CHAPTER 6

Vibrational Assignments and Normal Coordinate Analysis of Para Nitro Benzoic Acid
6.1 INTRODUCTION

Derivatives of benzoic acid have been the subject of investigation for many reasons. Derivatives of Benzoic acid is an essential component of the vitamin B complex. Benzoic acid occurs widely in plants and animal tissues along with vitamin B complex and is used to raise the salicylate level in blood. It is also used in miticides, contrast media in urology, cholecystographic examinations and in the manufacture of pharmaceuticals. It also finds application in dyes, in occurring tobacco, in preserving fruit juice, in many esters, as a mordant in cloth printing and as a reference in volumetric analysis. Because of its wide applications, the surface enhanced Raman scattering studies(1), vibrational spectra of benzoic acid (2) and nitro derivatives have been extensively investigated.

Verma et al., (3) studied infrared absorption spectrum of m-fluorobenzoic acid with the help of nujol mull in the region 250-4000 cm⁻¹. The assignments of the fundamentals were proposed for this compound by assuming C₆ symmetry. The infrared and laser Raman spectra of solid 3,4,5, and 2,3,5-triiodobenzoic acid in various solvents are reported by Goel et al., (4). The vibrational spectra of benzoic acid at low temperatures were studied by Kresimir Furic et al., (2). Ashok Babu et al., (5) carried out a zero order calculations of o- and p-nitrophenoxy acetic acid. The vibrational frequencies are reported with an average error of 15 cm⁻¹. The calculations are used to make vibrational
assignments on a quantitative basis. Ashok Babu et al., (6) have recorded the infrared spectra of phenoxy acetic acid, p-chlorophenoxy acetic acid, o-chlorophenoxy acetic acid, p-nitrophenoxy acetic acid and o-nitrophenoxy acetic acid using Perkin-Elmer model-283 double beam grating spectrophotometer equipped with CSI optics. They have analysed Mull technique for phenoxy acetic acid, p-chlorophenoxy acetic acid, o-chlorophenoxy acetic acid, p-nitrophenoxy acetic acid and o-nitrophenoxy acetic acid using fluorolube and nujol as mulling agents so as to cover different ranges of frequencies. The KBr pellet method has used for p-nitro phenoxy acetic acid. The Fourier transform far-infrared spectra of the sample have been measured with polytec FIR-30 Fourier transform far-infrared spectrometer in the range 650-20 cm⁻¹. They have confirm the frequencies for the compounds on the basis of qualitative considerations. Shabbir Ahmad ed al., (7) have recorded the infrared and far infrared spectra of o-, m- and p-iodonitrobenzene in the region 200-4000 and 50-00 cm⁻¹, and they have assigned vibrational frequencies. Singh et al., (8) have recorded the infrared and laser Raman spectra of 2,3-dichloronitrobenzene and they have assigned vibrational frequencies and internal modes of vibration of NO₂ group vibrations. Muralidhar Rao et al., (9) have recorded the Raman and infrared spectra of o-, m- and p-fluoronitrobenzenes, o-, m- and p-chloronitrobenzenes, m-and p-bromonitrobenzenes and m- and p-iodonitrobenzenes. They
have carried out a normal coordinate analysis for both in-plane and out-of-plane vibrations of these molecules using an 82 parameters modified valence force field. An overlay least squares technique was employed to refine the force constants using 378 frequencies of the molecules to obtain the converged set of meaningful force constants. They have also studied the reliability of the force constants obtained and tested by making a zero order calculation for o-bromonitrobenzene. The potential energy distribution and eigen vector calculated in the process were used to make unambiguous vibrational assignments of all the fundamentals. Recently Shabbir Ahmad et al., (10) have been recorded laser Raman and Fourier transform infrared spectra of 3,5-dinitrobenzoic acid in the region 25-4000 and 50-4000 cm\(^{-1}\), respectively in solid phase. The assignments of observed bands have been proposed. Again Shabbir Ahmad et al., (11) have been recorded laser Raman and Fourier transform infrared spectra of o-, m- and p-iodonitrobenzene in the region 50-4000 and 400-4000 cm\(^{-1}\), respectively. The vibrational analysis was carried out and assignments have proposed. Recently Mohan et al., (12) have recorded the Fourier Transform infrared and laser Raman spectra of para chloro benzoic acid in the regions 200-4000 and 30-4000 cm\(^{-1}\), respectively. They have assigned various modes of fundamental vibrations and also reported normal coordinate analysis with potential energy distributions.
As none of the above workers have given a complete vibrational assignments for para nitro benzoic acid, the present investigation has been undertaken to record and study the infrared and laser Raman spectra completely. Using the infrared, Fourier transform infrared together with laser Raman spectra, a complete vibrational assignments are given along with the normal coordinate analysis and potential energy distributions.

6.2 EXPERIMENTAL DETAILS

The para nitro benzoic acid was obtained in the solid form from SISCO - CHEM industries, Bombay and was used as such without further purification to record infrared, FTIR and laser Raman spectra. The infrared spectrum in a KBr disc was recorded using a Perkin-Elmer IR 521 double beam grating spectrophotometer in the region 4000-600 cm\(^{-1}\). The FT-infrared spectrum of the sample in the region 200-4000 cm\(^{-1}\) was recorded on Shimadzu FTIR 8101 spectrophotometer and the laser Raman spectrum was recorded in the region 30-4000 cm\(^{-1}\) on a Cary Model 82 grating spectrophotometer using 488 nm radiation from an Ar\(^{+}\) laser excitation, operating at 4W. The spectral width was 2 cm\(^{-1}\) and scanning speed was 5 cm\(^{-1}\) s\(^{-1}\). The frequencies of all sharp bands are accurate ± 1 cm\(^{-1}\). The recorded spectra of para nitro benzoic acid are shown in figs (6.1-6.3), and the molecular structure is illustrated in fig (6.4).
FIG. 6.1 INFRARED SPECTRUM OF PARA NITRO BENZOIC ACID
FIG. 64 STRUCTURE OF PARA NITRO BENZOIC ACID
The bond lengths and bond angles were taken from Sutton's tables (13). The normal coordinate calculations were performed using the modified programme given in an earlier work (14). Internal coordinates for the out-of-plane vibrations were defined as recommended by IUPAC. The general quadratic valence force field was adopted for both in-plane and out-of-plane vibrations. The initial force constants were taken from similar benzene derivatives (15,16).

6.3 RESULTS AND DISCUSSION

The observed frequencies of para nitro benzoic acid together with relative intensities, probable assignments and calculated frequencies are given in Table 6.1.

Assuming NO$_2$ group and COOH group as mass points, the present molecule belongs to C$_s$ point group and gives rise to 30 normal vibrations. They are distributed as:

$$\Gamma = 21 \alpha'(\text{planar}) + 9 \alpha'' (\text{non-planar})$$

All the vibrations are both infrared and Raman active. Apart from these vibrations there are also 6 group vibrations pertaining to NO$_2$ group and 10 group vibrations belonging to COOH group.
6.3.1  PHENYL RING VIBRATIONS

6.3.1.1  CARBON VIBRATIONS

Benzene has two doubly degenerate modes $e_{2g}$ (1596 cm$^{-1}$) and $e_{1u}$ (1485 cm$^{-1}$) and two non-degenerate modes $b_{2u}$ (1310 cm$^{-1}$) and $a_{1g}$ (995 cm$^{-1}$) due to the skeletal C-C stretching vibration (17). The doubly degenerate modes corresponding to C-C stretching in benzene are assigned to the observed bands at 1690, 1600, 1530, 1440, 1415 and 1400 cm$^{-1}$ in para nitro benzoic acid. These frequencies are in close agreement with the literature values (18,19).

The in-plane carbon bending vibrations are obtained from the non-degenerate $b_{1u}$ (1010 cm$^{-1}$) and degenerate $e_{2g}$ (606 cm$^{-1}$) modes of benzene. The $e_{2g}$ (606 cm$^{-1}$) degenerate modes split into two totally symmetric vibrations under $C_s$ symmetry and they are observed at 654, 520 and 315 cm$^{-1}$ in para nitro benzoic acid, which agree well with the literature values (20).

The carbon out-of-plane bending vibrations are described with reference to the non-degenerate $b_{2g}$ (703 cm$^{-1}$) and degenerate $e_{2g}$ (404 cm$^{-1}$) modes of benzene. The degenerate $e_{2g}$ (404 cm$^{-1}$) vibration splits into two non-totally symmetric components and the bands are observed at 548, 260 and 255 cm$^{-1}$ in para nitro benzoic acid. The results agree with earlier works (21,22).
6.3.1.2 C-H VIBRATIONS

The aromatic structure shows the presence of C-H stretching vibrations in the region 3000-3100 cm\(^{-1}\), C-H in-plane bending in the region 1000-1100 cm\(^{-1}\) and C-H out-of-plane bending in the region 800-880 cm\(^{-1}\), which permits a ready identification for this structure. In this region the bands are not affected by the nature of the substituents. The observed frequencies in this region 3200-3068 cm\(^{-1}\) are assigned to C-H stretching modes in para nitro benzoic acid. Weak bands are of little interest in the more complicated region in the spectra. Overtone and combination bands are characteristically weak except at Fermi resonance. The potential energy distributions associated with these normal vibrations also confirm the assignment. They are in good agreement with the literature values (23,24).

The C-H in-plane bending results from the degenerate \(e_{2g}\) (1178 cm\(^{-1}\)) and \(e_{1u}\) (1037 cm\(^{-1}\)) and non-degenerate \(b_{2u}\) (1152 cm\(^{-1}\)) and \(a_{2g}\) (1340 cm\(^{-1}\)) modes of benzene ring. The change in the frequencies of these deformations from their values in benzene are almost determined exclusively by the relative position of the substituents and are almost independent of their nature (25). Hence, the bands at 1108, 1075, 1051 and 1015 cm\(^{-1}\) are assigned to C-H in-plane bending vibrations in para nitro benzoic acid.
The C-H out-of-plane bending vibrations derived from the two degenerate $b_{2g}$ (985 cm$^{-1}$) and $e_{2u}$ (970 cm$^{-1}$) and two non-degenerate $e_{1g}$ (850 cm$^{-1}$) and $a_{2u}$ (671 cm$^{-1}$) modes of benzene and they are expected to occur in the region 600-1000 cm$^{-1}$. In the present work, these modes yield four non-planar bending vibrations involving hydrogen atom. The bands at 968, 878, 859 and 825 cm$^{-1}$ are assigned to C-H out-of-plane bending vibrations for the para nitro benzoic acid. They agree with the literature values (24).

6.3.1.3 C-NO$_2$ VIBRATIONS

Shabbir Ahmad et al (10) suggested that the bands at 1160 cm$^{-1}$, 280 cm$^{-1}$ and 183 cm$^{-1}$ in 3,5-dinitro benzoic acid be assigned to the C-NO$_2$ stretching, in-plane bending and out-of-plane bending vibrations, respectively. On this basis, the bands at 1110, 288 and 202 cm$^{-1}$ in para nitro benzoic acid are assigned to C-NO$_2$ stretching, in-plane bending and out-of-plane bending vibrations.

6.3.1.4 C-COOH VIBRATIONS

In para nitro benzoic acid the bands at 1196, 325 and 210 cm$^{-1}$ are assigned to C-COOH stretching, C-COOH in-plane bending and C-COOH out-of-plane bending vibrations, respectively. The above results are in good agreement with earlier work (10).

6.3.1.5 NO$_2$ GROUP VIBRATIONS

The NO$_2$ asymmetric and symmetric stretching vibrations...
generally gives rise to bands in the region $1500-1570 \text{ cm}^{-1}$ and $1300-1370 \text{ cm}^{-1}$ in nitro benzene and substituted nitro benzenes (26,27). In para nitro benzoic acid the bands appeared at $1555 \text{ cm}^{-1}$ and the strong band at $1367 \text{ cm}^{-1}$ are assigned to NO$_2$ asymmetric and symmetric stretching vibrations, respectively in the laser Raman spectrum. The NO$_2$ in-plane deformation and wagging vibrations in the present molecule are assigned at $840$ and $770 \text{ cm}^{-1}$ respectively. This is in agreement with the various substituted nitro benzenes (26,27). The band at $611 \text{ cm}^{-1}$ is a suitable choice for the NO$_2$ rocking vibration, while the frequency $98 \text{ cm}^{-1}$ is assigned as the NO$_2$ torsion mode. This is in close agreement with the assignments given by Andreev et al (28) and Ashok Babu et al (6).

6.3.1.6 COOH GROUP VIBRATIONS

The band observed at $3440 \text{ cm}^{-1}$ has its origin in the O-H stretching vibration. The C=O stretching is a characteristic frequency of the carboxylic group. The dipole moment derivatives of the COO in-plane bending mode and C=O stretching modes are very large, splittings with marked frequency differences may be expected for these modes and the out-of-plane C=O stretching mode should have a higher frequency than the in-plane mode (29). The band appearing at $1775 \text{ cm}^{-1}$ is assigned to the C=O stretching vibration. The O-H in-plane bending and C-O stretching vibrations are closely coupled. These are appearing at $1460$
and 1295 cm\(^{-1}\) in the present work. The bands at 800 and 575 cm\(^{-1}\) are assigned to the OCO in-plane bending and CCO rocking vibrations. Out-of-plane bending vibrations due to O-H and C=O give rise to the bands at 990 and 720 cm\(^{-1}\) in the present work. The O-H out-of-plane bending vibrations strongly couple with the C=O out-of-plane bending vibration. The C=O out-of-plane wagging mode of the carboxyl group probably involves motion of both the oxygen atoms. The C-OH in-plane and out-of-plane bending vibrations are assigned to 352 and 225 cm\(^{-1}\) in the present work. These are in close assignment with the literature values (26,29).

The general agreement between the observed and calculated frequencies for both in-plane and out-of-plane vibrations is reasonable.

6.4 POTENTIAL ENERGY DISTRIBUTION

To check whether the chosen set of vibrational frequencies contribute maximum to the potential energy associated with the normal coordinates of the molecules, the potential energy distributions (PED) have been calculated using the relation:

\[
PED = F_{ii} L_{ik}^2 / \lambda_k
\]

PED is the contribution of the \(i^{th}\) symmetry coordinate to the potential energy of the vibration whose frequency is \(\nu_k\). \(F_{ii}\) = force constants, \(L_{ik}\) = \(L\) matrix elements and

\[
\lambda_k = 4 \pi^2 c^2 \omega_k^2
\]