmittance in the range of 15%-70% in order to get a good IR spectra. This will correspond to about 0.02 mm cell thick in the case of most neat liquids, and concentration of 10% and cell length of 0.1 mm in the case of most solutions. The solvent selected must be transparent in the region of interest. Neat liquids can be analyzed between salt plates made of NaCl or KBr.

Non- or low volatility liquids can be analyzed by placing a drop of the sample onto specially prepared thin polyethylene (or other) polymer substrates. These supports (called "IR cards") are cheap and disposable. They absorb IR only in well-known, narrow bands, which depend on the material. These absorption can be accounted for using the clean substrate as a background. The absorptions are ratioed out in the final step of sample spectrum generation.

C. Solid Samples

The IR spectra of solid samples can be obtained using many different methods of sample preparation.

1. Solutions

Solids can be dissolved and measured in a manner described for liquids. However, this requires a suitable solvent. None of the solvents is completely transparent in the IR region. The most adequate solvents are carbon tetrachloride, carbon disulfide, and chloroform.

2. Cast Films

A film of the solid can be prepared by evaporating a solution of the material directly on an IR transmitting window, or on material from which dried film can be peeled. Water solution can be evaporated on ZnS or AgCl platets. This technique is most useful for soluble polymers.

3. Melts

Melting the sample and allowing it to resolidify is another technique for preparing solid samples. It is used mostly for vibrational analysis studies of orientation effects since preparing samples in this way may result in samples oriented in a specific way which is not desirable in qualitative and quantitative analysis.

4. Mulls

This method is especially valuable for preparing samples of crystalline powders. Radiation scattered by crystalline powders tends to obscure IR spectra. The most visible effects of scattered radiation include a gradual lowering of the "no absorption" background line at the short wavelength end of the spectrum and a nonsymmetrical band shape distortion. To reduce the scattering effects mulls are prepared by 1) finely grounding the powder to a particle size smaller than the used wavelength and 2) surrounding the particles by a material with a refractive index relatively similar to that of the sample.

In a mineral oil (Nujol) mull method a small amount of solid sample is mulled in a mortar with a small amount of Nujol to make a paste which is transferred to a rock salt plate. Alternatively the sample can be mulled directly between the rock salt plates. The mineral oil has the advantage of no reactivity with the sample. The disadvantage of this method include loss of the aliphatic carbon-hydrogen region of the spectrum because of the mineral oil used. If the carbon-hydrogen regions, 3000-2800 and 1500-1340 cm^{-1}, is of interest mull can be prepared using halogenated oils such as Perfluorokerosene or Halocarbon. which do not have C-H.

5. KBr Discs

The potassium bromide discs are prepared by mixing a very small amount of finely ground solid sample with powdered KBr and then pressed in an evacuated die under high pressure. The resulting disc are transparent and yield a very good spectra. The only infrared absorption by KBr matrix is from small amounts of water adsorbed in the powder. Adsorbed water is minimized by grinding KBr as little as possible. The sample is ground separately and them mixed with KBr, after which it is ground as little as possible to achieve good mixing.

A die which can be evacuated improves the lifetime of the disc clarity buy is not mandatory. Pressures of approximately 8 tons for a pressing time of 5 min or 10 tons for 1 min are suitable for producing 13-mm discs. For smaller diameter dies, a hydraulic press is not necessary, as suitable pressures can be generated with hand operated presses. The optimum sample concentration varies from 0.1 % to 3 % in some aromatic compounds. The proper concentration is best determined by trial and 0.5 % is a good starting point.

KBr discs have no absorption bands above 400 cm^{-1}. However, the small amount of water adsorbed in KBr gives a weak band about 3440 cm^{-1} and a weaker still band at 1640 cm^{-1}. In consequence one never knows if this is the water impurity in the sample or the KBr. Occasionally, KBr discs of crystalline materials can be less reproducible owing to the changes in crystallinity or sample polymorphism, or hydration state, or KBr reactivity.

Sample preparation is an important part of the processes of obtaining good IR spectra. Poor sample preparation can lead to so-called false spectrum. In which broadening of the most intense bands and strengthening of the weak bands is observed.

III. Instrumentation

A conventional IR spectrometer consists of three basic components: radiation source, monochromator, and detector. First commercial IR spectrometers used monochromators to disperse a broad spectrum of radiation and provide the desired wavelength band so that only the band of interest is detected and measured. Recently, Fourier transform infrared (FTIR) spectrometers replaced the dispersive instruments for most applications. In FTIR instruments use interferometers instead of monochromators. Interferometers allow to examine all frequencies simultaneously. A conventional IR spectrometer, dispersive infrared spectrometer, is shown in Figure 3.

A. Radiation source for IR

The common continuous radiation sources for IR spectrometers are electrically heated inert solids. The simplest source can be a coil of nichrome wire which emits IR radiation when heated by electric current. A globar source, silicon carbide rod, emits IR radiation when heated electrically to 1500°C. A Nernst glower is a cylinder of zirconium and yttrium oxides that emits IR radiation when heated to a high temperature by an electric current. However, the thermal sources are inefficient in the far infrared region, and the mercury arc, a quartz jacketed tube filled with Hg vapor has to be used.

B. Dispersive spectrometers

Conventional infrared spectrometers (Figure 3) or dispersive infrared spectrometers have two beams of radiation, one passing through the sample, the other passing through a reference cell or just air. A particular frequency is absorbed by the sample and less radiation is transmitted. Using an optical chopper (such as sector mirror) the two transmitted beams are alternatively dispersed by a monochromator into its component wavelength and focused on a detector. The detector compares the intensity passing through the sample with the intensity passing through the reference.

In monochromators a prism (Figure 4) or a diffraction grating (Figure 5) are used to disperse radiation into its component wavelengths. The radiation enters the monochromator through an entrance slit and the radiation beam is made parallel by a suitable mirror. The parallel radiation approaches the mirror or grating at one angle and leaves at angles that vary with the wavelength of the dispersed radiation. The dispersed spectrum is focused by a mirror onto an exit slit. In the prism monochromator the exit slit allows one wavelength element to pass through and reach the detector. The whole spectrum is measured one wavelength at a time. The same steps happen in a grating monochromator with the exception that the exit slit allows one wavelength and multiples of that wavelength to pass through. The unwanted wavelength multiples are removed by a selective filter.

The surface of the grating has a series of very closely spaced parallel grooves on its surface. The significant data of a grating are: the total number of grooves, the distance between neighboring grooves (grating constant), and the length of grooves. After the radiation strikes the surface each groove acts like a slit-like source of radiation, diffracting it a various angles. Only the radiation that leaves the grating at a specific angle can pass through the exit slit. A beam of monochromatic light of wavelength λ incident on two adjacent grooves is diffracted and leaves toward the exit slit displaced by the path length difference (Figure 6). Constructive interference will occur for the wavelengths for which the path length difference is equal to the integral number of wavelengths. This means that a given wavelength and its whole number multiples, or higher orders, will pass through the exit slit together. The path length difference depends on the groove spacing, the angle of incidence and the angle of reflectance of the radiation. By rotating the grating slightly, the path length difference for adjacent grooves will be changed and a slightly different wavelength will reach the detector. The spectrum is recorded one wavelength resolution element at a time. Usually for the whole spectral range more than one grating is used. The shorter wavelength radiation is reflected off the grating at sharper angle than the longer wavelength – that is, angular dispersion of radiation takes place at the grating surface.

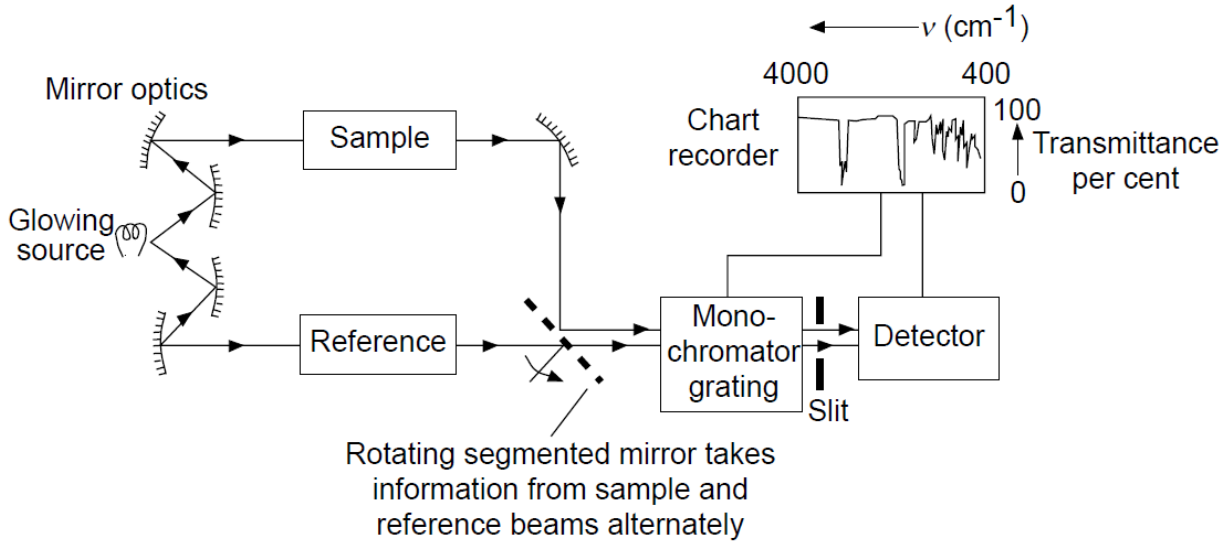

Figure 3. Double-beam dispersive IR spectrometer.

C. Fourier-Transform Spectrometers

Fourier-transform (FTIR) spectrometers were introduced in seventies and since then have become a commonplace in the laboratory. A schematic of a FTIR instrument is shown in Figure 10. Fourier-transform instruments contain no dispersing element, and all wavelengths are detected and measured simultaneously using a Michelson interferometer (Figure 7). The interferometer is used to split a beam of radiation into two beams and then recombining them after a path difference is introduced. To separate the wavelengths, it is necessary to modulate the source signal and pass it through a sample in such a way that it can be recorded as interferogram. The interferogram is subsequently decoded by a Fourier transformation, a mathematical operation conveniently carried out by a computer.

A beam from the source impinges on the beam splitter, which is tilted at 45° to the incoming beam. The beam splitter (half-transparent mirror in Figure 7) is coated on the right side so the beam enters the glass and is partially reflected off the back side of the coating (beam B) and partially transmitted (beam A). Beam B moves up toward the movable mirror, where it is reflected back down toward the beam splitter. Part of the beam is then transmitted down through the beamsplitter toward the detector. Beam A emerges to the right of the beam splitter toward the fixed mirror. It then is reflected back to the left to the beam splitter, where it is reflected down to the detector. With careful alignment, both beam A and B are collinear and impinge on the detector at the same spot. When the beams are recombined, an interference pattern is obtained as the Optical Path Difference (OPD) or the *retardation* δ is varied (OPD = 2 x mirror displacement). In the regions where they interfere constructively, bright bands appear, and where destructive interference occurs, dark bands form. Constructive interference occurs every time the value of the retardation δ is an integer multiple of the wavelength or δ = nλ; therefore, the energy arriving at the detector as a function of retardation I(δ) will be a maximum. On the other hand, if the position of the moving mirror is such that the optical pathlength of beam (B) is different from that of beam (A) by $\left(n+\frac{1}{2}\right)\lambda$ where n = 0, ±1, ±2… then the two beams are 180° out of phase and will exactly cancel each other on destructive interference. In this case the energy that reaches the detector is a minimum. The alternating light and dark bands are called *interference fringes*. When the movable mirror is moved down at constant velocity, the interference pattern remains the same, but the position of constructive and destructive interference are shifted as the path difference changes. As the mirror moves, the two wavefronts are shifted in space relative to one another, and alternate light and dark fringes sweep across the detector. For a monochromatic radiation (one frequency) the intensity of the radiation at the detector, I(δ), varies as a cosine function of the optical retardation δ (Figure 8). If the source emits more than one frequency (polychromatic radiation) every frequency is treated as if it resulted in a separate train of

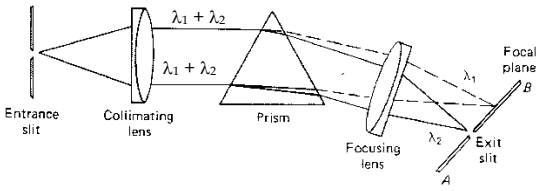

Figure 4. Prism Monochromator

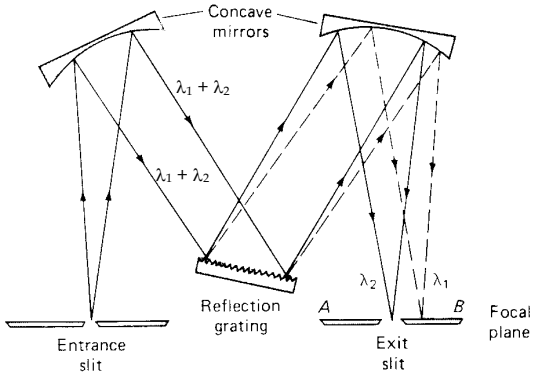

Figure 5. Refraction Grating.

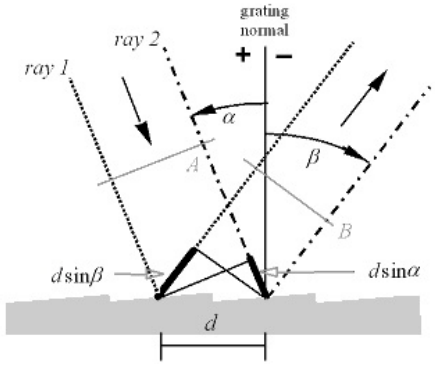

Figure 6. Two parallel rays, labeled 1 and 2, are incident on the grating one groove spacing *d* apart and are in phase with each other at wavefront A. Upon diffraction, the principle of constructive interference implies that these rays are in phase at diffracted wavefront B if the difference in their path lengths, *d*sinα + *d*sinβ, is an integral number of wavelengths.

cosine waves. If the original light intensity is denoted as $P(\lambda)$, the intensity $I(\delta)$ at the optical path difference δ can be expressed as burst" or the Zero Path Difference (ZPD) of the interferogram. Conversely, when the optical path difference is a half-integer multiple (integer + 1/2), the light becomes weaker as contributions from the various frequencies go in and out of phase with each other. The "spectrally meaningful" information is extracted from the wings of the interferogram.

$$I(\delta) = \frac{1}{2}P(\lambda)\left(1 + cos\left(\frac{2\pi\delta}{\lambda}\right)\right) \qquad (11)$$

Fourier transform is the process of calculating the wave intensity at each period from the sum at all wave periods. Applying Fourier transform to an interferogram obtains the intensity at each period, that is, at each wavelength. If an interferogram $I(\delta)$ for infrared light at continuous wavenumbers can be created using the wavenumber ν instead of the wavelength λ, $I(\delta)$ can be expressed as For a continuous infrared source this is mathematically expressed as in Equation (12).

$$I(\delta) = \int_{-\infty}^{\infty} B(\nu)cos(2\pi\nu\delta)d\nu \qquad (12)$$

$$B(\nu) = \int_{-\infty}^{\infty} I(\delta)cos(2\pi\nu\delta)d\delta \qquad (13)$$

Where $B(\nu)$ is the infrared light intensity at wavenumber ν and is calculated by Fourier transform. In practical experiments the interferogram is measured by recording the detector signal as a function of the optical path difference (OPD) between the two beams. The signal has to be sampled at precise intervals corresponding to equal steps in path difference. For signal averaging, successive interferograms have to be measured at exactly the same points. This is achieved by using a helium-neon laser as a reference. Radiation at exactly 632.8 nm traverses the same optical path as the IR beam. A separate detector measures the interferogram produced, giving a sinusoidal signal with maxima separated by the laser frequency at 15,803 cm^{-1}. This signal is used to trigger the sampling of the IR signal very reproducibly.

The resulting interferogram is subjected to Fourier analysis using a computer algorithm called fast Fourier transform (FFT) which produces a frequency spectrum (right panel of Figure 9). The relationship between the interferogram and the spectrum is given by equations (12) and (13). This equation is the Fourier Transform pair of equation (11). Essentially, the FFT takes amplitude signals in the time domain (interferogram) and converts them to power in frequency domain (spectrum).

The FT-IR spectrometer generates the infrared spectrum of a given sample by calculating the ratio of the

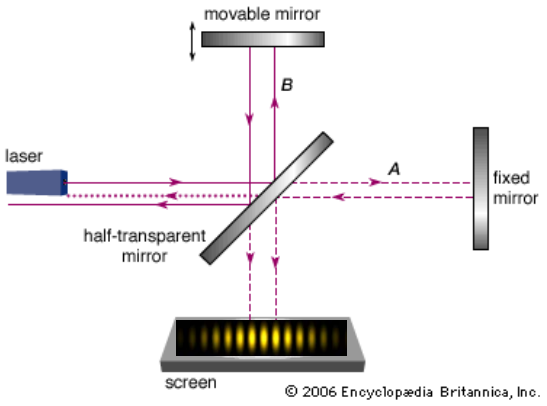

Figure 7. Michelson interferometer.

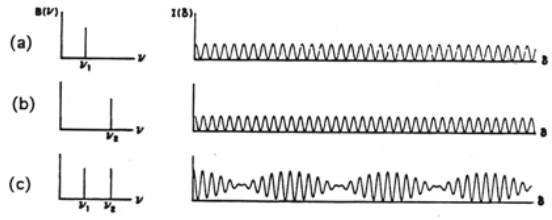

Figure 8. The interferogram of a single frequency source is a cosine function with a periodicity that varies with the frequency of the emitting source (a and b). The interferogram of a two-frequency source may be calculated by geometrically adding the cosine functions corresponding to each of the individual lines in the source (c).

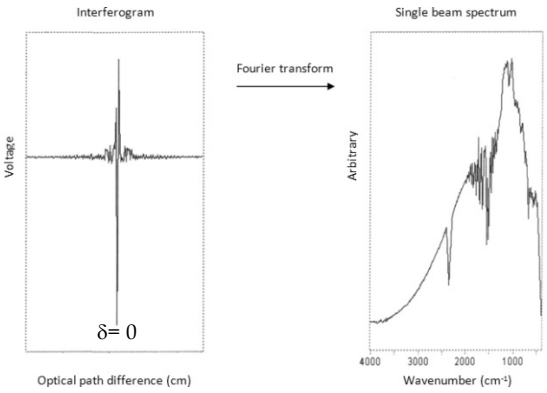

Figure 9. Interferogram (left) and its frequency spectrum (right).

signal obtained by scanning air (empty beam) to the signal obtained by scanning the sample. First an interferogram of the source (background) is scanned. This is a reference interferogram with no sample in the light path, its frequency spectrum is obtained after performing FFT. The right panel in Figure 9 shows a typical background in the FTIR spectroscopy observed by measuring the absorption of just air. Next, the sample is placed in the path and again we scan the mirror and acquire a second interferogram. In IR spectroscopy, the sample absorbs IR radiation, which attenuates the beam in the interferometer. The difference between the second (sample) interferogram and the reference interferogram is then computed in computer memory. Since the difference interferogram depends only on the absorption of radiation by the sample, the FFT is performed on the resulting data, which produces the IR spectrum of the sample.

The most important parameters of a FTIR instrument are listed below.

1) *Scanning time*. One scan taken with an FT-IR spectrometer is equivalent to a complete displacement of the moving mirror from the initial position to the final one. This change of position is referred to as the Optical Path Difference (OPD) or retardation because it sets the difference between the paths of the beams of light that come from the fixed mirror and from the moving mirror and recombine at the beamsplitter as explained above. The largest the distance traveled by the moving mirror, corresponds to the highest resolution that can be achieved. For this reason, the *scanning time* increases with resolution.
2) *Signal to noise ratio* (SNR). Indicates the quality of the baseline of the sample's infrared spectrum; mathematically, the SNR is a comparison of the size of the noise to the size of the signal. The SNR improves with the number of scans acquired because of the averaging nature of the data acquisition: after averaging each scan the signal increases in size while the noise diminishes. The dominant noise in

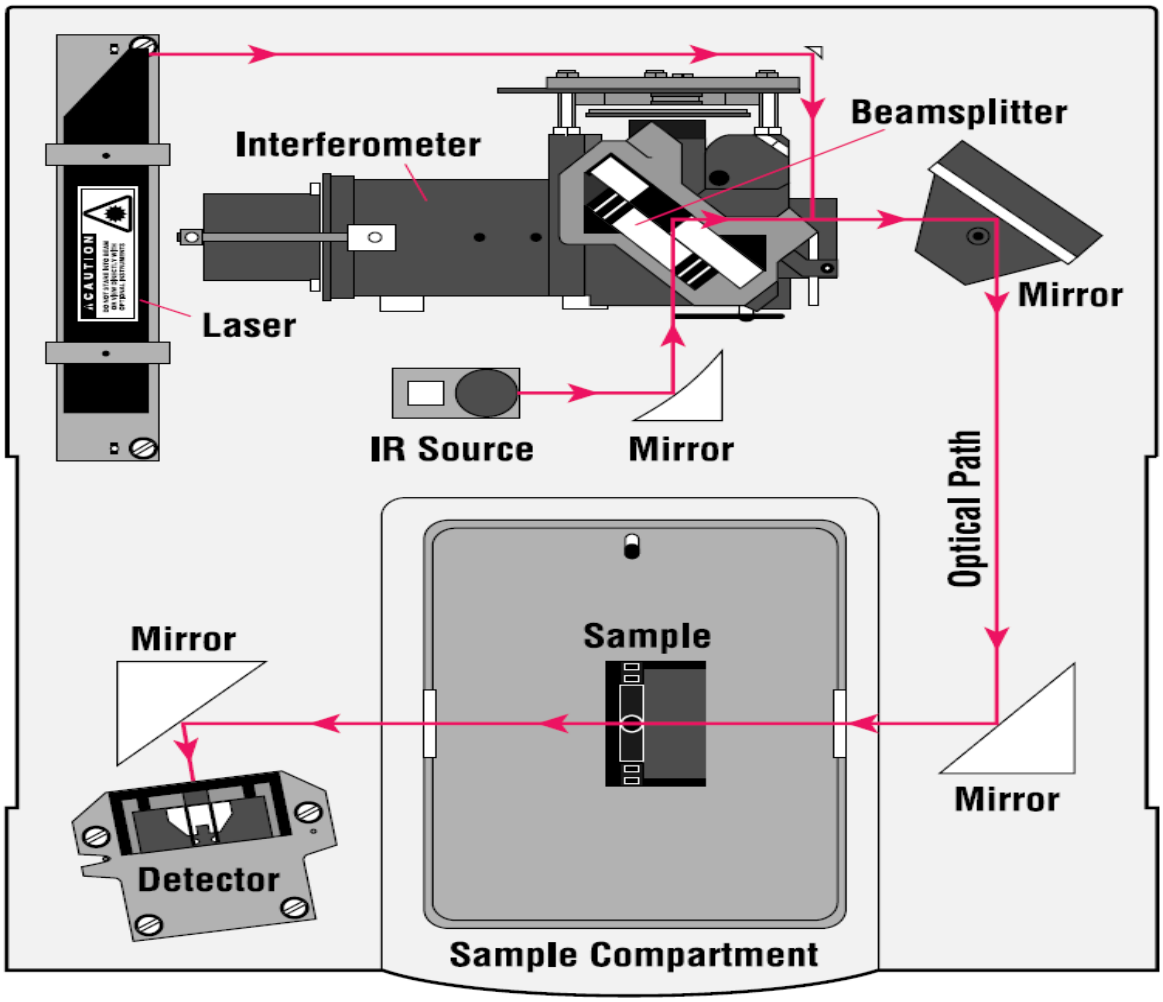

Figure 10. Thermo-Nicolet FTIR.

FT-IR is the detector-limited noise, which varies as the square root of the number of scans ($\sqrt{N}$ for N scans). Hence, combining these two factors, the SNR varies with the number of scans N as $\frac{N}{\sqrt{N}} = \sqrt{N}$. Acquiring a larger number of scans will improve the SNR. For transmission experiments of condensed phase samples, 4 scans will suffice to obtain a good SNR, because of the high energy involved in the measurement. For gases, at least 16 scans must be acquired to assure good SNR. When reflectance accessories such as Diffuse, Specular, or Total reflectance are used, a minimum of 64 scans must be collected due to the limitation on the energy that reaches the detector or optical throughput.

3) *Spectral Resolution*. Indicates the ability of the spectrometer to distinguish two closely spaced vibrational or rotational modes. The resolution of the interferometer increases with δ and therefore with the distance the movable mirror travels. To a good approximation, the best resolution is given by

$$\Delta\tilde{\nu} = \frac{1}{\Delta} cm^{-1}$$

Where: $\Delta = \delta_{max}$ is the maximum mirror travel distance. Since this mirror displacement cannot be infinite in an actual spectrometer, the resolution is somewhat less, as discussed below. For condensed samples acquired in transmission mode, a resolution of 8 cm^{-1} will resolve most vibrational modes, which full width at half height (FWHH) is about 10 cm^{-1}. This resolution also allows the acquisition of a large number of scans at a relatively short time improving the SNR. If the rotational fine structure is required for the calculation of molecular parameters for gas samples, the best resolution of the spectrometer must be utilized together with the acquisition of a large number of scans for good SNR. *Apodization* functions limit spectral resolution, as it will be explained below, so for gas samples a simple truncation function called boxcar must be used.

Apodization. The mathematical form of the Fourier pair, equations (12) and (13), sets the integration limits to retardation values from -∞ to +∞. However, such a movement is impossible. The moving mirror reciprocates through a finite distance from -Δ to +Δ, such that in practice this integration has to be cut off in a finite range. Setting these limits is equivalent to truncating the interferogram, or setting it equal to zero for all values greater than Δ and less than -Δ. This is known in mathematics as convoluting the complete interferogram (-∞< δ < +∞) with a function that has the value 1.0 for (-Δ<δ < +Δ) and zero for values of δ outside these limits. Because of its rectangular shape, this function is called boxcar and the process is called boxcar truncation (Figure 11). When the Fourier transform with boxcar truncation is performed, an infinitely narrow monochromatic line takes on width and acquires positive and negative side lobes, known as ringing - Ripples are formed around a large peak

The elimination of the ripples that result after truncating the interferogram with a boxcar function is known as apodization, and functions used for this purpose are called apodization functions. Triangular apodization is one of the simplest functions used (Figure 11 bottom). Triangular apodization further increases line width but reduces the magnitude of the side lobes and makes them all positive. Note that although the triangular function decreased the side lobes, the resultant line width is considerably increased, affecting the resolution. There are several apodization functions, which employ a degree of non-linearity or curvature in an effort to maintain resolution while reducing the ringing, these include Gaussian and Lorentzian functions, a raised cosine function (Hanning apodization), Happ-Genzel apodization and Norton-Beer functions.

Fourier-transform infrared (FTIR) spectrometers offer several basic advantages over classical dispersive instruments.

- Multiplex advantage (Fellgett advantage). All source wavelengths are measured simultaneously in an interferometer, whereas in a dispersive spectrometer they are measured successively. A complete spectrum can be collected very rapidly and many scans can be averaged in the time taken for a single scan of a dispersive spectrometer.
- Throughput advantage (Jacquinot advantage). For the same resolution, the energy throughput in an interferometer can be higher than in a dispersive spectrometer, where it is restricted by the slits. In combination with the Multiplex Advantage, this leads to one of the most important features of an FT-IR spectrometer: the ability to achieve the same signal-to-noise ratio as a dispersive instrument in a much shorter time.

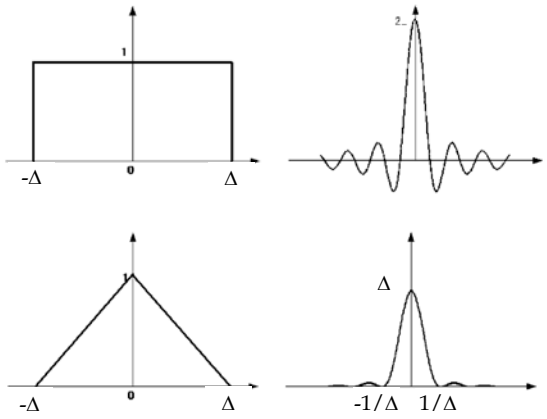

Figure 11. Box car waveform (top left) and its Fourier transform (top right). Triangular waveform (bottom left) and its Fourier transform (bottom right).

- Connes advantage. The wavenumber scale of an interferometer is derived from a HeNe (helium neon) laser that acts as an internal reference for each scan. The wavenumber of this laser is known very accurately and is very stable. As a result, the wavenumber calibration of interferometers is much more accurate and has much better long term stability than the calibration of dispersive instruments.
- Negligible stray light Because of the way in which the interferometer modulates each source wavelength. There is no direct equivalent of the stray light found in dispersive spectrometers.
- Constant resolution. Resolution is constant at all wavenumbers in the defined spectral range but the signal-to-noise ratio varies across the spectrum. FT-IR instruments have a much higher optical throughput than dispersive instruments and do not use slits to define the resolution. Instead, the resolution is defined by the Jacquinot stop aperture size, which does not change during data collection. In dispersive instruments, throughput is typically optimized by adjusting the slit width during the scan. Thus, signal-to-noise is constant but resolution varies.
- No discontinuities. Because there are no gratings or optical filters, there are no discontinuities in the spectrum.

D. Detectors for IR

FT-IR spectrometers use two basic types of detectors. The thermal detectors which measure the heating effects of radiation and respond equally well to all wavelengths and selective detectors whose response is wavelength dependent.

The thermal detectors include thermocouples, bolometers, and pyroelectric detectors. A thermocouple has a junction of two dissimilar metals. When incident radiation is absorbed on the junction, the temperature rise causes an increase in the electromotive potential developed across the junction leads. A bolometer is a detecting device which depends on a change of resistance with temperature. Pyroelectric detectors are a special kind of thermal detector consisting of single, thin, pyroelectric crystals such as deuterated triglycine sulfate (DTGS) or LITA (lithium tantalate). If such a material is electrically polarized in an electric field, it retains electrical polarization after the field is removed. The residual polarization is sensitive to changes in temperature. The pyroelectric detector operates at room temperature. Being a thermal device, it possess essentially a flat wavelength response ranging from the near infra-red through the far infrared. It can handle signal frequencies up to several thousand Herts and hence is well suited for Fourier transform infrared spectrometers.

The most important type of selective detectors is the photoconductive cell which has a very rapid response and a high sensitivity. An example is the mercury cadmium telluride detector (MCT) which is cooled with liquid nitrogen. These cells show an increase in electrical conductivity when illuminated by infrared light. These detectors utilize photon energy to promote bound electrons in the detector material to free states, which results in increased electrical conduction. There is a long wavelength limit to the response however, because photons with wavelengths longer than a certain limit will have insufficient energy to excite electrons.

E. Attenuated Total Reflectance (ATR)

Traditionally IR spectrometers have been used to analyze solids, liquids and gases by means of transmitting the infrared radiation directly through the sample. Where the sample is in a liquid or solid form the intensity of the spectral features is determined by the thickness of the sample and cannot be more than a few tens of microns. The technique of Attenuated Total Reflectance (ATR) has in recent years revolutionized solid and liquid sample analyses because it combats the most challenging aspects of infrared analyses, namely sample preparation and spectral reproducibility typically this sample thickness.

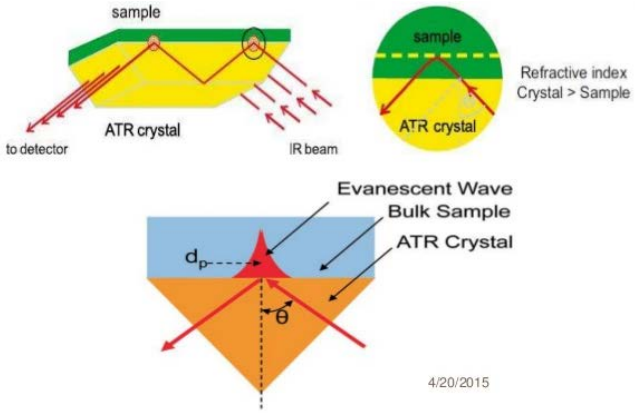

Figure 12. A multiple reflection ATR system.

An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample (Figure 12). With ATR sampling the IR beam is directed into a crystal of relatively higher refractive index. The IR beam reflects from the internal surface of the crystal and creates an evanescent wave, which projects orthogonally into the sample in contact with the ATR crystal. This evanescent wave

protrudes a few microns (0.5 µ - 5 µ) beyond the crystal surface and into the sample. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum. For the technique to be successful, the following two requirements must be met:

- The sample must be in direct contact with the ATR crystal, because the evanescent wave or bubble only extends beyond the crystal 0.5 µ — 5 µ.
- The refractive index of the crystal must be significantly greater than that of the sample or else internal reflectance will not occur – the light will be transmitted rather than internally reflected in the crystal. Typically, ATR crystals have refractive index values between 2.38 and 4.01 at 2000 cm^{-1}. It is safe to assume that the majority of solids and liquids have much lower refractive indices.

1. ATR accessories

In horizontal ATR (HATR) units, the crystal is a parallel-sided plate, typically about 5 cm by 1 cm, with the upper surface exposed. The number of reflections at each surface of the crystal is usually between five and ten, depending on the length and thickness of the crystal and the angle of incidence.

When measuring solids by ATR, it is essential to ensure good optical contact between the sample and the crystal. The accessories have devices that clamp the sample to the crystal surface and apply pressure. This works well with deformable materials and fine powders but many solids give very weak spectra because the contact is confined to very small areas. The effects of poor contact are greatest at shorter wavelengths where the depth of penetration is lowest.

The issue of contact between a solid sample and crystal has been overcome to a great extent by the introduction of ATR accessories with very small crystals, typically about 2 mm across. The most frequently used small crystal ATR material is diamond because it has the best durability and chemical inertness. These small area ATR crystal top-plates generally provide only a single reflection, but this is sufficient, given the very low noise levels of modern FT-IR spectrometers. Much higher pressure with limited force can now be generated onto these small areas. As a result, spectra can be obtained from a wide variety of solid materials including minerals.

2. Crystal materials used with ATR

There are a number of crystal materials available for ATR. Zinc Selenide (ZnSe) and Germanium are by far the most common used for HATR sampling. Zinc Selenide is a relatively low-cost ATR crystal material and is ideal for analyzing liquids and non-abrasive pastes and gels, but it is not particularly robust with a working pH range of 5–9. ZnSe scratches quite easily and so care must be taken when cleaning the crystal. It is recommended that lint free tissue is used.

Germanium has a much better working pH range and can be used to analyze weak acids and alkalis. Germanium has by far the highest refractive index of all the ATR materials available which means that the effective depth of penetration is approximately 1 micron. For most samples this will result in a weak spectrum being produced, however, this is an advantage when analyzing highly absorbing materials; carbon black filled rubbers are typically analyzed using Germanium ATR accessories.

Diamond is by far the best ATR crystal material because of its robustness and durability. The original purchase cost is obviously higher than that of other crystal materials available, but over the instrument's lifetime replacement costs should be minimal. The same cannot be said of Zinc Selenide or Germanium, both of which can scratch and break with improper use.

IV. Experiment

A. Materials and Chemicals

FTIR spectrometer with ATR accessory (NICOLET IS10)

Benzaldehyde	Cyclohexanone
Cinnamaldehyde	Acetophenone
n-butyraldehyde	*Benzoic acid
	*Salicylic acid
Benzophenone	(*unknown samples labeled "A" and "B")

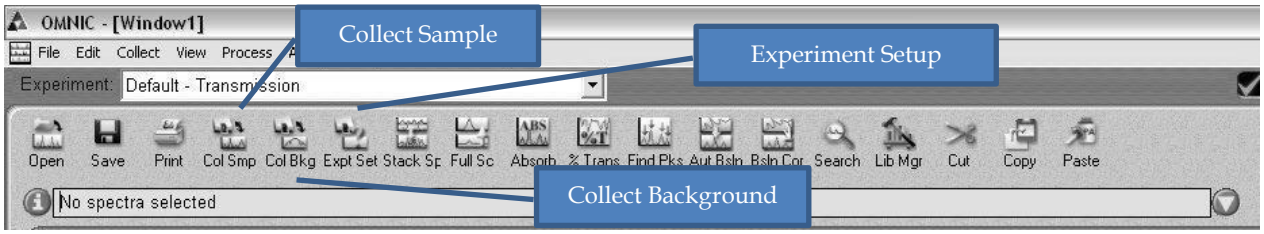

Figure 13. OMNIC Menu Bar.

B. Collecting Spectra with ATR accessory

1. Setting up an Experiment

1. Open OMNIC on the computer by double-clicking the OMNIC desktop icon.
2. Click the menu bar icon "Expt Set" (Figure 13) to enter the Experiment Setup window.
3. Under the **Bench tab** (Figure 14), set the accessory to *ATR* and click OK.
4. Under the **Collect tab** (Figure 15), set the number of scans to 64 or whatever you want and the final format to absorbance or transmittance.
5. Set the resolution for the measurements to 4. Resolutions of 0.5–2 are high resolution, 4–12 are medium resolution and 16–32 are low resolution. When you select a resolution, it will give you the data spacing and time for collection.
6. Enter a title for the experiment. Your window should be similar that shown in (Figure 15).
7. Set up the *Background handling*. There are four choices. Choose either *collect a background before each sample* or *Collect background after 100 minutes*. I recommend running a background before every sample. The number of scans for the background generally used is 16. If you choose to *collect a background before each sample* the software will prompt you to prepare a background every time you click "Col Sample", the software will measure the background and then prompt you to prepare your sample.
8. If you selected *Collect background after 100 minutes*, follow the steps in section *Acquire a Background Scan* below to collect the background before acquiring spectra of your samples. If you selected *collect a background before each sample* go to section *Collecting a Sample Spectrum* to acquire a background and sample spectra.

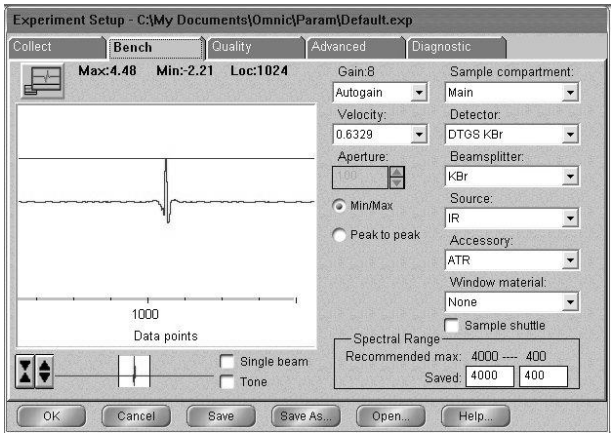

Figure 14. The Bench tab of the Experiment Setup.

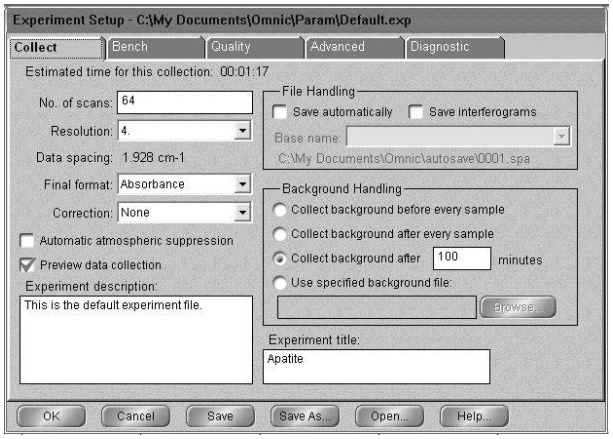

Figure 15. The Collect tab of the Experiment Setup window.

2. Acquire a Background Scan

1. Before a sample can be acquired, a background scan must be obtained. Water vapor and carbon dioxide in the air will produce interfering bands which must be subtracted from the spectrum.
2. Collect an infrared background from the **clean ATR crystal**. The crystals are usually cleaned by using a solvent soaked piece of tissue. Typically, acetone, methanol or isopropanol are used to clean ATR crystals. The ATR crystal must be checked for contamination before sample presentation, this is true for all liquids and solids. The solvent should not be applied in

a way that the setup is soaked since it will leak into the optics as well.

3. Make sure nothing is touching the diamond; click the menu bar icon "Col Bkg" (Figure 13) to collect the background and click OK to indicate start to collect the background. You should see a window similar to that shown in Figure 16.
4. When the background looks stable – no major changes in peaks – click *Start Collection* in the top right corner of the window (Figure 16).
5. Click *No* when prompted about adding the background to Window 1, unless you are troubleshooting the peaks of a spectrum already on hand.

3. Collecting a Sample Spectrum

1. If you choose to collect a background before each sample when you click "Col Sample" (Figure 13) the software will prompt you to prepare background and then prompt you to prepare your sample. If you choose to collect background after 100 minutes the software will prompt you to prepare your sample.
2. Background and sample spectra must be collected from **clean ATR crystal**. The crystals are usually cleaned by using a solvent soaked piece of tissue. Typically, acetone, methanol or isopropanol are used to clean ATR crystals. The ATR crystal must be checked for contamination before sample presentation, this is true for all liquids and solids.
3. Make sure nothing is touching the diamond and click *OK* to collect background.
4. Click *No* when prompted about adding the background to Window 1, unless you are troubleshooting the peaks of a spectrum already on hand.
5. After the background spectrum is collected the software will prompt you to prepare your sample in a popup screen; do not hit *OK* until you have placed your sample on the crystal.
6. Place the solid material onto the crystal area. The ideal results from powder samples are achieved by placing just enough sample to cover the crystal area. The sample height should not be more than a few millimeters. The beam reaches only two microns above the top of the crystal, so a thick layer of sample or sample on the metal base should be avoided. Hard inorganic solid material must be ground to a very fine powder in a mortar and pestle before applying it to the crystal.
7. Do not allow a metal spatula to touch the diamond surface.
8. If your sample is liquid; put a drop on the crystal.
9. For liquid samples do **not** use pressure applicator. For solid samples; lower the sample clamp into place and tighten it gently. This is especially important for solid, powder or gel samples. The clamp is engineered to exert force onto your sample to place it into close contact with the crystal. Increase the pressure applied to the sample by turning the pressure control clockwise.
10. Click OK when prompted and click Start Collection.
11. Click Yes when prompted Add to Window 1.
12. Save the spectrum by clicking the Save icon. If multiple spectra are open in a window, you will need to click on the desired spectrum before clicking Save.

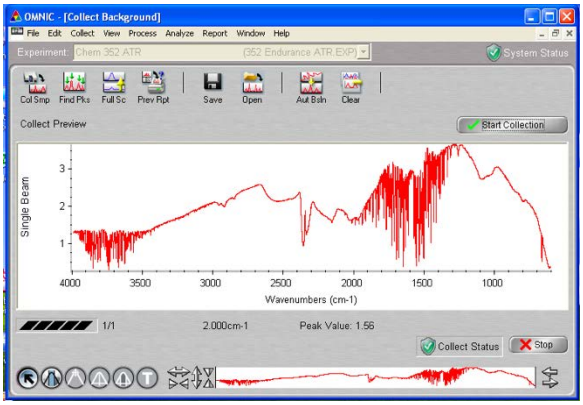

Figure 16. Background Collection.

4. Processing the spectra

From your spectrum, which is automatically background subtracted, you can:

Zoom in and out of particular regions by selecting the upper and lower bounds on the spectrum shown at the bottom of the screen (simply click onto blue border and move to desired location with the mouse).

Define frequencies by clicking **"find peak"** icon on the top tool bar. To get out of this window, simply close window and answer **"No"** to question that pop out.

Print spectrum by clicking the printer icon on the toolbar.

5. Cleaning up

1. Close OMNIC
2. Turn the thumbscrew counterclockwise to lift the pressure applicator to its maximum height.
3. Clean the pressure foot. Use a small piece of lens tissue or a Q-tip wetted with acetone, methanol or isopropanol or a suitable solvent
4. Clean the crystal. Do not rub the crystal, as that will scratch it. Dab at the crystal with a solvent (acetone or methanol) soaked lint-free cloth.
5. Do not forget to clean up mortar and pestle if you used them.

C. Part A. Spectra of Aldehydes and Ketones

The C=O stretching band is relatively constant and owing to its high intensity, easily recognizable in IR spectra. Aldehydes and ketones exhibit a strong C=O band in the region from 1870 to 1540 cm^{-1}. The actual position of the C=O band is affected by several factors: the physical state, neighboring substituents, conjugation, hydrogen bonding, and ring strain.

Aliphatic aldehydes absorb in the region from 1740 to 1720 cm^{-1}. Electronegative substitution on the α-carbon increases the frequency of absorption of the C=O bond. For example, acetaldehyde absorbs at 1730 cm^{-1}, whereas trichloroacetaldehyde absorbs at 1768 cm^{-1}. Conjugation of a double bond with the carbonyl group reduces the frequency of the carbonyl absorption. Aromatic aldehydes absorb at lower frequencies. Internal hydrogen bonding also shifts the absorption to lower frequencies.

In this experiment comparison of the carbonyl frequencies for selected aldehydes and ketones will be made to illustrate these effects.

1. Procedure

Determine the FTIR spectra of benzaldehyde, cinnamaldehyde, *n*-butyraldehyde, benzophenone, cyclohexanone, and acetophenone with ATR accessory. Refer to section Collecting Spectra with ATR accessory for instruction on how to obtain the spectra.

2. Analysis of the Spectra and Discussion

Determine the carbonyl absorption frequency for each compound and write the structure of each compound on each spectrum.

On the spectrum of benzaldehyde, make assignments to the main bands found in the region around 3000 cm^{-1} and between 675 and 750 cm^{-1}. Indicate the bonds or groups of bonds in the molecule responsible for these bands.

On the spectrum of cyclohexanone, make similar assignments in the region around 2900 cm^{-1} and 1460 cm^{-1}.

Compare the carbonyl frequencies of the aldehydes. Comment on the effect of conjugation and aromaticity on the frequency of absorption of the carbonyl group for cinnamaldehyde and benzaldehyde as compared with *n*-butyraldehyde.

Make a similar comparison of the carbonyl frequencies of the ketones with regard to conjugation and aromaticity.

D. Part B. Salicylic and Benzoic Acids

1. Procedure

Determine the FTIR spectra of the samples labeled "A" and "B" with ATR accessory. Refer to section Collecting Spectra with ATR accessory for instruction on how to obtain the spectra. You will have to determine based on the spectra which sample is benzoic acid and which is salicylic acid.

2. Spectra Analysis and Discussion

Determine what functional groups are most likely present by examining the group frequency region (3600–1200 cm^{-1}) and using the correlation chart. Identification of a substance can also be achieved by comparing the spectrum to a library of IR spectra.

Tabulate identified functional groups, type of vibrations and their vibrational frequencies.

List and discuss the differences in the IR spectra and structures of the two aromatic compounds.

E. Discussion

Explain how a shift in the carbonyl frequency also can occur by replacement of an alkyl group with a chlorine atom.

At what frequency would you expect the overtone for the C=O stretch of acetophenone.

Using a simple harmonic oscillator approximation calculate expected frequency shift upon substitution of O^{18} for O^{16}. Compare the magnitude of the isotopic shift with the shift caused by conjugation and aromaticity.

What is the significance of fingerprint region in the IR spectra?

Refer to text, **Principles of Instrumental Analysis** by Douglas A. Skoog, 5th ed. Saunders, Philadelphia (1998), Chapters 16 & 17, for more details on the theory and applications of IR spectroscopy.

Table 2. Typical Infrared Absorption Frequencies.

Functional Class	Stretching		Bending	
	Range (cm^{-1})	Assignment	Range (cm^{-1})	Assignment
Alkanes	2850-3000	CH3, CH2 & CH (2 or 3 bands)	1350-1470 1370-1390 720-725	CH_2 & CH_3 deformation CH3 deformation CH2 rocking
Alkenes	3020-3100 1630-1680 1900-2000	=C-H & $=CH_2$ C=C C=C asymmetric stretch	880-995 780-850 675-730	=C-H & $=CH_2$ out-of-plane bending cis-RCH=CHR
Alkynes	3300 2100-2250	C-H C≡C	600-700	C-H deformation
Arenes	3030 1600 & 1500	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 3200-3550 970-1250	O-H (free) O-H (H-bonded) C-O	1330-1430 650-770	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 3300-3400 1000-1250	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	NH_2 scissoring (1°-amines) NH_2 & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	2690-2840 1720-1740 1710-1720 1690 1675 1745 1780	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone) aryl ketone α, β-unsaturation cyclopentanone cyclobutanone	1350-1360 1400-1450 1100	α-CH_3 bending α-CH_2 bending C-C-C bending
Carboxylic Acids & Derivatives	2500-3300 (acids) 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1040-1100 1735-1750 (esters) 1000-1300 1630-1695(amides)	O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks) C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide)	1395-1440 1590-1650 1500-1560	C-O-H bending N-H (1°-amide) II band N-H (2°-amide) II band

Table 3. IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O).

Functional Group	Type of Vibration	Characteristic Absorptions (cm-1)	Intensity
Carbonyl			
C=O	stretch	1670-1820 (conjugation moves absorptions to lower wave numbers)	strong
Acid			
C=O	stretch	1700-1725	strong
O-H	stretch	2500-3300	strong, very broad
C-O	stretch	1210-1320	strong
Aldehyde			
C=O	stretch	1740-1720	strong
=C-H	stretch	2820-2850 & 2720-2750	medium, two peaks
Amide			
C=O	stretch	1640-1690	strong (unsubstituted have two bands)
N-H	stretch	3100-3500	
N-H	bending	1550-1640	
Anhydride			
C=O	stretch	1800-1830 & 1740-1775	two bands
Ester			
C=O	stretch	1735-1750	strong (two bands or more)
C-O	stretch	1000-1300	
Ketone			
acyclic	stretch	1705-1725	
cyclic	stretch	3-membered - 1850 4-membered – 1780 5-membered - 1745 6-membered - 1715 7-membered - 1705	strong
α,β-unsaturated	stretch	1665-1685	
aryl ketone	stretch	1680-1700	