CHAPTER - II

EXPERIMENTAL TECHNIQUES

2.1 INFRARED SPECTROPHOTOMETER

The infrared spectra were recorded on the Perkin-Elmer 521 spectrophotometer (Instruction Manual, 1965) at the central Optical Spectroscopy Laboratory of I.I.T., Kanpur. It is a self-recording, high performance, double-beam grating spectrophotometer, covering the range 4000 - 250 cm\(^{-1}\). There are two gratings fixed back to back, with 100 lines/mm and 25 lines/mm. The first grating is used in the first order for range 630 - 2000 cm\(^{-1}\) and in the second order for the range 2000 - 4000 cm\(^{-1}\). The second grating is used in the range 250 - 630 cm\(^{-1}\) in the first order. Suitable interference filters are used in the instrument to eliminate radiations of extraneous orders from the grating.

The instrument has spectral resolution of 0.3 cm\(^{-1}\) at 1000 cm\(^{-1}\). The accuracy of the frequency scale is ± 0.5 cm\(^{-1}\) with reproducibility of 0.25 cm\(^{-1}\). The detector is a high speed sensitive thermocouple fitted with blackened gold-leaf strip (2 x 0.2 mm) and a CsBr lens. The optical diagram of the instrument is shown in Fig. 2.1.

For the calibration of the frequency scale we used the standard sharp peaks of polystyrene and indene. The spectra of the former were recorded using a thin film provided by the Perkin Elmer Corporation and those of the latter were recorded by placing a few drops of the liquid between two CsBr plates and interposing the film thus made into the optical path.

2.2 SAMPLING TECHNIQUES FOR RECORDING THE SPECTRA

The three main considerations in the sample preparation for recording the IR spectra of solids are the following -
(1) The particle sizes must be quite small (compared with $\lambda$) in order to avoid scattering losses.

(2) The matrix in which the salt is situated must be transparent in the region of sample absorption.

(3) The refractive indices of the matrix and the sample must match.

Keeping these in view the techniques generally employed in recording the transmission spectra (Brugel 1962, Szymanski 1964) are (a) suspensions (or mulls), (b) pellets (or discs), and (c) thin films. The first two are more conventional. In the mull technique one needs some non-interacting organic liquid of high boiling point and having few specific absorption peaks in the region of interest. Nujol, a liquid paraffin, was used by us in most of the spectra, and bands belonging to nujol have been marked by N in the spectra reproduced. The mull is placed between two plates (called windows) which are transparent to IR. The materials generally used for windows are NaCl ($>600$ cm$^{-1}$), KBr ($>400$ cm$^{-1}$), CsBr ($>200$ cm$^{-1}$), CsI ($>200$ cm$^{-1}$) and KRS-5 ($>250$ cm$^{-1}$).

In the pellet technique the sample is mixed with some non-interacting solid (KBr, KCl, etc) in an appropriate proportion and ground in ball-mill grinder (vibrator) to a particle size of a few microns. This powder is then finally put in a pellet-making die and subjected to a pressure of several atmosphere. The pellet-making often encounters effects like ion-exchange, stress relaxation, partial dehydration etc. (Dwyckaerts 1959, Srivastava 1976). In our samples we encountered partial dehydration in the case of ZnSO$_4$$\cdot$H$_2$O and we switched to the nujol mull technique, except when bands near the nujol mull absorption regions were to be especially recorded. In anhydrous salts no problem was encountered with the KBr pellet method.
2.3 LOW TEMPERATURE CELL

A Wagner-Hornig (1950) type cell was used for recording the low temperature spectra. This cell is shown in Fig. 2.2. The cell was connected to a vacuum system, shown separately in Fig. 2.3. The sampling assembly (nujol mull or KBr pellet) was placed in the 'cold finger' block of the cell. This block is connected through a highly conducting metallic rod (copper) to a chamber at the bottom. Liquid nitrogen poured into this chamber cools the 'cold finger' (and hence the sample) by conduction, without itself coming in the optical path. Temperature at the cold finger was measured using a calibrated copper-constantan thermocouple, the accuracy being ±5K.

2.4 DEUTERATION OF THE SAMPLES

For deuteration the principle of vacuum distillation was employed. The vacuum system used for this purpose, shown in Fig. 2.3, provided a vacuum of \( \sim 10^{-5} \) mm of Hg. The salt to be deuterated was first thermally dehydrated up to the anhydrous stage by baking in an oven at the appropriate temperature. Three inter-connected flasks were used – one contained pure D_2O, the second the dehydrated salt and the third was empty. First, the whole system was evacuated and D_2O was frozen using liquid nitrogen. The vacuum pump was then disconnected from the system and under low pressure D_2O was transferred to the sample flask to dissolve the sample in D_2O at an appropriate temperature maintained by dipping the flask in an oil bath. In the third stage D_2O from the aqueous solution was transferred to the empty flask by a similar method, leaving the deuterated salt.
It is to be noted that if the anhydrous salt is dissolved in D₂O in the open atmosphere, exchange of H₂O takes place from the atmosphere. Hence the vacuum system is advisable. The temperature of the oil bath determines which of the possible deuterates for a given salt is formed.

2.5 RESOLUTION OF THE OVERLAPPING BANDS

Very few of the bands of interest appear as distinct isolated bands in the IR absorption spectrum. Often the neighbouring bands overlap considerably. It was therefore necessary to resolve such spectra geometrically. Such work depends on the expected shapes of the components. In the condensed phase theoretical considerations justify the Lorentzian shape for the band contour (Lorentz 1906). Gaussian curves are found to be good for the description of electronic absorption bands but not of IR bands (Vitek 1974). In fact, neither of these two functions is found to give a complete fit to the experimental curves and hence their Voigt like combinations (Voigt 1912) have been often used. However in those cases where the actual band-width is much larger than the instrumental slit, the Lorentzian shape alone gives a reasonably good fit, especially if we are not to go far into the tail of the band. This was the situation in the present case. Hence we used the Lorentzian analysis to resolve out components in the overlapping regions. A Lorentzian function is given as:

\[ I(\nu) = I(\nu_0) \frac{b_c^2}{b_c^2 + (\nu - \nu_0)^2} \]

Here \( \nu_0 \) is the frequency at peak intensity \( I(\nu_0) \) and \( 2b_c \) is the full band-width at half the maximum intensity, designated in our tables as \( \Delta\nu_{1/2} \) (half-width). Fig. 2.4 shows the significance of \( I(\nu_0) \) and \( b_c \).
The product of $I(\nu')$ and $\Delta \nu_{1/2}$ is a measure of the intensity of a band, usually called integrated intensity. It is useful for comparison within a spectrum to evaluate the relative integrated intensities (RII) of different bands assigning $\text{RII} = 100$ to one typical band or group. This procedure is adopted by us.

The first thing in proceeding for the analysis of an overlapping band is to choose a proper baseline. Two main considerations for this were the following: (1) The base should not touch the tails of absorption profile; margin should be left for absorption at the tails. (2) Selecting a base line with increasing absorption towards lower frequency region is to be avoided because if scattering is a contributor then on the high frequency side could tilt the base only in opposite sense. Having chosen a base and after accounting for it, the region to be analysed is replotted on a linear absorbance scale. Analysis is now made starting with the more obvious components, affixing some $I(\nu')$ and $\Delta \nu_{1/2}$ parameters to them, obtaining the residues, proceeding to more bands, and so on. Three main criteria used in this analysis were the following:

1. We tried to search for the minimum number of Lorentzian components warranted by the observed contour. Minor residues or deviations were not used to introduce bands with doubtful existence, since Lorentzian shape was only an approximation.

2. In case of alternative analyses giving equally good fit, the one which maintained the peak positions nearer the observed humps was preferred.

3. A component which was not obvious in the band contour by showing a hump or a clear shoulder was introduced only in those cases where repeated Lorentzian trials otherwise failed by wide margins and there were other spectral evidences also for such a component.
The inaccuracies of the derived parameters vary from situation to situation. For frequencies the estimated error level is $\pm 1 \text{ cm}^{-1}$ for sharp peaks, to $\pm 5 \text{ cm}^{-1}$ for broad but distinct bands and to $\pm 10 \text{ cm}^{-1}$ for the shoulders, bulges and bands with weak evidence. For intensities the error level may be 5 to 10% in the case of envelopes with weak overlapping and 15 to 30% in the case of envelopes with strong overlapping.

2.6 LASER RAMAN SPECTROMETER.

Raman spectra were recorded on Cary - 82 Raman spectrophotometer at the usual 90° geometry with 488 nm Ar$^+$ laser light ($\sim 1$ Watt power) as the exciting source. Fig. 2.5 shows the optical diagram for the instrument. On the right is the prefilter assembly (prisms $P_1$, $P_2$, $P_3$ and slit $S'$) to isolate the exciting line. The scattered light is collected by an f/1 aperture lens and mirror combination ($L_4$ and $M_1$). Three monochromators in succession ($S_1$ to $S_2$, $S_2$ to $S_3$ and $S_3$ to $S_4$) are used, reducing the background by a factor of $10^5$.

The detection is achieved with an electronically cooled ITT-FW-130 photomultiplier and photon counting electronics is used to obtain the record of the spectra.

The polarization scrambler (Fig. 2.5) remained in the optics while taking the spectra, but was not useful because our samples were microcrystalline, not single crystals.
REFERENCES


Duyckaerts G, Analyst, 84, 201 (1959).


PERKIN-ELMER-521 INFRARED SPECTROPHOTOMETER.

Glower (Source); Mirrors (M_1, M_2, M_3, M_4, M_5, M_6, M_7, M_8, M_9, M_{10}, M_{11}, M_{12}, M_{13} and M_{14}); Entrance slit (S_1); Exit slit (S_2), Grating (G_1 and G_2).

Fig. 2.1
Fig. 2.2 Low temperature cell
Fig. 2.3: Vacuum system used for deuterating the samples and also with the low temperature cell. The oil diffusion pump is not shown.
Fig. 2.4: Defining $I_0$, $b_0$ and $\Delta \nu_2$ of a Lorentzian absorption band.
FIG. 2.5
Optical diagram
Cary 82 system