CHAPTER 6
CHAPTER-6

VIBRATIONAL ANALYSIS OF BENZONITRILE AND ITS ISOTOPES

INTRODUCTION

Benzonitrile is, as it is obvious from fig.1., a phenyl cyanide compound. Benzonitrile is a colourless liquid, boiling at 197°C, having smell of bitter almonds. Benzoic acid, the main product of benzonitrile is used in medicine as urinary antiseptic in the form of its salts and in vapour form for disinfecting bronchial tubes, in dye industry for making aniline blue and for preserving food products (1). Because of its structural simplicity, a large number of studies on benzonitrile and its derivatives were reported. Aqucel et al.(2) studied the Laser Raman spectra of liquid m-fluoro benzonitrile and calculated depolarisation ratios of Raman lines. Further the Vibrational frequencies observed in the Raman spectra were assigned to various normal modes of vibrations assuming C\textsubscript{S} symmetry for the molecule by them.

The near U.V absorption spectrum of 2-chloro-6-methyl-benzonitrile in vapour phase was reported and analysed by Goel et al.(3). The spectrum corresponds to 2600 Å transition in benzene. The 0.0 band was observed at 34471 cm\(^{-1}\). It was reported that the strong bands at 130, 283 and 388 cm\(^{-1}\) towards the longer wavelength side of the 0.0
band correspond to ground state fundamentals while those at 215, 312, 519, 592, 902, 1028 and 1120 cm\(^{-1}\) towards the violet side represent the excited electronic fundamentals. The assignments of the ground and excited state fundamental frequencies to the probable modes of vibrations were also made.

Towns (4) studied the mid-infrared spectrum of 1,3,5-triamino-2,4,6-trinitro benzene and four of its isotopic derivatives. The relative simplicity of the spectra, in conjunction with the various isotopic shifts, made easy to assume that thirteen of the seventeen principal spectral features can be attributed to vibrational modes originating in the amino- and nitro-moieties; the remaining four bands to skeletal vibrations. In comparison with spectra of aniline and nitrobenzene, the assignments were found consistent with predicted spectral changes due to both hydrogen bonding and the presence of canonically electron withdrawing and electron donating substituents.

Abramazyket al(5) studied the Raman spectra of benzonitrile in phenol solution. The authors discussed the hydrogen bond effect on vibrational relaxation of the proton accepting group C=N of benzonitrile in phenol and deuterated phenol-OD solutions using Raman spectroscopy. The Raman bands of totally symmetric \(\nu(C=N)\) stretching modes at 2230 cm\(^{-1}\) and \(\nu_{12} (A_1)\) at 460 cm\(^{-1}\) were measured as a function
of concentration. Additional bands, shifted about 6 cm\(^{-1}\) to higher frequencies were found formed in both cases.

Raman and IR spectra of 1,3,5-triamino-2,4,6-trinitro benzene from 10 to 4000 cm\(^{-1}\) were reported by Vergoten et al\(^{\text{(6)}}\). They have carried out a normal coordinate analysis using a modified Urey Bradley force field, taking into account the cyclic redundancies and intramolecular hydrogen bonds for the assignment of various vibrational modes. In the same way, they have also studied 2,3,5-trinitro benzene \(^{\text{(7)}}\). Assignments were made with particular emphasis on low frequencies and over all vibrations with the local symmetry force field described in their work.

Ram et al\(^{\text{(8)}}\) reported the vibrational spectra of three isomeric hydroxy-benzonitriles. Infrared spectra were recorded in the region 35 - 4000 cm\(^{-1}\) and the Laser Raman spectra in the region 0 - 4000 cm\(^{-1}\), in the solid phase. Complete assignment of the frequencies observed were made assuming C\(_5\) point group for all the three isomers.

Upathy et al\(^{\text{(9)}}\) analysed Infrared spectra of 2,5- dibromo and 3,4-dichloro-nitro benzene, recorded in the region 200 - 4000 cm\(^{-1}\) in liquid and solution phase. The observed bands were assigned to different modes assuming C\(_5\) symmetry to the molecules. The carbonyl doublet observed in
the spectra was explained in terms of fermi resonance.

The torsional potential function of dimethyl-amino benzonitrile and related compounds in their $S_1$ states were studied by Gordon et al(10). Passingham et al(11) reported the Raman spectra of some aromatic nitro compounds. Correlations were found between frequencies of the NO vibrations and the electron donating and withdrawing effects of substituents on the phenyl rings. Further, relations were discussed between the highest frequency CH stretching mode and the electron density in number of nitro groups.

Joshi et al(12) reported the Infrared and electronic absorption spectra of 2,6-, 3,5- dichloro benzonitriles and 3-chloro-4-methyl benzonitrile. The various modes of vibrations were assigned and the effects of substitution are analysed. In the same way, 2-chloro-6-fluoro benzonitrile was analysed with help of UV and Raman spectra by Huded et al(13).

Sharma et al(14) studied the photo acoustic spectra of benzonitriles. The spectra were recorded using the commercial EDT OAS 400 photo acoustic spectrometer in the near IR region, 3850 - 10000 cm$^{-1}$. The observed bands were assigned in terms of combinations of fundamentals and overtones.
Bottcher et al (15) carried out a microwave Fourier transform study of the rotational spectrum of 3-fluoro benzonitrile to study the $^{14}N$ quadrupole coupling and to give improved rotational constants and centrifugal distortion parameters. It was found that the CN – bond in benzonitrile and in 3-fluoro-benzonitrile show a smaller deviation from cylindrical symmetry than in 2- and 4-fluoro-benzonitrile.

Green et al (16,17) and Jakobson (18) extensively studied the infrared and Raman spectra of $C_6H_5CN$ and $C_6D_5CN$ and their data has been used to assign the vibrational frequencies of benzonitriles. The spectra of $o$-D-$C_6H_4CN$, $m$-D-$C_6H_4CN$ and $p$-D-$C_6H_4CN$ was recorded by Bak and Nielsen (19) in the infrared region and assigned the frequencies approximately. A normal coordinate analysis for the in-plane vibrations of $C_6H_5CN$ and $C_6D_5CN$ was attempted by Danchinov et al (20) using a few force constants. They assigned the lowest possible frequency 170 cm$^{-1}$ to $b_2$ species in contrast to Green and Harrison’s (17) value 381 cm$^{-1}$. Kuwae and Macnida (21) recorded the infrared and Raman spectra of $p$-D-$C_6H_4CN$ and $C_6D_5CN$ and assigned the frequencies with the help of Normal coordinate analysis.

In the present work an attempt has been made to obtain a reliable intermolecular valence force field for benzonitrile and its four deuterated molecules. A normal
coordinate analysis is also carried out using 150 vibrational frequencies of benzonitrile. The statement "Since the isotopic molecules have the same electronic structure, the potential function under the influence of which the nuclei are moving is the same to a very high degree of approximation" by Herzberg (22) has been taken as guide line for checking the assignments of dueterated and undeuterated molecules. This approach helps us in obtaining not only a reasonable force field but also for reassigning few assignments for the benzonitriles in the present work.

NORMAL COORDINATE CALCULATIONS

Wilson's (23) F-G matrix method was used for the normal coordinate calculations using the observed vibrational frequencies (16, 17, 19, 21). The molecules under investigation possesses C_{2v} and C_{s} symmetry and the types of vibrations are distributed as follows:

Benzonitrile - d_{0} (C_{6}H_{5}CN) C_{2v} \Gamma = 12a_{1} + 3a_{2} + 7b_{1} + 11b_{2}
Benzonitrile - d_{s} (C_{6}D_{5}CN) C_{2v} \Gamma = 12a_{1} + 3a_{2} + 7b_{1} + 11b_{2}
Benzonitrile - p-d (C_{6}H_{4}CN) C_{2v} \Gamma = 12a_{1} + 3a_{2} + 7b_{1} + 11b_{2}
Benzonitrile - o-d (o-D-C_{6}H_{4}CN) C_{s} \Gamma = 23a' + 10a''
Benzonitrile - m-d (m-D-C_{6}H_{4}CN) C_{s} \Gamma = 23a' + 10a''

The conformation adopted for normal coordinate calculations is shown in fig.1 in which the internal displacement coordinates are also indicated.

Mink's (24) computer program for normal coordinate calculations are modified and used in the present

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FIG. 1. INTERNAL COORDINATES OF BENZONITRILE
work to study the vibrational analysis of benzonitriles. Internal coordinates for the out-of-plane bending vibrations are defined as recommended by IUPAC. The structural parameters employed in the present work are taken from the literatures; C-C = 1.397 Å, C-H = 1.073 Å, C-CN = 1.450 Å, C≡N = 1.161 Å and all the ring angles are 120°. The potential energy was expressed by SGVFF with 40 parameters. The initial set of valence force constants and the corresponding off-diagonal constants were transferred from related molecules. A zero-order calculation with the transferred force constants was performed and except for some deformational modes and low frequency modes, the result showed a reasonable agreement between the calculated and observed frequencies. The initial set of force constants were subsequently refined by the least square technique. The final set of force constants which gives a good agreement between the observed and the calculated frequencies are given in Table 1. The force constant thus obtained in the present work agree well with the literature values and also lie in the expected range. To check whether the chosen set of vibrational frequencies contribute the maximum to the potential energy associated with normal coordinates of the molecules, the potential energy distribution has been calculated. The observed and the calculated frequencies as well as potential energy distribution (PEDs) for the diagonal force constants are shown in Table 2.
VIBRATIONAL ASSIGNMENTS

It is the practice to assign the vibrational normal modes of conjugated systems by comparing the chemical bonds of similar molecules. It is well known that potential energy distribution is a measure of bond assignments rather than the normalised vibrational amplitudes. In the earlier work, the weak infrared band at 959 cm\(^{-1}\) of C\(_6\)D\(_5\)CN was assigned to ring breathing mode by Jakobson (18) in analogy with the sharp infrared band 1178 cm\(^{-1}\) of C\(_6\)H\(_5\)CN. Subsequently, Danchinov et al. (20) and Kuwae and Machida (21) suggested these modes to C-H deformations. From the potential energy distribution of the present work, it is concluded that 995 cm\(^{-1}\) is a mixed mode consisting ring breathing and C-C stretching. In our work this corresponds to 1001 cm\(^{-1}\) for C\(_6\)H\(_5\)CN. King and So (25) proposed C-H inplane deformation vibration at 1170 cm\(^{-1}\) and 870 cm\(^{-1}\) in ethynylbenzene and its deuterated species respectively. In line with their work, the weak band at 871 cm\(^{-1}\) and 1178 cm\(^{-1}\) of C\(_6\)D\(_5\)CN and C\(_6\)H\(_5\)CN are assigned to C-H inplane deformation vibration.

It is well known that the stretching frequencies involving various bonds except the substituted one do not change much on substitution while the stretching and deformed frequencies should decrease considerably on substitution.

Jakobson (18) and Danchinov et al. (20) assigned medium sharp and weak infrared bands at 1289 cm\(^{-1}\) and
1040 cm$^{-1}$ of C$_6$D$_5$CN to C-C stretching and C-D deformation modes respectively and similarly the medium intense bands at 1337 cm$^{-1}$ and 1289 cm$^{-1}$ are assigned to C-C stretching and C-H deform respectively for C$_6$H$_5$CN.

But, Kuwae and Machida (21) contradicted the above assignment and assigned 1289 cm$^{-1}$ and 1040 cm$^{-1}$ to C-H in-plane deformation ($\beta$C-H) and C-C stretching for C$_6$D$_5$CN and the corresponding modes at 1337 cm$^{-1}$ and 1289 cm$^{-1}$ to C$_6$H$_5$CN. In light of above discussion as well as from PED calculations from the present work, it is suggested that the modes at 1040 cm$^{-1}$ of C$_6$D$_5$CN (1337 cm$^{-1}$ of C$_6$H$_5$CN) and 1289 cm$^{-1}$ of C$_6$D$_5$CN (1289 cm$^{-1}$ of C$_6$H$_5$CN) should correspond to C-H in-plane deformation and C-C stretching vibration. Our conclusion can also be confirmed from Painter et al (26, 27) from their normal coordinate treatment on C$_6$H$_6$ and C$_6$D$_6$. They have suggested 1350 and 1309 cm$^{-1}$ of C$_6$H$_6$ and 1059 and 1282 cm$^{-1}$ of C$_6$D$_6$ corresponds to $\beta$C-H and $\nu$C-C modes respectively. The quantum mechanical ab initio calculations carried out by Pulay et al (28) further confirms our present assignment. According to him, 1350 and 1309 cm$^{-1}$ of C$_6$H$_6$ and 1059 and 1282 cm$^{-1}$ of C$_6$D$_6$ belong to C-H in-plane deformation and C-C stretching vibration respectively.

In Wilson's notation, Jakobson (18) assigned the liquid phase medium weak infrared band at 695 cm$^{-1}$ of C$_6$D$_5$CN to the mode 10a ($a_2$ species). Painter et al (25, 26)
and Pulay et al (28) showed that the band at 664 cm$^{-1}$ in C$_6$D$_6$ should correspond to 849 cm$^{-1}$ in C$_6$H$_6$ for mode 10a in benzene. In the liquid phase Raman spectra of C$_6$D$_5$CN, Jakobsen (18) observed 662 cm$^{-1}$ as 10a mode in $a_2$ species. Contrary to this assignments Kuwae and Machidae (21) assigned 692 cm$^{-1}$ band to the overtone of the fundamental at 351 cm$^{-1}$ in Fermi resonance with the $a_1$ fundamental at 716 cm$^{-1}$. From our work, the calculated frequency corresponding to the fundamental comes to 658 cm$^{-1}$. Based on the PED calculation, we propose the band at 662 cm$^{-1}$ ($\gamma$ C-D) to mode 10a in the $a_2$ species.

The liquid phase infrared spectra gives a sharp band at 488 cm$^{-1}$ which was assigned to torsion $\phi$C-C band in C$_6$D$_5$CN (548 cm$^{-1}$ in C$_6$H$_5$CN) (18). The PED calculation from our work reveals that the wavenumber 549 contributes to out-of-plane C$\equiv$N bending vibration. The next wavenumber 388 2 contributes to mixed mode with $\phi$(C-C), $\gamma$ C-CN and $\gamma$ C-H. Mannfords et al (29) have already suggested the mixed mode trends for certain bands. Considering their work, it is proposed in the present work that the band at 549 cm$^{-1}$ (484.1 cm$^{-1}$ in C$_6$D$_5$CN) can be assigned to mixed mode involving $\gamma$C$\equiv$N and $\gamma$C-H. It is interesting to note the same trend in benzonitrile-o-d(o-D-C$_6$H$_5$CN), benzonitrile- m-d-(m-D-C$_6$H$_5$CN) and in benzonitrile- p-d-(p-D-C$_6$H$_5$CN) molecules.
CONCLUSION

On the basis of normal coordinate analysis, using a simple valence force field and transferability of the potential constants, a few earlier assignments are revised for benzonitriles and its isotopes.