Chapter-II

Experimental

Instruments and Materials

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

(i) Production Techniques
   (a) Thermal Excitation Technique
   (b) Microwave Technique

(ii) Detection Techniques
   (a) Plane Grating Spectrograph (PGS-2)
   (b) Fourier Transform Spectrometer (FTS)

Vacuum Graphite Furnace

This furnace is essentially a high temperature vacuum graphite tube furnace, capable of providing temperature of the order of 3000°C in vacuum or in any desired atmosphere. It was used for the first time in this laboratory to carry out experiments on Saha’s theory of thermal ionization by Saha, Sur and Majumdar [1] in the year 1927. After a series of modification, this furnace is now being consistently used by various workers [2-4] for high temperature work in molecular spectroscopy. A sectional view of graphite furnace has been depicted in Fig. 2.1(a).

The body of the furnace is divided in three sections:

(a) The base – bottom plate, B
(b) The main body with four side walls, W
(c) The lid, L

Each of these parts is provided with outlets and inlets for circulating cooling water in the space between the walls. The direction of the inflowing water through various sections is represented by arrows towards and that of the out flowing by arrows from the body of the chamber. The tube, fixed at the base provides an outlet for creating the vacuum as well as for introducing the desired
inert gas. This is necessary at high temperature since the graphite tube would otherwise burn out rapidly.

The entire body of the furnace is double walled and a water circulation system is maintained throughout the intervening space. E and E’ are two hollow electrodes made by copper and fitted with inlet and outlet pipes for circulating cold water. P and P’ represent two horizontal rectangular plates drilled with two parallel rows of holes at regular distances. Two quartz windows Q are provided in order to allow the radiation from the experimental vapor to reach the slit of the spectrograph. There are also two windows (not shown in the Fig.) one on the front and the other on the back side through which visual observation is made of the glowing wall of the graphite tube and its temperature is measured with the help of an optical pyrometer of vanishing type.

(b) The Graphite Tube: The heating unit of the furnace is a cylindrical graphite tube through which a high current is passed. For high temperature work graphite has a unique property. Its specific resistance is high $9.0 \times 10^{-4}$ ohm cm at room temperature, rising to about $11.0 \times 10^{-4}$ ohm cm at $2000^\circ$C. It is, therefore, possible to construct heating elements using graphite which conveniently withstand temperature of the order of $4000^\circ$C. Also, the small value of its temperature coefficient of resistance favours to make electrical equipment simple. Graphite is however very reactive with oxygen and with nitrogen at a high temperature, it forms the toxic cyanogens. So, due precautions should be taken about the furnace chamber atmosphere.

The graphite tubes are constructed to suitable shapes and sizes from the solid graphite rods supplied by Acheson Graphite Company Ltd. of New York, U.S.A. The end walls of the tube were machined a bit thicker so as to fit accurately in a pair of carbon blocks C, C’. These are clamped into the corresponding holes by means of screw driven through the platform of the electrode. The arrangements are depicted in Fig. 2.1(b)
Fig. 2.1 Sectional View of Vacuum Graphite Furnace
(c) **The Power Supply**: The electrodes are connected to the secondary of a 10 kW step down transformer which supplies the necessary current to the furnace. The current is adjusted by the variac for attaining different temperatures.

**Shape, Size and Life Time of Graphite Element**

Thin wall tubes were found to give better performance though such tubes were structurally weaker and their life time was also relatively short. Further smaller bore and size of these tubes were also found to favour high temperature production.

The dimensions of the tube used in our experiments have been as follows:

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<table>
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<tbody>
<tr>
<td>Length</td>
<td>9.5 cm</td>
</tr>
<tr>
<td>Outer diameter</td>
<td>10.0 mm</td>
</tr>
<tr>
<td>Inner diameter</td>
<td>7.5 mm</td>
</tr>
</tbody>
</table>

The vapour pressure of the graphite is $10^{-6}$ mm Hg at 2000°C and $10^{-3}$ mm Hg at 2500°C. As a result, the rapidly increasing vapor pressure of graphite at the above 2500°C becomes the dominating factor for the life of the tube. The higher the temperature shorter will be the life of the resister.

**Experimental Procedure**

(a) **Loading of the Furnace**: The substance under study is placed uniformly spread in the central portion of the heating graphite tube which is clamped between the carbon blocks at the electrodes. Due care should be taken that the graphite tube uniformly fixed between the carbon blocks, otherwise flickering takes place at higher current input and the temperature is lowered down after a few seconds. The furnace chamber is now closed by the lid L, sealed with plasticine, evacuated and then filled with argon gas to prevent effusion of experimental vapors from the open end of the tube. It may be mentioned here that nitrogen was found less favorable for better performance of thermal emission experiments. Water circulation is kept on as the operation is started. It is necessary
to leave the cooling water running for at least 30 minutes after the furnace is turned off to prevent melting of the rubber parts.

(b) **Optical Arrangements**: A quartz lens was placed between the furnace and the spectrograph so that the central portion of the graphite tube could be focused on the slit of the spectrograph. Two asbestos sheet discs, with about 0.5 cm holes drilled through in the centre were used to keep the black body radiation emitted by the walls of the graphite tube away being focused on the slit. A copper or iron arc was placed on the common optical axis of the furnace and the spectrograph for recording the standard comparison spectrum.

For larger exposure it was found desirable to introduce experimental substance two or three times in the furnace before the desired total exposure time was over. It was particularly needed while using high dispersion grating spectrograph and in recording spectra of the ultra violet region.

Two meter Ebert Plane Grating Spectrograph (2m PGS -2) Carl Zeiss was used for photographing the spectra in the visible as well as ultraviolet region with a grating blazed at $\lambda\,5600$ Å and total lines 45600. All the final records of spectra from which the measurements were made, were taken in first and second order on this spectrograph. The reciprocal linear dispersion for this spectrograph varied from 7.3 Å/mm to 3.7 Å/mm corresponding to first and second order respectively. The visible and ultra violet spectra were recorded on ILFORD 400 ASA black and white films. The measurements of the spectrum records were made on C.Z. Abbe Comparator (Carl Zeiss) with a least count of 0.0001 cm.

**Electrodeless Discharge Lamp (EDL)**

The Microwave was used for the both Electrode less Discharge Lamp (EDL) and discharge tube excitation of transient molecular species. The 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.

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 ELD 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 $^{80}$Se$_2$ EDL we had experimented with natural ‘Se’ metal to work out the exact quantity of 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 ‘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 $^{80}$Se$_2$ were excited and recorded on DA8 BOMEM F.T. Spectrometer.

**Plane Grating Spectrograph (PGS-2)**

The plane grating spectrograph is used for spectral analysis in the ultraviolet, visible and near infrared spectral region. The optical principle of the
spectrograph is the Ebert mount of the plane grating with mirror optics [5]. The rays travel from slit to a deflecting mirror and then to the lower section of a large concave mirror, where they are collimated and reflected to the grating. After diffraction by the reflection grating the dispersed beams strike the upper section of the concave mirror, which recombines the parallel rays so that a spectrum is produced in the plane of plate above the grating. The grating is rotatable so that it can be set for various wavelength ranges and spectral orders.

The material to be investigated is excited by suitable exciting device and the emission is brought to the spectrograph via an illumination system. In the spectrograph it is dispersed into a spectrum that is photographed.

**Fourier Transform Spectroscopy**

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).

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, hollow cathode discharge, DC or AC electric discharge etc. The emission of radiation occurs when chemical species makes transition from excited states to lower states. The FTS system consist of two distinct system [6-10]

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:

<table>
<thead>
<tr>
<th>Beam splitters and its ranges</th>
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<tbody>
<tr>
<td><strong>Beam Splitter</strong></td>
</tr>
<tr>
<td>Mylar film</td>
</tr>
<tr>
<td>KBr</td>
</tr>
<tr>
<td>KCl</td>
</tr>
<tr>
<td>CaF$_2$</td>
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<tr>
<td>Quartz</td>
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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 distance between two beam traveled is same, then they recombine constructively. If the beam from moving mirror traveled a different distance then the beam from fixed mirror, then recombination will results 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 [5] is given below:
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 wavenumber and so wavenumber 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 wavenumber, 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

<table>
<thead>
<tr>
<th>Working temperature</th>
<th>Detector</th>
<th>Working wavenumber range (cm(^{-1}))</th>
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<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>
“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
\[
I(\delta) = \int_0^{\infty} B(v) e^{2\pi i v \delta} dv
\]
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
\[
B(v) = 2 \int_0^\delta I(\delta) e^{-2\pi i v \delta} d\delta
\]
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:
\[
B(v) = 2 \int_0^\delta A(\delta) I(\delta) e^{-2\pi i v \delta} d\delta
\] (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 beamsplitter act as slit and beamsplitter 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 wavenumber 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 M₂ relative to M₁ 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 wavenumber 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 may be detected are 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