Chapter-II

Experimental

Instruments used for the production and detection of molecular species have been divided into two parts:

(i) Production Technique: Electrodeless Discharge Lamp (EDL)

(ii) Detection Technique: Fourier Transform Spectrometer (FTS)

Electrodeless Discharge Lamp (EDL)

The electrodeless discharge lamp (EDL) is a sealed tube, to be used when the sample is available in small quantity because of its cost etc. like isotopes or if the sample itself is costly or hygroscopic. Among the line like radiation source, it exhibits the highest radiation intensity and the narrowest emission line widths. The biggest advantage of the EDL is the high intensity of the radiation which can be several orders of magnitudes higher than hollow cathode lamp, especially, for easily vapourizable elements. The signal to noise ratio is generally improved which gives higher precision.

To make an EDL we need a vacuum system of the order of $10^{-4}$ to $10^{-5}$ mm Hg. A quartz tube of about 6 mm diameter and 5-6 cm length was attached to quartz end of a graded seal (of which one side was quartz and other side glass). Before attaching the quartz tube a contraction was made so that afterwards by glass blowing the EDL could be sealed and detached from the vacuum line. The glass end of the graded sealed was attached to a U–shape trap, which was then connected to a vacuum line by means of a Cone and Socket arrangement. 4-5 mg sample was kept in a small capillary tube. The sample side of this sample tube (~3mm dia x 3cm length) was opened whereas on the other side a small iron rod was encased and the end was closed. The embedded iron rods helped in putting the sample inside the EDL in the end when the complete degassing was achieved. The U-shape trap was made of glass and very carefully after putting the sample in the sample capillary tube, sample facing the EDL side, the sample tube was slide in
the graded seal tube and then the trap was attached by glass blowing. Now the trap to which the EDL and sample tube was attached and placed in a Dewar flask then only the pumping started. Before hand provisions was made so that through the vacuum system a desired quantity of buffer gas could be let in at the EDL side after baking and complete degassing. Then by means of a magnet the sample was lowered in the EDL by tilting the EDL end. To get a good EDL, the quantity of sample and buffer gas was varied and a number of EDLs were sealed by glass blowing. For making $^{78}$Se$_2$ EDL we had experimented with natural ‘Se’ metal to work out the exact quantity of $^{78}$Se isotope metal required. Also the quantity of buffer gas Ne was varied from 2-5 mm of Hg.

The sealed EDL containing the optimum quantity of isotopic $^{78}$Se and the buffer gas was excited by means of microwave power (150 W, 2450 MHz). The EDL was placed in vertical position by means of clamps and the microwave cavity was placed below it. With this arrangement very intense spectra of $^{78}$Se$_2$ were excited and recorded on DA8 BOMEM F.T. Spectrometer.

**Fourier Transform Spectroscopy**

The conventional spectrometer is of dispersive type which uses prism or grating monochromator. The dispersive instrument is of characteristics of slow scanning. Here, the energy of radiation is varied over the desired range and response is plotted as a function of radiation energy (or frequency). Fourier Transform Spectrometry (FTS), a non-dispersive Doppler limited technique based on interferometry has some inherent characteristic features such as wide spectral range (UV-to-FAR IR), very high resolution capability, extensive data averaging, ability of fast data acquisition etc., which make it as one of the most versatile spectroscopic techniques for Molecular Spectroscopy, Atomic Spectroscopy, Analytical tools etc. The incorporation of an interferometric spectrometer in time-resolved studies allows rotationally resolved multiple vibrational frequencies to be monitored simultaneously across a wide spectral window. The availability of synchrotron radiation source which has characteristic properties such as low
divergence, high brilliance, almost constant intensity versus wavelength widens the application of FTS to infrared microscopy for studying biological molecules, high pressure studies of material etc.

In spectroscopic experiments, the emission source is all containing transient molecules that emit electromagnetic radiation. The transient species are excited by various means such as microwave discharge; hallow cathode discharge, DC or AC electric discharge etc. The emission of radiation occurs when chemical species makes transition from excited states to lower states. To overcome the limitations of dispersive instruments, Fourier transform infrared (FT-IR) spectrometers were developed in the 1960s, but it was confined to few laboratories in the world. This was due to the unavailability of an efficient algorithm for FT computation, cost of the instrument components and the large computers required to run them. With the development of FFT algorithm in 1965 and gradual technology advancements in computers and instruments have reduced the cost and enhanced the capabilities of an FT-based instrument (FT-IR, FT-RAMAN, FT-NMR, FT-MS).

There are several commercial FT spectrometers being used in the high resolution spectroscopy of diatomic molecules. The design of most instruments is based on the two beam interferometer originally designed by Michelson in 1891. A typical FTS system consist of two distinct parts [1-5]:

1. Optical transducer along with input/output optics
2. Fourier transform computer

The optical transducer consist of basic Michelson interferometer input and output serve the purpose of introducing parallel radiation into interferometer, to couple the output radiation into sample under study and subsequently into a detector.

The radiation from source passes through Michelson interferometer optics which generates an optical path difference for input signal and produces interferogram as measured with detector. The light from the source strikes the beam splitter and produces two beams of nearly same intensity. Depending on
working frequency range different type of beam splitter are used. The working range of different kind of beam splitter is summarized below:

**Beam splitters and its ranges**

<table>
<thead>
<tr>
<th>Beam Splitter</th>
<th>Range (in cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mylar film</td>
<td>0-1000</td>
</tr>
<tr>
<td>KBr</td>
<td>350-6000</td>
</tr>
<tr>
<td>KCl</td>
<td>750-6000</td>
</tr>
<tr>
<td>CaF(_2)</td>
<td>1000-7000</td>
</tr>
<tr>
<td>Quartz</td>
<td>4000-30,000</td>
</tr>
</tbody>
</table>

One of the beams strikes a fixed mirror and returns while the second strikes a moving mirror. A laser parallel to source radiation also goes through the interferometer. These two reflected beam recombine at beam splitter. If the
If the beam from moving mirror traveled a different distance then the beam from fixed mirror, then recombination will result in some destructive interference. The movement of mirror thus generates an interference pattern during motion. Thus Michelson interferometer in Fourier transform spectrometer converts the source emission (intensity versus frequency) into interferogram (intensity versus optical path difference). Thus the spectral information in source is preserved in interferogram. The interferogram is found to be different for different type of sources. The beam finally arrives at detector and is measured by detector. The different kind of detector and their working range [1] is given below:

**Working temperature and range of detectors**

<table>
<thead>
<tr>
<th>Working temperature</th>
<th>Detector</th>
<th>Working wavenumber range (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid helium (4K)</td>
<td>Si Bolometer</td>
<td>0-400</td>
</tr>
<tr>
<td>Liquid helium (4K)</td>
<td>Si:B detector</td>
<td>350-2,000</td>
</tr>
<tr>
<td>Liquid nitrogen (77K)</td>
<td>MCT</td>
<td>800-2,400</td>
</tr>
<tr>
<td>Liquid nitrogen (77K)</td>
<td>InSb</td>
<td>1,850-6,000</td>
</tr>
<tr>
<td>Room temperature</td>
<td>Si Photo diode</td>
<td>9,000-45,000</td>
</tr>
<tr>
<td>Room temperature</td>
<td>PMT</td>
<td>13,000-25,000</td>
</tr>
</tbody>
</table>

The decoding of frequency into spectrum (length→frequency domain conversion) is done by Fourier transform algorithm. Fourier transform spectrometer allows information in one domain to be converted to that in inverse domain. In case of Michelson interferometer, the interferometer is measured in the length domain i.e. function of retardation. The inverse of length is wave number and so wave number and length are complementary Fourier variables. In other words, if the light intensity at detector is measured as function of retardation, Fourier transformation can convert this into intensity versus wave number, i.e. into
a spectrum. A reference beam or background beam is always collected without sample as it is induced by instrument and environment. To eliminate the instrumental and atmospheric contribution to the spectrum, beam spectrum must be normalized against background spectrum.

**Apodization**

Apodization, sometimes also called tapering, is a mathematical technique used to reduce the Gibbs phenomenon “ringing” which is produced in a spectrum obtained from a truncated interferogram. Since interferograms can only be measured out to some finite distance, all laboratory interferograms are truncated. The observed spectrum is related to the true spectrum by a convolution with the “instrument function” (or “apparatus function”) obtained by Fourier transforming the apodization function. The instrument function corresponding to the simplest apodization - the rectangle function produced by a finite-length interferogram - is a sine function. Because of the large sidelobes of this function, it is sometimes desirable to multiply the original interferogram by some other function which goes smoothly to zero at the end of the interferogram (e.g., Schnopper and Thompson 1974). Thus the process of apodization is removal of sidelobes of the lines in a spectrum by multiplying the interferogram with a suitable function prior to Fourier transform. The Fourier transform integral which is given by 

$$I(\delta) = \int_{-\infty}^{\infty} B(v) e^{2\pi i \delta v} dv$$

has infinite limits for optical path difference and experimental limits are finite so the interferogram has to be truncated, so some error arises in the resulting spectrum. The function 

$$B(v) = \int_{0}^{\delta} I(\delta) e^{-2\pi i \delta v} d\delta$$

can be considered as best approximation to the spectrum. $\delta_o$ is the maximum path difference in a particular instrument. The sharp cut off at $\delta_o$ introduces spurious side lobes into spectrum. The effects are most pronounced as spurious side lobes near the sharp absorption or transmission peaks. These side lobes can suppress by multiplying the ideal
interferogram with an apodization function which results in convolution of the true spectrum with sine function. Thus the spectrum is technically free from side lobes but the peaks get broadened which decreases the resolution. Any function that has value of unity at zero path difference and decreases with increasing retardation will serve as apodization function. The integral can be modified by using an apodising function $A(\delta)$ as follows:

$$B(v) = 2\int_0^\delta A(\delta)I(\delta)e^{-2\pi iv\delta}d\delta$$  \hspace{1cm} (2.1)

**Phasing**

Fourier transform of an arbitrary function is a complex function which has both a real and imaginary part. The symmetric component of interferometer contributes to the real cosine part and an antisymmetric component of interferogram brings about the imaginary sine part. In Fourier transform spectroscopy, an ideal interferometer produces interferogram about zero path difference, and only the cosine part is present in transformed results. A lack of symmetry is indicative of subtle difference in optical characteristics of various components of the instrument changes in condition during data acquisition. The imperfection of real world interferometer always brings about a nonzero imaginary parts in the transformed results which mean that the real component is distorted (phase correction). Therefore prior to actual experiment, the phase response of the instrument is determined by recording a low resolution phase spectrum. This phase spectrum is used to correct the interferogram during the experiment. A cosine Fourier transform is then performed.

**Advantages**

(I) **Throughput Advantage (Jacquinot advantage)**

The circular aperture of FTS and beam splitter act as slit and beam splitter as dispersive element respectively. Therefore there is less loss of energy so signal intensity is high and hence increases signal to noise ratio.
(II) Multiplex advantage

Signal of all frequencies enter the FTS and arrive at detector at same time with same S/N ratio therefore measurement is faster. This saved time can be used to do more scan to reduce noise. As number of scan increases by $n$, the S/N ratio increases by root of $n$. FTS doesn’t separate light into individual frequency before measurement. This means each point in interference contains information from each wavelength in the input light. In other word if 1000 data points along the interferogram are collected, each wavelength in input light is sampled 1000 times. Thus, increases the brightness of signal.

(III) Conne’s advantage

Conne’s advantage makes use of He-Ne laser to measure frequency precisely. As a result repetitive scans can be made with high precision so that data from number of scan can be co-added without any error. In grating instrument, this is not possible because of error from backlash, intensity fluctuation etc.

(IV) Stray light advantage

In measurement of strong band any amount stray light can have adverse affect on photometric accuracy of measurement. Here interferometer modulates each wavelength at different frequency, so there is no equivalent to stray light.

(V) Precision advantage

The accuracy of wave number measurement is determined, in principle by accuracy with which the moving mirror position is known at all points in its motion. In FTS, the relative position of mirror $M_2$ relative to $M_1$ is also measured interferometrically. This is achieved by sending a reference laser beam along the same path as signal beam. The moving mirror generates interference fringes from laser beam beyond the beam splitter and if the wave number of laser is accurately known, then the relative position of mirror is easily deduced by fringe counting. Its accuracy is better than 0.0001 cm$^{-1}$.
(VI) Computation and software advantage

The high resolution spectrum is obtained through powerful signal processing technique such as apodization, phase correction, zero filling etc.

(VII) Mechanical simplicity

The moving mirror in interferometer is only continuously moving part in instrument. Thus, there is very little possibility of mechanical breakdown.

Applications of FTS

The measurement made by FTS is extremely accurate and reproducible. The FTS created renewed interest in the field of UV-VIS-IR spectroscopy. It is one of the most widely used analytical tools available today. Thus it is a reliable technique for identification of even smallest of contamination. This makes FTS an invaluable tool for quality control or quality assurance application. In addition, the sensitivity and accuracy of FTS detector along with a wide variety of software algorithm have dramatically increased the practical use in qualitative analysis. Qualitative methods can be incorporated into simple procedures for routine analysis. FTS is used to study the events that occur at the blood biomaterial interface. In another system for antibiotic biosynthesis, an FT spectrometer is used in quantify the level of product in fermentation mixture. FTS is now extensively used in areas such as toxicology, mutagenesis and general cellular research. The simultaneous data collection helps one to investigate the spectrum of transient species such as unstable molecules or intermediaries in a chemical reaction and for the analysis of environmental samples etc. The rapid scanning property of FT Spectrometer has its greatest impact in the field of gas chromatography-FTS.

High sensitivity helps one to investigate species observed on metal oxide and supported metal catalysts, pharmaceuticals, protein etc. Its potential for the detection of photoacoustic signal and for biochemical research is enormous. The possibility for high resolution in infrared permits a more detailed knowledge of molecular vibrations and energetic. High resolution FTS spectra has enable one to
measure the presence of components in the atmosphere to the limit of few parts per billion.

The incorporation of a computer in the instrument allows rapid spectral searches as high as 10,000 in about 6 to 7 seconds at the end of a run. The subtraction of the spectrum of a reference sample from the spectrum of a mixture, determination of the number of component in a mixture, curve fitting routines etc are some of the other popular operations possible with a FT Spectrometer.

References


